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

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

General Comments

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

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 $\sim 5.6 \times 10^4\ cm^{-3}$ 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 $5 \times 10^6\ cm^{-3}$ 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 17-18 Lines 311-314
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.

Page 20 Lines 354-362
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. 6b). 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 Distribution 2, 3, and 4 are lower in concentration. 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. (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.) The counting efficiency was then calculated for each case and aerosol diameter in CPC Distribution 1.

Page 23 Lines 407-408
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 25 Lines 450-453
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 $4 \times 10^4 cm^{-3}$ and $1 \times 10^4 cm^{-3}$, respectively.

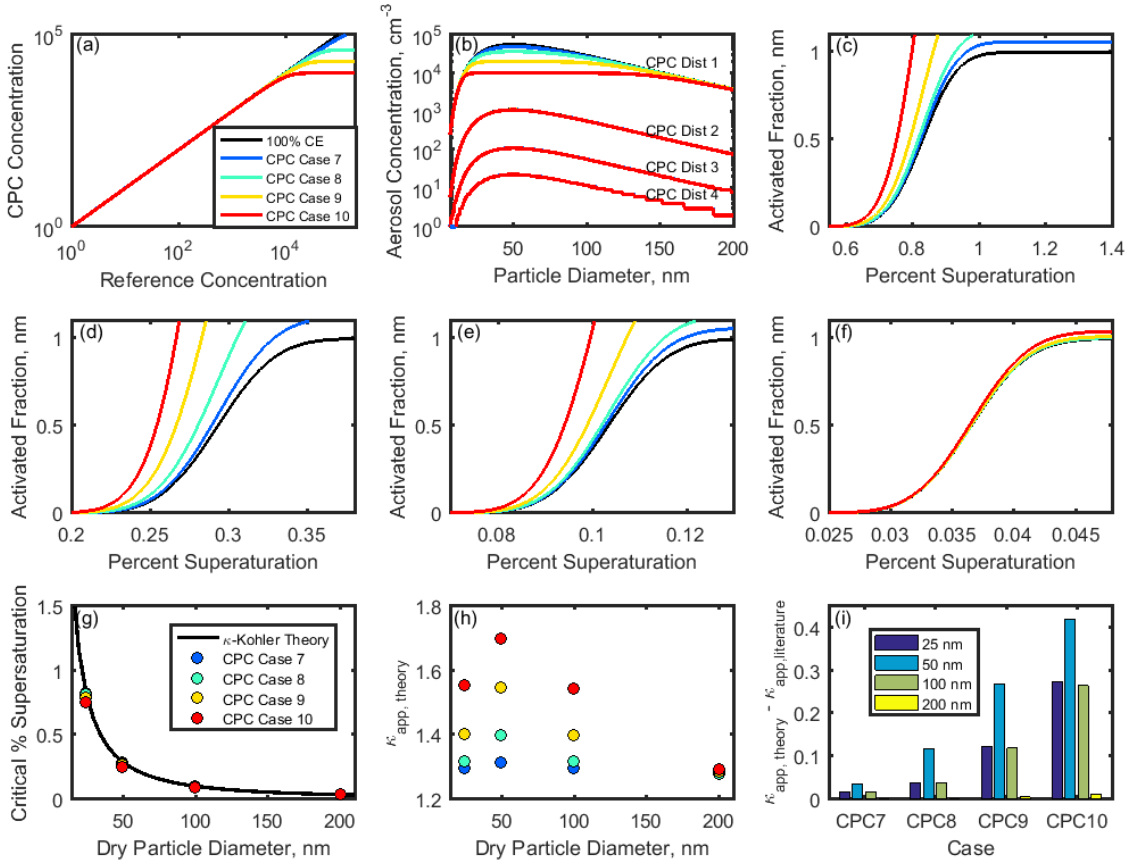
Page 25 Lines 456-458
The text now reads: It should be noted that undercounting was only observed for one of the four upstream distributions studied, CPC Distribution 1. No undercounting was observed when CPC Cases 7-10 were applied to CPC Distributions 2-4.

Page 43: 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.

Table 5 Total concentrations used in theoretical aerosol distribution for CPC operation at high concentration and CCN-derived $\boldsymbol{\kappa_{app}}$ artifacts.

CPC Distribution	CCN Case	Total Concentration (particles cm^{-3})
CPC Distribution 1	CCN 1	5×10^6
CPC Distribution t 2	CCN 2	1×10^5
CPC Distribution 3	CCN 3	1×10^4
CPC Distribution 4	CCN 4	2×10^3

Page 45: Three more (total aerosol) distributions have been added to Figure 6b in order to demonstrate the effect of CPC undercounting on lower aerosol concentrations. Figures 6c-i are only applied to the first distribution, CPC Distribution 1, because this is the only distribution in which undercounting occurs.



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.

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) a) The approach used to derive artifacts from DMA in this study is significantly different from the real CCN measurement. 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 κapp 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?

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) Secondly, I am not sure whether the method used to calculate κapp 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 kappa should be relatively invariant.

