

Authors' response to referee comments on "Instrument Artifacts Lead to Uncertainties in Parameterizations of Cloud Condensation Nucleation"

Referee #1

We thank the Reviewer for her/his detailed suggestions which we feel have improved the manuscript. Specific modifications are discussed below.

General Comments

1) Reviewer comment: This study used a pure theoretical approach to assess the artifacts in various CCN operating scenarios. However, many scenarios are not common in the real CCN activation measurement.

A. For example, is very rare that the particle number concentrations at the output of DMA reach $1e4 \# \text{ cm}^{-3}$, or even $5e6 \# \text{ cm}^{-3}$ as investigated in the section of artifacts derived from CPC and CCN.

B. The authors suggested in the introduction section that the discrepancy in experimental results for ammonium nitrate and some organics in the literature are contributed by the artifacts in CCN measurement. An interesting question is to what extent the artifacts investigated here can explain the discrepancies in the kappa of ammonium nitrate, for example, in the literature.

A. Authors' response: As the Reviewer correctly points out, the scenarios in this study include conditions which are rare, as well as more typical conditions. Specifically, a DMA output aerosol concentration of $\sim 5.6 \times 10^4 \text{ cm}^{-3}$ is very high. We intentionally include this concentration, because such conditions have been encountered in the field under certain conditions, such as new particle formation events (Hameri, O'Dowd, and Hoell 2002). Also, in our original manuscript, we attempted to clearly qualify all conclusions according to "standard" vs. "high concentration" situations. We have now modified the text to make these delineations clearer, as specified below. In order to assess CPC operation at more typical concentrations, as well as the initially assessed $5 \times 10^6 \text{ cm}^{-3}$ total particles, three more total particle distributions have been added to the analysis in Section 4.2 CPC operation at high concentration.

Authors' changes in manuscript:

We have added the following statements for clarification:

Page 24-25 Lines 449-452 the text now reads: "CPC undercounting issues which arise even at relatively low concentrations (which one would expect to encounter under standard experimental conditions) will be discussed in this section. Concentration-dependent effects encountered at higher concentrations will be explored in Sect. 4.2."

Pages 26-27 Lines 488-496 the text now reads: "In order to assess the importance of undercounting in CPC Cases 7-10, four theoretical aerosol distributions with a peak concentration at 50 nm were employed (Table 5, Fig. 8b). CPC Distribution 1 represents a worst-case scenario of similar magnitude to the highest particle concentrations measured during a coastal nucleation event (Hameri et al., 2002; Sem, 2002), while CPC Distributions 2, 3, and 4 are lower in concentration (due to the lack of undercounting in CPC Distributions 2, 3, and 4 as demonstrated in Figure 6b, the remaining analysis for CPC operation at high concentration considers only CPC Distribution 1.) CPC Cases 8-10 were applied to CPC Distribution 1 in order to determine the concentration measured by the CPC

for 25, 50, 100 and 200 nm aerosols. The counting efficiency was then calculated for each case and aerosol diameter in CPC Distribution 1.”

Page 29 Lines 541-543 the text now reads: “Note that CCN Cases 1-4 are identical to the aerosol distributions. CPC Distributions 1-4 used for the high-concentration CPC cases.”

Page 33 Lines 605-608 the bolded section was added to the following sentence: “In contrast, κ_{app} artifacts are negligible ($< 0.10\%$ of κ_{app}^{NaCl}) in CPC Case 3, where maximum counting efficiency = 100%. CPC Cases 8 and 10 (**applied to the highest-concentration case, CPC Distribution 1**) represent undercounting at high concentration with CPCs where saturation is observed at $4 \times 10^4 \text{ cm}^{-3}$ and $1 \times 10^4 \text{ cm}^{-3}$, respectively.”

Page 33 Lines 611-613 the text now reads: “It should be noted that undercounting was only observed for one of the four upstream distributions studied, CPC Distribution 1. No undercounting was observed when CPC Cases 7-10 were applied to CPC Distributions 2-4.”

Page 55: CPC distributions for operation at high concentration have been added to Table 5, which in turn has been moved earlier in the manuscript to coincide with the first mention of these aerosol distributions. These CPC distributions are identical to the distributions used for CCN Cases 1-4.

Page 56: Three more (total aerosol) distributions have been added to Figure 8b in order to demonstrate the effect of CPC undercounting on lower aerosol concentrations. Figures 8c-i are only applied to the first distribution, CPC Distribution 1, because this is the only distribution in which undercounting occurs.

B. Authors’ response: The ammonium nitrate kappa value comes from Svenningsson et al 2006 (Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance), in which the DMA sample/sheath ratio was maintained between 1.2 and 2, and the DMA-selected diameters fell in the range 50-180 nm. The apparent hygroscopicity for ammonium nitrate was found to be 0.577-0.753, with a mean value of 0.67. If 0.67 is assumed to be the true kappa for ammonium nitrate, then this sample/sheath ratio could lead an experimental kappa as low as 0.65 or as high as 0.69, which would not fully explain the actual experimental range. This assessment ignores possibility of under/over counting which could introduce additional errors. Since CPC and CCN spectrometer concentrations are not discussed in Svenningsson et al 2006, we cannot evaluate the likelihood of under/overcounting. Alternatively, the observed range of values could also arise (to some degree, at least) from fitting the activated fraction data in order to calculate kappa.

- 2) Reviewer comment: The approach used to derive artifacts from DMA in this study is significantly different from the real CCN measurement.

A. Firstly, in the real CCN measurement, uncertainties in SScrit (accordingly kappa) are “produced” in the fitting of activated fraction of particles (either activated fraction vs. supersaturation(SS) for particles of a given size or activated fraction vs. particle size at a given SS). The artifacts derived from DMA was calculated by Eq. 12 based on “volume-weighted diameter-specific perceived κ_{app} values”. I am not sure whether the artifacts in this study can reflect the real uncertainties in CCN measurement. Could the authors assess the uncertainties in kappa using the way that kappa is derived in the real CCN measurement?

B. Secondly, I am not sure whether the method used to calculate κ and (and to derive SScrit) is appropriate. Why the authors used “volume-weighted” approach? In my opinion, when the particle size distribution broadens, the number of both the larger particle and smaller particles increase in a largely similar rate. Then the ratio of activated particles (larger particles) to total particles (measured by CPC) as well as SScrit and κ should be relatively invariant.

A. Authors’ response: To clarify, the uncertainties in critical saturation that arise from fitting the activated fraction data may be produced by several physical factors. First, the size of the aerosols will affect the fit. A broader size distribution will lead to a larger standard deviation in the sigmoid curve fit. Secondly, composition will also affect the standard deviation in the fit; a pure aerosol (one compound) may be fit with a sigmoid curve characterized by a smaller standard deviation, and the sigmoid curve fit for a mixture will have a larger standard deviation. Pure compounds were analyzed in this theoretical study, so the broadened size distribution was the only factor taken into account. The uncertainties in critical supersaturation are determined experimentally rather than theoretically in CCN experiments.

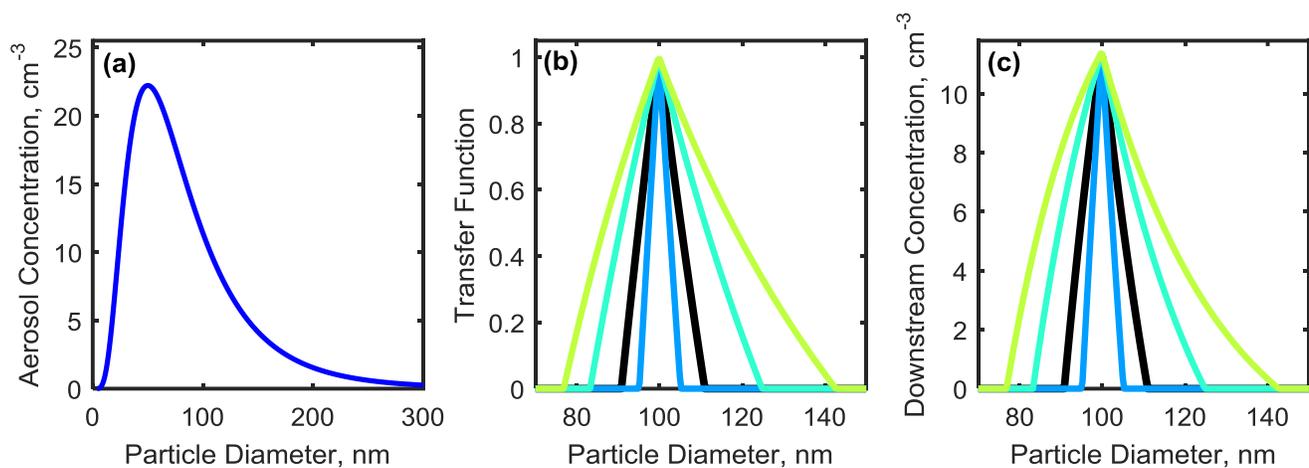
B. Authors’ response: The volume-weighted approach accepted as a standard convention of κ theory. The κ for a mixture consisting of i components is calculating using a volume-weighted mixing rule (Petters and Kreidenweis 2007):

$$\kappa = \sum_i \epsilon_i \kappa_i$$

Where ϵ_i is the volume fraction of each component, and κ_i is the hygroscopicity of each component. In this case, a pure compound is used instead of a mixture; instead, each component is an aerosol with a specific diameter, and each κ_i is the perceived κ that would be calculated using the diameter selected at the DMA.

When the particle distribution broadens, smaller and larger electrical mobilities are favored equally/symmetrically, but this is not the case for smaller and larger particles. We have included Figure 3 from my paper below as an illustration. Figure 3b demonstrates that the transfer function is broadened more dramatically for larger diameters than for smaller diameters, and that this effect increases as the aerosol/sheath flow increases in the DMA (aerosol/sheath ratios: blue line = 0.05, black line = 0.1, mint green line = 0.2, yellow-green line = 0.3). Under recommended operating conditions (aerosol/sheath ratio ≤ 0.1), this effect is relatively small.

The aerosol distribution at the DMA inlet must be considered as well. A theoretical distribution was used in this analysis (Fig. 3a below). In this distribution, aerosols larger than the selected diameter would be favored over smaller aerosols if the selected diameter is less than 50 nm (the distribution peak); if the selected diameter is larger than 50 nm, smaller aerosols would be overrepresented compared to larger aerosols. This effect would be diminished if the aerosol distribution at the DMA sample inlet was broader than the theoretical distribution shown; conversely, this effect would be more dramatic if the aerosol distribution was narrower than the one shown.



- 3) Reviewer comment: In the CCN activation measurement, the supersaturation of CCN counter is often calibrated using the theoretical data of (NH₄)₂SO₄ or NaCl in the literature (Rose, Gunthe et al. 2008). The kappa of the standards ((NH₄)₂SO₄ or NaCl) and the sample aerosol would have the bias of the same direction. This may largely compensate the artifact of CCN measurement and thus lessen the role of instrument artifacts in the discrepancy between different measurements. It may be helpful to discuss this aspect.

Authors' response: This is an interesting point, and the bias in the kappa determined from the standards should be in the same direction as the bias in an experimental CCN measurement. However, the magnitude of this bias may not be the same for the standards and the aerosol studied in a CCN experiment (for pure compounds or mixtures). The biases ($\kappa_{app,theory} - \kappa_{app,literature}$) observed in this study, as shown below in Figure 4, are not equal for the two ionic compounds studied. The relative bias may be similar (for example, if the experimental apparent hygroscopicity of sodium chloride is calculated to be 10% higher than the true value, one might expect ~10% overestimation of the apparent hygroscopicity of an aerosol sample calculated using data from the same CCN instrument). This would not necessarily lead to 100% compensation in the experimentally-determined apparent hygroscopicity for the aerosol sample being studied. However, some compensation would be reasonable to expect. This study considers two compounds that are used as standards for CCN instrument calibration. A further analysis could apply these results to an experimental setting, in which such compensation is discussed.

Authors' changes in manuscript:

Page 34 Lines 627-631 the text now reads: "We note that Fig. 4c-d demonstrated that κ_{app} error may result from instrument artifacts for ammonium sulfate and sodium chloride, two standard compositions used in calibration of CCN instruments (Rose et al., 2008). Therefore, the κ_{app} error encountered while calibrating the CCN instrument may compensate for the CCN measurement bias of aerosol samples. However, as also demonstrated in Fig. 4c-d, the magnitude of this instrumentally-derived bias varies by compound.

Specific comments

1. Reviewer comment: L62, why do the authors particularly mention sea spray aerosol among various aerosol types?

Authors' response: Sea spray is an important natural source of aerosols, but our initial discussion left out other common aerosol types. To broaden the discussion, a reference has been added to another study which summarizes the apparent hygroscopicity values of continental aerosols (Andreae and Rosenfeld 2008).

Authors' changes in manuscript:

Page 6, Lines 79-81, the text now reads: "Another study, which included a survey of observational CCN data, proposed that marine and continental aerosols could be described by κ_{app} values of 0.7 ± 0.2 and 0.3 ± 0.1 respectively (Andreae and Rosenfeld 2008)."

2. Reviewer comment: L457, it is worth noting that these values are for the artifacts of CPC or CCN alone. The artifacts from CPC and CCN counting at high aerosol concentration counteract. Therefore, the combined effect of the CPC and CCN is much lower as the authors mentioned in L445-447. Please also state that these values (" $-0.57 < \kappa_{app,artifact} < 0.42$ ") are for NaCl.

Authors' response: We thank the reviewer for this interesting point and have modified the text accordingly.

Authors' changes in manuscript:

Page 36, Lines 650-652 the text now reads: "The largest artifacts ($-0.57 < \kappa_{app,artifact} < 0.42$ for sodium chloride) in this study arise from undercounting by condensation particle counters and cloud condensation nuclei counters at high concentration."

Page 35, Lines 650-652 the text now reads: "It should be noted that these artifacts are for individual instruments and do not take combined operation of the CPC and CCN into account; when both instruments undercount, artifacts in $\kappa_{app,artifact}$ are reduced."

3. Reviewer comment: L137, the literature of the kappa values is not provided.

Authors' response: the apparent hygroscopicity is taken from Svenningsson et al 2006, which was previously group with other literature citations on line 139. This reference has been moved for clarity.

Authors' changes in manuscript:

Page 10, Lines 153-157 The text now reads: "Experimental results for ammonium nitrate are inconsistent with reported values ranging from $0.577 \leq \kappa_{app} \leq 0.753$ (Svenningsson et al., 2006). Also, large ranges are often observed for organic compounds, such as glutaric acid ($0.054 \leq \kappa_{app} \leq 0.16$) and malonic acid ($0.199 \leq \kappa_{app} \leq 0.255$) (Koehler et al., 2006; Kumar et al., 2003; Hartz et al., 2006)."

4. Reviewer comment: L202, L is not defined.

Authors' response: Corrected. Thank you for pointing this out.

Authors' changes in manuscript:

Page 14 Line 232 The text now reads: "where L is the distance between the DMA inlet and outlet."

5. Reviewer comment: L216, the detailed motivation of design these 7 cases are not available (although they are mentioned in the conclusion section).

Authors' response: We agree that the logic for choosing these cases warrants further explanation. We have added a few sentences to explain the motivation for these seven cases.