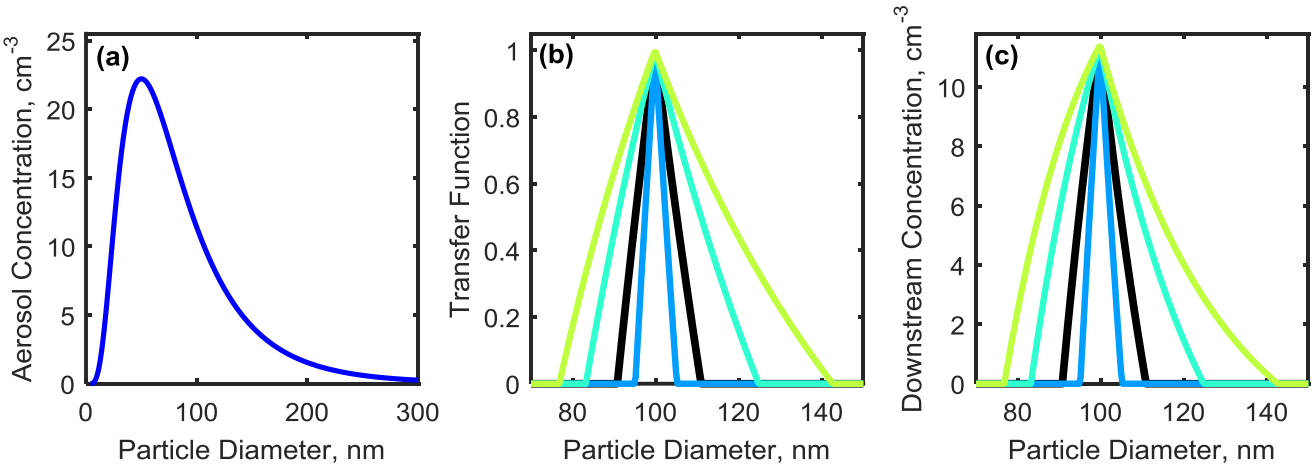
Authors' response: The volume-weighted approach accepted as a standard convention of kappa theory. The kappa for a mixture consisting of i components is calculating using a volume-weighted mixing rule (Petters and Kreidenweis 2007):

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

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 kappa 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.



2) 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 26 Lines 471-479
The following paragraph was added: It should be noted Fig. 4c-d demonstrated that κ_{app} bias may result from instrument artifacts for ammonium sulfate and sodium chloride. These two species are standards used in calibration of CCN instruments (Rose et al., 2008). Therefore, the κ_{app} bias 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. Experimental CCN measurement bias would only truly be compensated if the aerosol sample was of the same composition as the standard used for calibration. A further analysis could apply the results of this study, which considers two CCN calibration standards, to an experimental setting in order to determine the effectiveness of such compensation.

Specific comments

1. 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 5, Lines 64-66, added:
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. 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 ("$-0.57 < \kappa app,\mathrm{ar}tifact < 0.42$") are for NaCl.

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

Authors' changes in manuscript:

Page 27, Lines 488-490 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 27, Lines 492-495 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. 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 9, Lines 138-141 The text now reads: Experimental results for ammonium nitrate are inconsistent $0.577 \leq \kappa_{app} \leq 0.753$ (Svenningsson et al., 2006), and 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. L202, L is not defined.

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

Authors' changes in manuscript:

Page 12 Line 209 The text now reads: Where L is the distance between the DMA inlet and outlet.

5. 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 13 Lines 219-226 The text now reads:

Added: "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, though in practice, small discrepancies may occur."

6. L253, it is not clear how exactly the κapp, theory (and κi) is derived. εi and κi 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 15 Lines 265-266 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. 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.

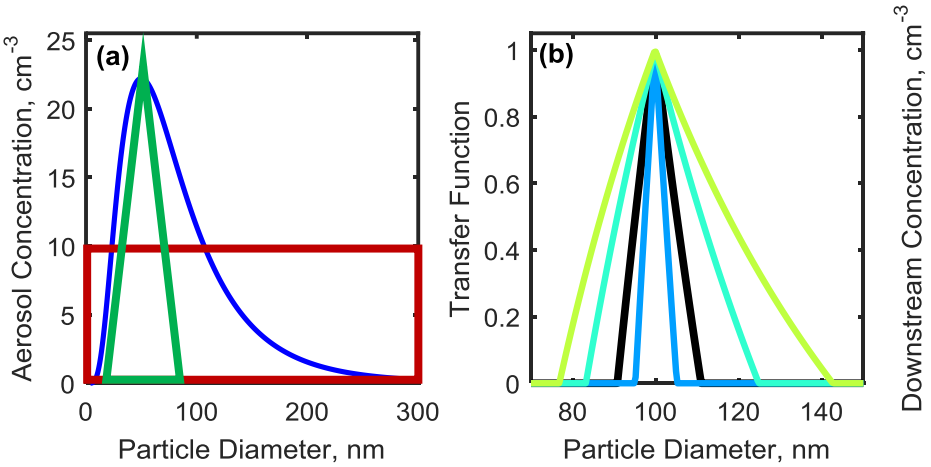
Authors' changes in manuscript:

Pages 15-16, Lines 278-283 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. L412-416, why would "a distribution with a narrower peak than the one generated for this analysis be at risk for larger κapp artifacts for any total aerosol concentration…"?

AR: 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. 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.