Authors' changes in manuscript:

Page 14 Lines 242-249 The text now reads: "These seven cases were chosen to represent possible measurements scenarios that may be encountered in a CCN experiment. The aerosol/sheath ratio is varied in Cases 1-4 in order to study the effects of chosen experimental parameters. Sheath flow is predetermined in some DMAs (for example, the Grimm Vienna DMA considered in this study), but can be varied in other instruments. The aerosol flow rate may also be selected in an experiment. Cases 5-7 vary the excess/sheath ratio in order to take proper instrument operation into account. The excess and sheath flow should be identical, but small discrepancies may occur."

6. Reviewer comment: L253, it is not clear how exactly the κ_{app} , theory (and κ_i) is derived. ϵ_i and κ_i are not defined. Please elaborate. And why do the authors use volume-weighted kappa?

Authors' response: Thank you for pointing out our mistake. These definitions have now been added to the manuscript (see below). A fuller explanation for volume-weighted kappa is given in my response to General Comment 2b.

Authors' changes in manuscript:

Page 16 Lines 288-289 the text now reads: "where ϵ_i is the volume fraction of aerosol of each diameter i , and κ_i is the perceived κ_{app} for each diameter (adapted from Petters and Kreidenweis [2007])."

7. Reviewer comment: L266-268, the artifacts due to the ratio of excess flow to sheath flow are not really discussed here, even less than in the abstract.

Authors' response: We have commented further on artifacts that may arise due to unequal sheath and excess flow rates.

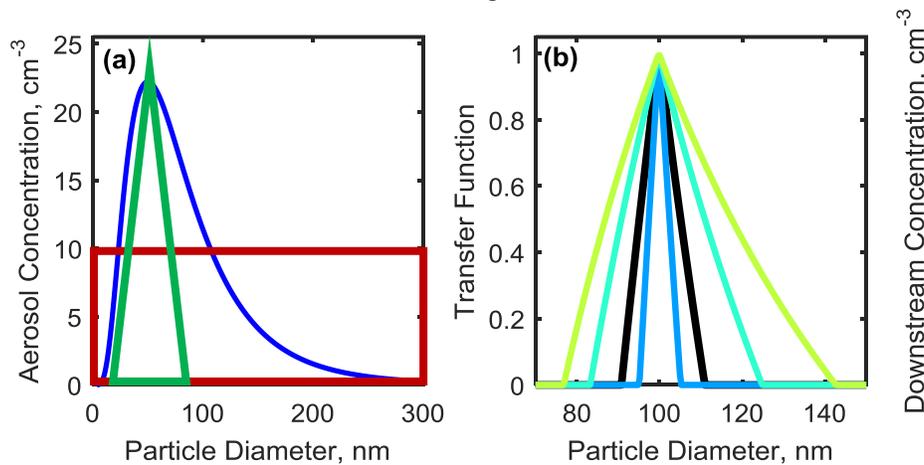
Authors' changes in manuscript:

Page 17, Lines 301-306 the text now reads: Artifacts were also high for DMA case 6 ($-0.025 \leq \kappa_{app,artifact}^{(NH_4)_2SO_4} \leq -0.018$) and DMA case 7 ($0.016 \leq \kappa_{app,artifact}^{(NH_4)_2SO_4} \leq 0.017$), where sheath and excess flow were unequal. This result demonstrates that artifacts may still occur when low aerosol/sheath flow ratios are chosen (0.15 and 0.08 for DMA cases 6 and 7, respectively) due to small differences between sheath and excess flow rates (5% and 2% for DMA cases 6 and 7, respectively).

8. Reviewer comment: L412-416, why would “a distribution with a narrower peak than the one generated for this analysis be at risk for larger κ_{app} artifacts for any total aerosol concentration...?”

Authors’ response: We will use Figure 3 (parts a and b), shown below, to illustrate this concept. To make it more clear, the theoretical distribution used in this study is the blue curve in Figure 3a. We have now added a red rectangle to represent an extremely broad distribution, where the concentration of an aerosol does not depend on its diameter, and a green triangle to represent a much narrower distribution, where the concentration of an aerosol depends strongly on its diameter.

In the extremely broad case (red), the DMA output would have the same shape as the transfer function, with a peak concentration at 100 nm of 10 cm⁻³. This is because the transfer function varies with particle diameter, but the concentration at the DMA inlet does not vary with concentration. In the theoretical case used in this study (blue), particles smaller than 100 nm would be favored over particles larger than 100 nm due to the shape of the aerosol distribution at the DMA inlet; this is because the concentration at the inlet and the transfer function both vary with diameter. In narrowest distribution (green), only particles smaller than 100 nm would be represented. This would skew the experimental activated fraction and hygroscopicity more dramatically than in the theoretical distribution (blue), and no skewing would occur in the broadest case (red).



Technical comments

1. Reviewer comment: I suggest numbering the section from the “Introduction”.

Authors’ response/change to manuscript: This is a good suggestion. The Introduction has now been changed to Section 1, and the numbering throughout the manuscript has been adjusted accordingly.

- Andreae, M. O., and D. Rosenfeld. 2008. "Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols." *Earth-Science Reviews* 89 (1-2):13-41. doi: 10.1016/j.earscirev.2008.03.001.
- Hameri, K., C. D. O'Dowd, and C. Hoell. 2002. "Evaluating measurements of new particle concentrations, source rates, and spatial scales during coastal nucleation events using condensation particle counters." *Journal of Geophysical Research-Atmospheres* 107 (D19):11. doi: 10.1029/2001jd000411.
- Petters, M. D., and S. M. Kreidenweis. 2007. "A single parameter representation of hygroscopic growth and cloud condensation nucleus activity." *Atmospheric Chemistry and Physics* 7 (8):1961-1971. doi: 10.5194/acp-7-1961-2007.

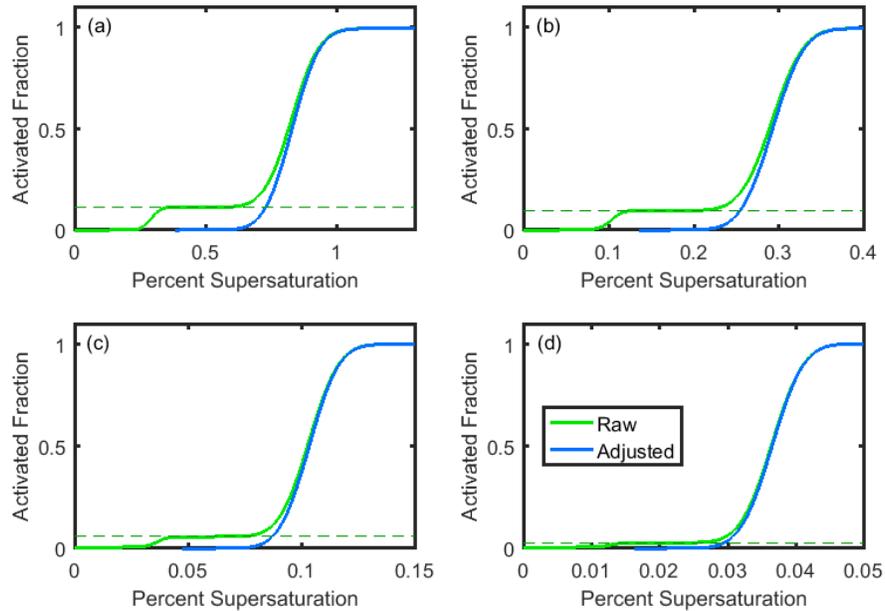
Authors' response to referee comments on "Instrument Artifacts Lead to Uncertainties in Parameterizations of Cloud Condensation Nucleation"

Referee #2

Authors' response: We thank the Reviewer for her/his feedback, which we feel have improved the manuscript. New sections have been added to the manuscript in order to address the recommended revisions. While it is beyond the scope of this manuscript to address very possible source of uncertainty in detail, we have added significantly to the discussion of errors. In particular, to address the Reviewer's concern that we had not included uncertainties which arise due to multiple charging in the DMA, we have now performed calculations and added a new figure and addition text to the manuscript. Multiple charging uncertainties are incorporated into our overall analysis and conclusions. Additional specific modifications are discussed below.

- 1) Reviewer comment: Even though more discussion about artifacts and good practice in CCN measurements are needed, this is not the first paper dealing with the issue and with the role of DMA flow ratio in determining the precision in fitting step functions for evaluating number of CCN as a function of supersaturation. I would recommend that this literature is summarized and that results in this paper are discussed in perspective of this literature.

Authors' response: We thank the reviewer for this suggestion. The previous literature regarding the role of flow ratio in precision of fitting the step functions include the works of Petters et al. (2007b), Rose et al. (2008) and Zhao-Ze and Liang (2014) which are now discussed in the text. To summarize, the DMA sample/sheath flow ratio increases, the DMA transfer function broadens, allowing particles that area both larger and smaller than the selected diameter to exit the DMA. This in turn broadens the CCN activated fraction curve (Rose et al., 2008). DMA transfer function broadening may be significant enough to also increase the concentration of multiply-charged particles downstream of the DMA, resulting in the appearance of "plateaus" in the activated fraction curves. An example of a plateau is shown in the figure below, where the green lines correspond with raw activated fractions and the dashed lines on each plot correspond with the activated fraction plateau for 25, 50, 100, and 200 nm diameter particles. This figure is further discussed in a new section in the manuscript, 3.1.3 Effect of double and triple charges on particles. The effects of multiple charges are addressed in more detail in the response to Question 4. A new section has also been added to the manuscript to address particles with multiple charges, 3.1.3 Effect of double and triple charges on particles.



Authors' changes to the manuscript

Pages 21-22 Lines 393-404 the text now reads: “The aerosol/sheath ratio within the DMA also modulates the effect of multiple charges on κ_{app} . As the aerosol/sheath ratio increases, the transfer function broadens, allowing particles that are both larger and smaller than the selected diameter to exit the DMA. This in turn broadens the CCN activated fraction curve (Rose et al., 2008). The larger particles will activate as CCN at lower supersaturations than particles with the selected diameter, resulting in an increase in the activated fraction plateau due to multiple-charged particles and a further decrease in the determined SS_{crit} . Petters et al. 2007b showed that CCN activated fraction curves are significantly skewed by multiply-charged particles when the mode diameter of the aerosol population upstream of the DMA exceeds the critical diameter of the size-selected particles. In an example CCN activated fraction curve, Rose et al. 2008 demonstrated that a 1:6 ratio of doubly-to-singly charged particles resulted in an underestimated of the critical activation diameter by 2%. Zhao-Ze and Liang, 2014 also showed that multiply-charged particles can introduce significant uncertainty in values of kappa (~17%) into hygroscopicity calculations.”

- 2) Reviewer comment: Also, the use of hygroscopicity parameterizations goes much further back in time than indicated in this manuscript. The parameter epsilon is originally adopted from the work by Fitzgerald (1975) and in 1982 Fitzgerald et al. suggested a single hygroscopicity parameter (Bc). There might be even older literature.

Authors' response: This is a good point, thank you. The Reviewer is referring to hygroscopicity parameterizations which precede the "kappa" notation but are nonetheless about hygroscopicity, and yes, we agreed that these references should be included. A number of references to earlier works have been added to the manuscript's introduction. Specific changes are described in the revised text below.

Authors' Changes to the manuscript:

Page 5 Lines 59-72 the text now reads: “Parameterizations of hygroscopicity that pre-date Petters and Kreidenweiss 2007 exist as well. Winkler 1973 developed an equation for approximating the growth of an aerosol particle with relative humidity, based on the quantity and physical characteristics of the

soluble species in the particle. Another approximation for the relationship between the equilibrium size of a particle and relative humidity was derived by Fitzgerald in 1975, in which the soluble fraction and composition of the soluble component(s) are taken into account. Fitzgerald et al., 1982 derived a particle composition parameter using the mass fraction and physical properties of soluble material in a particle. Kreidenweis et al., 2005 determined that the critical activation diameter of dry aerosol particles can be calculated from simplified Köhler theory using the physical properties of water and the solute in a solution droplet. This parameterization has been used in CCN closure studies (Bougiatioti et al., 2009; Moore et al., 2011; Moore et al., 2012a). The earliest prediction of CCN concentrations for specific particle diameters and hygroscopicity used this parameterization as well (Mochida et al., 2006).”

3) Reviewer comment: I also recommend that the authors state the limitations of the paper clearly:

A) All CCN measurements are not done with the set up indicated in figure 1. Lab studies can be performed with an SMPS instead of CPC if evaporation from the particles is suspected.

B.) Field studies at low particle concentrations are made without a DMA upstream the CCNC. These measurements have their own issues.

A. Authors’ response: We now state the scope of limitation of the paper clearly. The scope of this manuscript includes only CCN measurements that are used to calculate apparent hygroscopicity from critical supersaturation, which in turn is determined from activated fraction curves for monodisperse (or near-monodisperse) aerosol. Other setups can be used for CCN measurements, as the reviewer correctly points out. For example, if evaporation is a concern, an SMPS can be used to determine the size distribution of the aerosol particles. An SMPS can also be used in conjunction with unsized CCN measurements. A clarification has been added to section 3. Artifacts derived from CCN measurements (now titled “Artifacts derived from size CCN measurements”).

Authors’ changes to the manuscript:

Page 11 lines 162- the text now reads (additions are bolded): “CCN measurements **used for calculating apparent hygroscopicity from monodisperse aerosol** require accurate operation of three instruments: the CCN, the differential mobility analyzer (DMA), and the condensational particle counter (CPC). The setup for laboratory CCN experiments is shown in Fig. 1. First, a polydisperse population of aerosols is generated by an atomizer and dried using a desiccant tube packed with silica gel. A near-monodisperse flow is obtained through size-selection in the DMA. The flow is then split between a CPC (which measures aerosol concentration) and a CCN counter (which measures the concentration of particles that activate as cloud condensation nuclei at a given percent supersaturation). **Instrument artifacts will first be assessed separately for the DMA, CPC, and CCN counter. In the concluding section of the paper (and Fig. 10), the overall uncertainty due to the combination of these is presented and discussed.**

We note that this study considers sized CCN measurements which may be used for the determination of κ_{app} . In contrast, a number of earlier CCN studies conducted on the full ambient aerosol population without sizing the aerosol (Jennings et al., 1996; Hudson and Xie, 1998; Modini et al., 2015; Duan et al., 2017; Schmale et al., 2018; Leng et al., 2013). While useful, such studies do not produce the data required for accurate determination of κ_{app} from the CCN measurements.”

B. Authors' response: The Reviewer is correct that a large number of field studies have been conducted without a DMA to size-select the aerosol prior to CCN measurements, Although these are somewhat different than the sized CCN measurements which are the focus of this paper, it is a good idea to mention them here. Examples which we now cite in the text include Jennings et al., 1996; Hudson and Xie, 1998; Modini et al., 2015; Duan et al., 2017; Schmale et al., 2018; Leng et al., 2013. However, our manuscript focuses on sized CCN measurements which may be used for the determination of κ_{app} . This is now clearly stated on page 10.

Authors' Changes to the manuscript:

Page 11 Lines 175-182 the text now reads: "This study considers sized CCN measurements which may be used for the determination of κ_{app} . In contrast, CCN studies are often conducted on the full ambient aerosol population without sizing the aerosol (Jennings et al., 1996; Hudson and Xie, 1998; Modini et al., 2015; Duan et al., 2017; Schmale et al., 2018; Leng et al., 2013).

Instrument artifacts will first be assessed separately for the DMA, CPC, and CCN counter. In the concluding section of the paper (and Fig. 10), the overall uncertainty due to the combination of these is presented and discussed."

4). Reviewer comment: Another limitation is that the paper does not treat all the important artifacts.

A. An example is uncertainty in sizing due to evaporation of particle material or residual water in the particles while sized in the DMA. I can understand if this is out of scope for this article, but they could be mentioned.

B. Other sources of errors are closer to the focus of this paper and could be included or at least references made to papers discussing them. I am mainly thinking about three effects. The first is the role of doubly charged particles, especially in lab studies in which atomized aerosols can be overcharged in comparison to equilibrium charge distribution and radioactive sources normally used are not strong enough to neutralize the aerosol.

C. Voltage offset in the DMA is sometimes an issue, especially when working with high supersaturations and small aerosol particle sizes.

D. The role of counting variability due to sampling statistics at low concentrations and how it influences the determination of SSc in different cases (for example different flow ratios).

A. Authors' response: While we cannot address all possible artifacts in this manuscript, a new section has been added to the manuscript to address sources of artifacts that are beyond the scope of the study, but should still be considered (3.1.4 Additional artifacts resulting from DMA measurements). We have included a short discussion of particle evaporation and growth due to volatility and hygroscopicity, respectively.

Authors' Changes to the manuscript:

Pages 22-23 Lines 408-426 the text now reads: "Several other factors that may impact experimental κ_{app} are beyond the scope of this study, but are worth mentioning as they represent additional potential sources of error in some cases. First, volatile aerosols may partially evaporate inside the DMA, resulting in a decrease in particle size exiting the DMA. DMA sizing error due to aerosol volatility (defined as the ratio of sampled diameter to the selected diameter) increases with volatility, though sizing error can be decreased by increasing the sheath flow rate in the DMA. Conversely, hygroscopic aerosols may grow inside the DMA, resulting in larger particles existing the DMA.

Operationally, errors in DMA sizing due to hygroscopic growth can be mitigated if aerosols entering the DMA inlet are in wet metastable states (higher aerosol RH at DMA inlet), and if DMA sheath flow rates are kept low (Khlystov, 2014)."

B. Authors' response: The reviewer has a valid point. On further consideration, we now include full consideration of one additional significant artifact, effects of multiple charging, in our analysis. We have added an analysis of multiple particle charges to the manuscript in a new section (3.1.3 Effect of double and triple charges on particles). In addition, 3 new figures have also been added (Figure S2 in supplement, Figures 5 and 6 in manuscript, all shown below).

Authors' Changes to the manuscript:

Pages 17-21 Lines 316-397 the text now reads: " During normal operation, the Grimm DMA employs a bipolar charger (also known as a neutralizer) to charge aerosol particles through the capture of gaseous ions. The analysis in Section 3.1.2 assumes that each particle carries a single (+1) charge. In reality, the methods used to charge particles prior to entering a DMA may impart two, three, or more charges to individual particles (Fuchs, 1963). The charge distribution resulting from a bipolar charger is roughly approximated using the Boltzmann law (Keefe et al., 1959). However, the Boltzmann law assumes symmetric aerosol particle charging (equal concentrations of negatively and positively charged particles). Deviation from symmetric charging is observed in regions of high ionizations, and this deviation becomes more pronounced as particle size increases (Hoppel and Frick, 1990). A more accurate estimation of stationary charge distribution has been calculated using an approximation formula for the charge distribution produced by a bipolar charger:

$$f(k) = 10^{\left[\sum_{i=0}^{i=5} a_i(k)(\log_{10} D_{nm})^i\right]} \quad (13)$$

where $f(k)$ is the fraction of particles carrying k charges, $a_i(k)$ are approximation coefficients determined using a least-squares regression analysis, and D_{nm} is the particle diameter in nanometers (Wiedensohler, 1988). The approximation coefficients only apply to particles with 0, ± 1 , and ± 2 charges. In a separate study, **Maricq et al., 2008** determined approximation coefficients for poly (α -olefin) oligomer oil droplets with ± 1 , ± 2 , and ± 3 charges. The approximation coefficients reported by these two studies were in excellent agreement for particles with ± 1 and in weak agreement for ± 2 charges (+2 and -2 charging efficiencies were overestimated by 50% and 100%, respectively). Therefore, this analysis will use the approximation coefficients from Wiedensohler, 1988 for particles with +1 and +2 charges, and the approximation coefficient for particles with +3 charge from Maricq et al., 2008.

In order to assess the impact of multiple charges on κ_{app} , Eq. (13) and the approximation coefficients from Wiedensohler, 1988 and Maricq et al., 2008 were used to calculate the charge distribution of the representative aerosol population shown in Fig. 3a. The resulting charge distribution is shown in Fig. S2a. An increase in multiple charging is observed as particle diameter increases, though this is offset somewhat by the decrease in concentration with particle size above 50 nm.

It follows that aerosols incorrectly sized due to double and triple charging will be passed from the DMA to the CCN and result in an additional uncertainty in the CCN measurements. To illustrate this, activated fraction curves, were generated for 25, 50, 100, and 200 nm sodium chloride particle selection by the DMA (Fig. 5). The activation of sodium chloride is represented by sigmoid curves, where the midpoint of each activation curve is the κ -Köhler-derived critical supersaturation of sodium chloride, and the standard deviation of each curve is one-tenth of this value (consistent with the

standard deviation/midpoint ratio observed from our instrument's ammonium sulfate CCN calibration data). For each particle diameter, D , the observed activated fraction, $AF_{D,weighted}^{SS}$, for each percent supersaturation SS was determined by weighting the activated fraction $AF_{D,i}^{SS}$ of each particle diameter/charge at that percent supersaturation, by the fraction of particles of that diameter:

$$AF_{D,weighted}^{SS} = \sum_{i=1}^{i=3} \frac{\text{concentration of particles with charge } i \text{ and diameter } D}{\text{concentration of particles with charge } +1, +2, +3, \text{ and diameter } D} AF_{D,i}^{SS} \quad (14)$$

The raw data shown in Fig. 5 (green curves) can be corrected for multiple charging by determining the fraction of particles with $> +1$ charge from the lower plateau in each plot (dashed lines). The adjusted activated fraction for each percent supersaturation, $AF_{adjusted}$, is calculated using the equation:

$$AF_{adjusted} = \frac{AF_{raw} - AF_{plateau}}{1 - AF_{plateau}} \quad (15)$$

where AF_{raw} is the raw activated fraction at that percent supersaturation, and $AF_{plateau}$ is the activated fraction corresponding to the lower plateau (Rose, 2008). The adjusted activated fraction curves are shown in Fig. 5 (blue curves). These are in good agreement with the theoretical κ -Köhler-derived activation curves for sodium chloride (not shown).

Critical supersaturation was determined for each diameter by calculating the percent supersaturation at which the raw $AF_{D,weighted}^{SS} = 0.5$. These critical supersaturations are shown in Fig. 6a, and the theoretical critical supersaturations calculated from κ -Köhler theory are shown for comparison. Eq. 4 was used to calculate apparent hygroscopicity for each particle diameter, shown in Fig. 6b. A dashed line in Fig. 6b indicates the literature value for κ_{app}^{NaCl} . It is apparent that failing to account for multiply-charged particle in the activated fraction curves shown in Fig. 5 leads to an overestimation of κ_{app} . Artifacts in κ_{app} are shown in Fig. 6c.

For the theoretical aerosol distribution used in this analysis (Fig. 3a), small, positive deviations from κ -Köhler theory and the literature value for κ_{app}^{NaCl} were observed ($0.01 \leq \kappa_{app,artifact}^{NaCl} \leq 0.04$, 1 – 3 % of κ_{app}^{NaCl}). As shown in the figure, κ_{app} artifacts resulting from unaccounted-for multiple charges decrease with particle diameter for this theoretical aerosol population. Greater κ_{app} artifacts would be expected for aerosol populations with more prevalent accumulation modes.

The aerosol/sheath ratio within the DMA also modulates the effect of multiple charges on κ_{app} . As the aerosol/sheath ratio increases, the transfer function broadens, allowing particles that are both larger and smaller than the selected diameter to exit the DMA. This in turn broadens the CCN activated fraction curve (Rose et al., 2008). The larger particles will activate as CCN at lower supersaturations than particles with the selected diameter, resulting in an increase in the activated fraction plateau due to multiple-charged particles and a further decrease in the determined SS_{crit} . Petters et al. 2007b showed that CCN activated fraction curves are significantly skewed by multiply-charged particles when the mode diameter of the aerosol population upstream of the DMA exceeds the critical diameter of the size-selected particles. In an example CCN activated fraction curve, Rose et al. 2008 demonstrated that a 1:6 ratio of doubly-to-singly charged particles resulted in an underestimation of the critical activation diameter by 2%. Zhao-Ze and Liang, 2014 also showed that multiply-charged particles can introduce significant uncertainty into hygroscopicity calculations.”

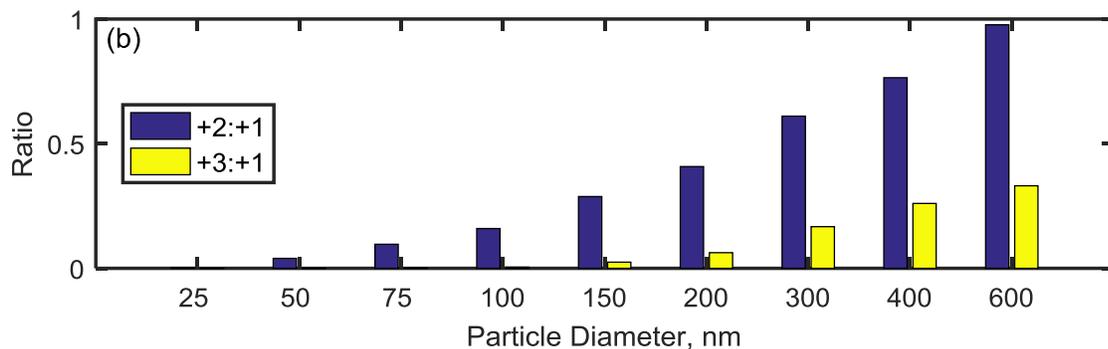
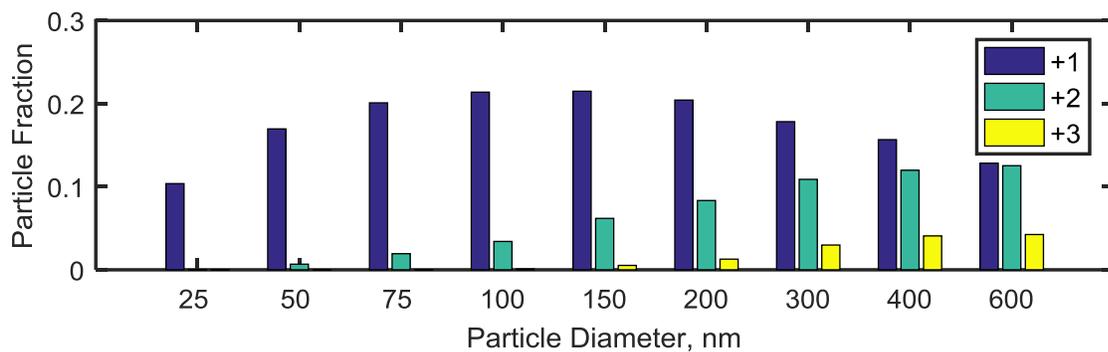


Figure S2 (a) Stationary charge distribution on particles shown in Fig. 3a. The particle diameters were chosen to represent particles that would be present due to single, double, and triple charging for the DMA selected diameters 25, 50, 100, and 200 nm. (b) Ratio of multiple charged particles to single charged particles.

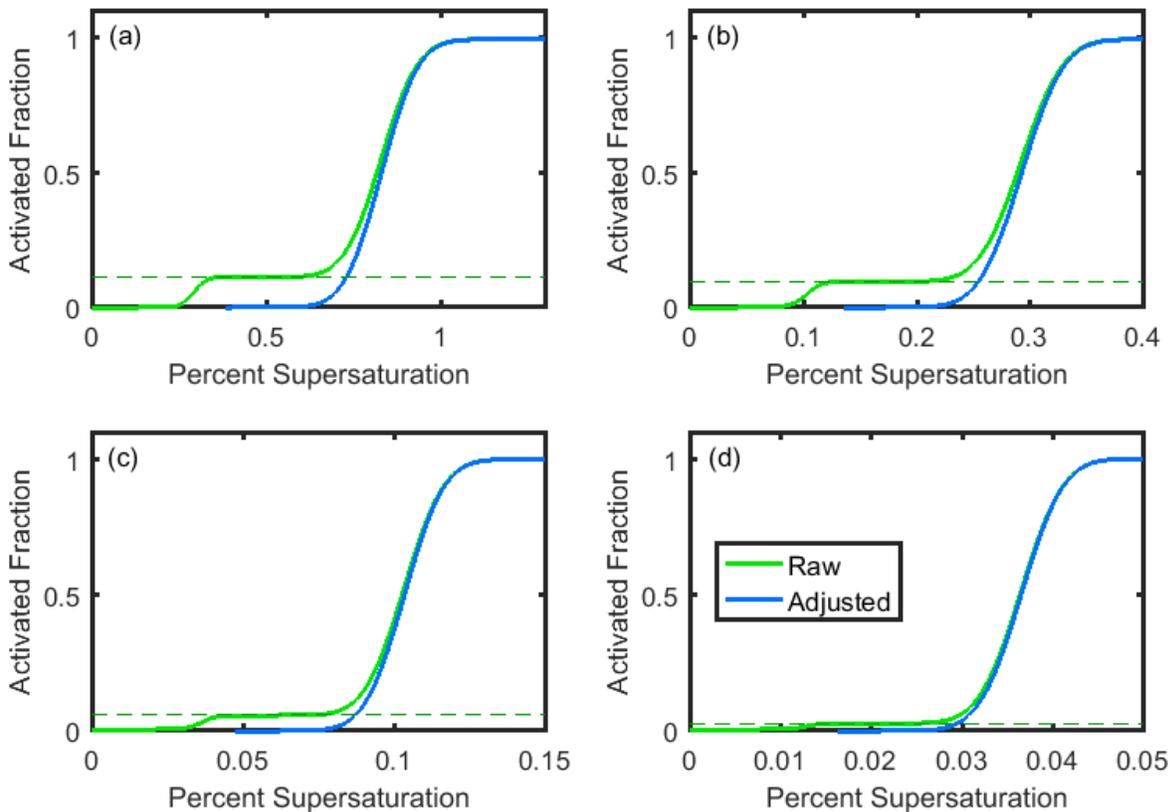


Figure 5 (a) Theoretical raw and adjusted activated fraction curves for single charged 25 nm particles, double charged 50 nm particles, and triple charged 75 nm particles; (b) single charged 50 nm particles, double charged 100 nm particles, and triple charged 150 nm particles; (c) single charged 100 nm particles, double charged 200 nm particles, and triple charged 300 nm particles; (d) single charged 200 nm particles, double charged 400 nm particles, and triple charged 600 nm particles. All particles are pure sodium chloride.

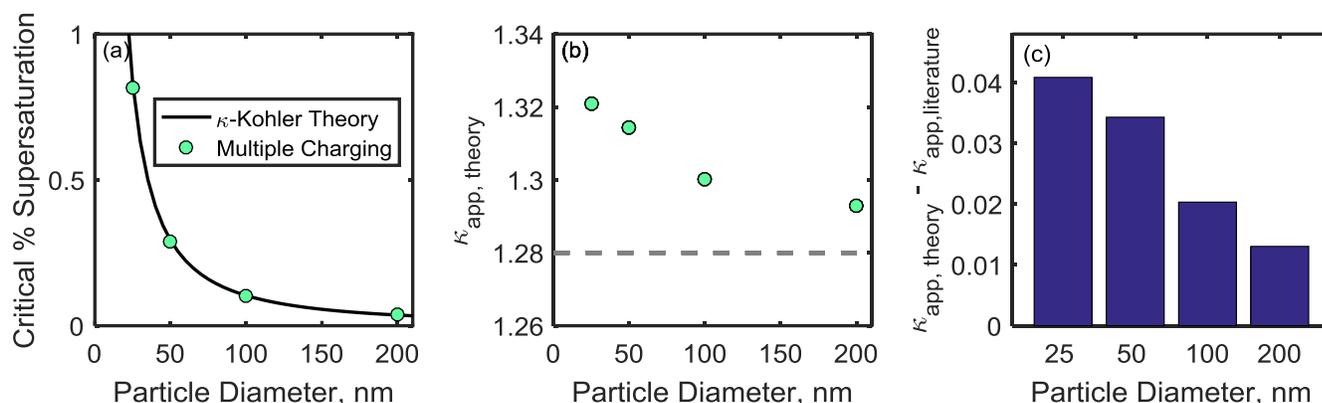


Figure 6 (a) The critical supersaturation of sodium chloride particles determined from the activated fraction curves in Fig. 5. A sodium chloride curve calculated using κ -Köhler theory is shown for comparison. (b) κ_{app} was calculated for the charge distribution; the gray dashed line indicates the literature value for the κ_{app} of sodium chloride. (c) κ_{app} artifacts resulting from multiple particle charges.

C. Authors' response: A new section has been added to the manuscript (3.1.4 Additional artifacts resulting from DMA measurements) that includes a short discussion of voltage shifts that may result from the space-charge field observed due to separation of the charged aerosol particles.

Authors' changes to the manuscript:

Pages 21-22 Lines 411-419 the text now reads: "Voltage shifts within the DMA (differences between the selected voltage and the actual voltage inside the DMA) can lead to discrepancies between selected and sampled particle diameters. Voltage shifts may result from a space-charge field generated by the motion of charges within the DMA. Particles charged by the neutralizer will either be attracted towards or repelled away from the inner column of the DMA, depending on whether they are positively or negatively charged. This charge separation creates a space-charge field which shifts the actual voltage within the DMA from the selected voltage. The impact of the space-charge field on the midpoint and spread of the DMA transfer function increases as particle mobility increases (as particle size decreases), and as particle concentration increases (Alonso and Kousaka, 1996; Alonso et al., 2000; Alonso et al., 2001)."

D. Authors' response: New text has been added to the manuscript in order to address this issue (6. Counting statistics in CCN and CPC measurements).

Authors' changes to the manuscript:

Page 31 Lines 572-577 the text now reads: "Though it is beyond the scope of this analysis, it should be mentioned that sampling at very low particle concentrations ($< 200 \text{ cm}^{-3}$ total particle concentration) can introduce additional error into CCN and CPC measurements. This error can be mitigated by increasing scan times (Moore et al., 2010). For example, Moore et al., 2010 averaged CCN and particle concentrations over 5-second intervals for monodisperse particle concentrations $<$

10 cm⁻³, and increased averaging time to 20-second intervals when the monodisperse particle concentration reached < 6 cm⁻³”

- 5) Reviewer comment: I also have a comment that might sound nerdy, but I find it important that we stick to the definition of an aerosol as a population of solid and/or liquid particles and the surrounding gas. Thus, we should not talk about aerosol size, when referring to the size of the particles. Please check the manuscript in line with this.

Authors’ response: the reviewer is correct about the technical difference between aerosols and particles, but we respectfully disagree that the term needs to be changed in the manuscript. “Aerosol” is often used synonymously with “aerosol particle”. In keeping with convention, we will not change the current wording. Doing so would likely make the text less clear.

- 6) Reviewer comment: It is not clear how the critical supersaturation is determined: is it defined as the supersaturation at which #CCN/#CN is 0.5 or when its value is 50% of the level reached at high supersaturation (the later often being used in experimental work)? This will in some of the examples make a large difference, and need to be discussed. An example is line 346-348.

Authors’ response: Activated fraction data is fit with a sigmoid error function to determine the supersaturation at which 50 % of the particles have activated as CCN (activated fraction = 0.50), which is considered the operationally defined critical supersaturation SS_{crit} (Rose et al., 2008). An alternative approach is to define critical supersaturation as the value of supersaturation corresponding to 50% of the maximum observed value. However, this alternative method has a caveat in cases of external aerosol mixtures which include non-hygroscopic members. In such cases, the highest CCN/CN reached will be much lower than 1 (due to the inactive member aerosols) and thus the resulting value of critical supersaturation would be lower than the SS required to the active aerosol members to become CCN. A clarification has been added to the Background section of the manuscript.

Authors' changes to the manuscript: Page 9 Lines 139-141 the text now reads (clarification bolded): "Activated fraction data is fit with a sigmoid error function to determine the supersaturation at which 50 % of the particles have activated as CCN (**activated fraction = 0.50**), which is considered the operationally defined critical supersaturation SS_{crit} (Rose et al., 2008)."

Additional clarification was added to Section 4.1 CPC operation at low concentration.

Page 24 Lines 461-462 the text now reads (additions are bolded): “ SS_{crit} was determined for each CPC case by **finding the percent supersaturation at which activated fraction = 0.50.**”

- 7) Reviewer comment: Please check the plots with particle size distributions. The y-axis should be dN/dDp (with the unit cm⁻³ nm⁻¹) if a linear diameter scale is used. Why are you using a linear diameter scale and not a logarithmic? Also, see my comments to figure 6 and 7 below. I think that these are critical for the quality of the paper and the conclusions!

Authors’ response: We see the Reviewer's point here. Employing dN/dDp is one of the standard way to plot an aerosol size distribution and readers are likely to be comfortable viewing such graphs. It is advantageous to view instrumental data in dN/dlogDo format, in which the normalization accounts for differences in the widths of size bins employed by various instruments and in various size ranges. However, our analysis is based on a theoretical aerosol distribution in which there are no disparate

ranges in size bins to account for, and thus normalization is not necessary. For the purposes of this analysis, it is more straightforward to plot concentration in lieu of $dN/d\log D_p$.

In the original text, logarithmic scales were used for particle size distribution plots in Figures 8a and 8b (previously Figures 6a and 6b) and in Figure 9b (previously Figure 7b). A linear scale is used in Figures 3a and 3c because we feel that it clearly demonstrates “visual multiplication” (combining the distribution in 3a with the transfer function for 100 nm particles in 3b) performed in our analysis. In addition, given the small range of concentrations observed in Figure 3c, this is the clearest presentation of the data.

8) Reviewer comment: Also, make sure that the figure captions and legends are sufficient.

Authors’ response: Several figure captions have been edited for clarity as specified below.

Authors' changes to the manuscript: figure captions have been changed as indicated below (changes are shown in bold).

“Figure 1 Experimental setup used for obtaining sized CCN and particle concentration measurements from an aerosol sample.”

“Figure 2 Simplified flow diagram of a DMA with an inner electrode radius r_1 , outer electrode radius r_2 , distance between aerosol inlet and sample outlet L , clean sheath air flow Q_{sh} , aerosol flow Q_a , excess air flow Q_e , and sample air flow Q_s .”

“Figure 3 (a) A theoretical aerosol distribution generated using a lognormal function centered at 50 nm. (b) The transfer function calculated using Eq. (7). (c) Multiplying the distribution by the transfer function gives the downstream aerosol concentration (cm^{-3}).”

“Figure 4 (a) Apparent hygroscopicity κ_{app} for DMA cases 1-7 for sodium chloride (triangles) and ammonium sulfate (circles) [see legend in (b)]. (b) Critical supersaturation of ammonium sulfate and sodium chloride particles calculated using κ_{app} values derived in (a). Ammonium sulfate and sodium chloride curves from κ -Köhler theory are shown for comparison. Legend colors apply to both salts. (c,d) DMA-flow-derived artifacts in κ_{app} are shown for each DMA case and both salts.”

“Figure 7 (a) Counting efficiency curves for CPC Cases 1-6 (shown in Table 3).

(b-e) CCN activated fraction curves for 25, 50, 100, and 200 nm NaCl, respectively. (f) Critical supersaturation calculated for each particle diameter. (g) Theoretical κ_{app} for each CPC case and particle diameter. (h) Artifacts in κ_{app} for each CPC case and particle diameter.”

“Figure 8 (a) Theoretical relationships between the reference aerosol concentration and CPC concentration. (b) Concentration-dependent counting efficiencies from (a) were applied to four theoretical aerosol distributions. (c-f) Activated fraction curves for CPC Distribution 1 and particle diameters 25, 50, 100, and 200 nm NaCl aerosol, respectively. (g,h) Critical supersaturation and κ_{app} for each case. (i) Artifacts in κ_{app} for each case.”

“Figure 9 (a) Counting efficiencies of the DMT CCN-100 for specific supersaturations. (b) Lognormal aerosol distributions used to study CCN undercounting at high concentrations. (c-f) Activated fraction curves for 25, 50, 100, and 200 nm NaCl particles. Supersaturation-specific counting efficiencies from (a) applied to theoretical sigmoid curves for NaCl CCN activation. Activated fraction in the case of 100 % counting efficiency is shown for comparison. (g) Critical supersaturation for each case. (h) Theoretical κ_{app} calculated for each case. (i) Artifacts in κ_{app} artifacts for each case.”

9) Reviewer comment: Figure 6 b. As I understand it, the CPC counting limitations relevant here relate to the number concentration after the DMA.

A. Are the DMA transfer function and the charge distribution taken into account when determining these curves? And if so, for which aerosol to sheath flow ratio are they made?

B. Is it just a coincidence that the size distribution is cut at the same value of dN/dDp (in $\text{cm}^{-3} \text{nm}^{-1}$?) as the CPC concentration saturates (in the unit cm^{-3}). And how can the “saturated size distribution” be a horizontal line? Both charging probability and transfer function width (in a linear scale) are size dependent.

A. Authors’ response: Yes, the CPC instrument is positioned after the DMA. The DMA transfer function is not taken into account in the CPC concentration analysis here.

Author’s changes to the manuscript:

Page 11 Lines 180-182 the text now reads: “Instrument artifacts will be assessed separately for the DMA, CPC, and CCN counter. In the concluding section of the paper (and Fig. 10), the overall uncertainty due to the combination of these is presented and discussed.”

B. Authors’ response: This is not a coincidence; this concentration is the concentration at which the CPC can no longer count additional particles (and is not related to charging probability or the transfer function). An additional sentence has been added to the manuscript for clarification.

Author’s changes to the manuscript:

Page 26 Lines 484-486 the text now reads: “It should be noted that the CPC concentration (the concentration that would be measured and recorded by the CPC in Cases 7-10) levels off at the saturation concentration for each case.”

10) Reviewer comment: Figure 7 and the calculations behind them: How is dN/dDp transferred into a concentration after the DMA? Which flows are used?

Author’s response: To clarify, we have only used concentration in this manuscript, not dN/dDp . If we understand this question correctly, the reviewer is referring to the fact that particles are lost in the DMA which leads to error in particle concentration measured by the CPC placed downstream of the DMA. Indeed, particle losses within the DMA are substantial. If aerosol concentration were the measurement objective then a more accurate measurement of concentration would simply use a CPC, thus minimizing particle losses. However, for the purposes of this manuscript, we consider activated fraction (the ratio of particles measured by the CCN instrument to those measured by the CPC for a given particle diameter and supersaturation). In this case, losses in the DMA impact the CPC and CCN concentrations exactly the same way, so no error is introduced in the resulting activated fraction. In this analysis, the actual CCN and aerosol particle concentrations are only used for determining how activated fraction is effected in each CPC or CCN case, if at all. We acknowledge that estimation of particle losses in the DMA, and between the DMA and CPC/CCN, are worth considering but the treatment of these particle losses is beyond the scope of this manuscript.

11) Reviewer comment: You use both saturation ratio and supersaturation in the theoretical discussion. As I can see you are using them correctly, but sometimes you use only saturation for saturation ration. I would recommend that you stick to saturation ratio in order to avoid confusing the readers.

11. Authors' response: We thank the reviewer for finding this error. All mentions of "saturation" have been revised to "saturation ratio".

12) Reviewer comment: Line 184. With a truly monodisperse aerosol the concentration would also be 0.

12. Authors' response: This is true, and the sentence indicated has been changed for clarification.

Author's changes to the manuscript:

Page 13 Lines 208-209 the text now reads: "In other words, Q_s would ideally consist only of aerosols with diameters equal to, or very nearly equal to, the selected diameter."

13) Reviewer comment: The discussion and the conclusion section is mainly a repetition of the results (which might well be a part of these sections), but I would have liked to see a discussion on what should be considered good practice in CCN measurements, based on this work and the literature.

Authors' response: Good practice in CCN measurements was originally addressed in the Conclusion section of the original manuscript, in terms of minimizing kappa artifacts. Based on the reviewer's comment, we have expanded on the discussion and conclusions, including references to DMA sample/sheath ratios recommended in other studies for comparison.

Authors' changes to the manuscript:

Page 33 Lines 591-595 the text now reads: "The results demonstrate that limiting Q_a/Q_{sh} to ≤ 0.10 will result in a narrow particle size distribution downstream of the DMA. Other studies have recommended employing DMA sample/sheath ratios of 0.2 (Petters et al., 2007; Carrico et al., 2008; Moore et al., 2010) or 0.1 (Moore et al., 2010; Zhao-Ze and Liang, 2014) in order to minimize measurement aerosols due to transfer function broadening.

Page 32 Lines 597-601 the text now reads: "The effects of multiply-charged particles on κ_{app} calculations were also quantified, as shown in Fig. 10. Small, positive κ_{app} artifacts (1 – 3 % of κ_{app}^{NaCl}) were observed when particles with +2 and +3 charges were not accounted for. This analysis considered a theoretical aerosol distribution in which most of the particles measure less than 100 nm in diameter. Actual aerosol distributions vary temporally and spatially, and often include accumulation and coarse modes that would result in larger κ_{app} artifacts."

Page 33 Lines 621-625 the text now reads (additions are bolded): "The combined artifacts for the cases where the highest artifacts were observed (DMA Case 4, **multiple particle charging**, CPC Case 4, CPC Case 10, CCN Case 1) are 0.21, 0.24, 0.32, and 0.21 for 25, 50, 100, and 200 nm particles respectively, as shown in Fig. 10. The combined artifacts for the lowest-artifact cases (DMA Case 2, CPC Case 3, and CCN Case 4) are < 0.001 except for 200 nm particles, where $\kappa_{app,artifact} = 0.0013$."

Page 37 Lines 681-683 the text now reads (**additions are bolded**): "Under optimal operating conditions, where the DMA sample/sheath ratio is 0.10 and excess/sheath ratio is 1.0, and in the absence of undercounting by the CPC or CCN, uncertainties in κ_{app} are within ± 1.1 % for 25 to 200 nm particles. When the DMA sample/sheath ratio drops to 0.05, κ_{app} uncertainties decrease to ± 0.01 %. **Additionally, errors in activated fraction (and therefore κ_{app}) resulting from the bipolar**

charge distribution can be corrected by determining the fraction of particles with multiple charges.”