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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Uncertainty in counting ice nucleating particles with continuous diffusion flow chambers" *by* Sarvesh Garimella et al.

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We would like to thank both Reviewers for their careful reading and thoughtful comments on our manuscript. We have made the changes they suggested and provide a point by point response below with the comment directly followed by the response. We believe this is a much improved paper as a result.

Reviewer 1 (Major points extracted from first paragraph with overview text omitted for clarity; we quote these points here and refer the Reviewer / Editor to the comment in the main body of the review where they apply.)

Major Points

1. First, no description of the ice growth model was given, including equations and

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assumptions on condensation coefficient for ice growth, habit, or at what size particles were started for growth.

This point is repeated and addressed in response to that for Page 9, line 23.

2. Second, no demonstration data is given to provide confirmation the errors predicted by the particle transfer studies using ice nucleation data collected in the chambers. Are there any conditions for which higher RH operation is possible in order to confirm that activation appears as predicted in the SPIN instruments (i.e., data consistent with a cf of 2.6-9.5 times)? Past data seems to exist for ZINC in workshops. Can any of these data be utilized?

This point is repeated and addressed in response to the first point in the Conclusions.

Specific Comments

Abstract Line 13: suggest “instrument theory of operation”

Change made.

Line 14-16: The sentence ends oddly following the “and”. This is a product of the machine learning or the combination of flows? Should there be separate sentences here?

Sentence broken at “and” with wording changed to “We use a machine learning approach to show that non-ideality is most likely due to small scale flow features where the aerosols are combined with sheath flows. Machine learning is also used to minimize the uncertainty in measured INP concentrations. We suggest that detailed measurement, on an instrument-by-instrument basis, be performed to characterize this uncertainty.”

Introduction Page 3, line 20 – Concerning the need for accurate and unbiased measurements, the need exists, but it may or may not be achievable. Why not frame it as "assessing the accuracy and bias of such measurements"?

Change made.

Page 5, line 3: The referenced study of DeMott et al. (2015) did not only discuss the effect of aerosol spreading outside the lamina, so perhaps this should read “discussed the effect of aerosol “spreading” outside the lamina and other possible factors that together result in a low bias: : :”. This is the first mention of the hypothesis that it is the lamina spreading that is primarily responsible or most important.

We agree with the reviewer; we have concentrated on the spreading issue in this paper but did not intend to ignore the other possible factors outlined by DeMott et al. We have made the suggested change to “DeMott et al. (2015) discussed the effect of aerosol “spreading” outside the lamina as well as other possible factors that, in combination, could contribute to a low bias in the number of INP measured.”

Methodology Page 6, lines 6-8: Is there a reason that this ZINC test is done at such a low temperature below that of the mixed phase cloud regime where one thinks of the need to exceed water saturation. Was the thinking just to cover a broad range?

To demonstrate our thinking we have added “This temperature was used to determine effect of temperature on particle loss from the lamina and because it is in the homogeneous freezing regime where all test particles are able to nucleate ice. At this lamina temperature the difference between the wall temperatures is larger for a given supersaturation than at a higher temperature and this maximized any resulting turbulence effect on particle migration from the lamina.”

Page 6, lines 14-17: Is there any reason to test different sizes of particles for transfer? For example, would there be any difference expected for 100 nm versus 1000 nm for whatever phenomenon is responsible for spreading outside of the lamina or whatever leads to undercounting?

We did not observe differences from 100 to 200 nm and could not definitively attribute effects when using polydisperse aerosol in the field. We do not believe diffusive or

other effects are equivalent to the mixing/turbulence effects we have qualified this at the end of this section with “We note that diffusive and other forces may differ across particle sizes. Monodisperse particles were tested under laboratory and polydisperse particles under field conditions; future studies may consider a full range of particle sizes applicable to particular CFDCs.”

Page 6, lines 18-19: In creating a lamina profile of particle arrival times, it is not clear how you decide the position of a particle coming from either side of the central lamina.

The text has been expanded: “Combining information from a measured particle pulse and a calculated velocity profile, the corresponding distribution of particles across the width of the chamber for that particular pulse can be inferred (Figure 3). Buoyancy effects on mean chamber flow and mean particle position are accounted for in the calculation of the velocity profiles (Rogers, 1988). The particle distributions are reconstructed by assigning the first detected particles to the maximum velocity position in the calculated flow profile and the assigning peak particle concentration to the calculated lamina position (about which spreading occurs). The particles in the tail of the pulse are assigned positions corresponding to their relative velocities, which are derived from their relative arrival times.”

Page 7, lines 20-21: What thermodynamic variables besides wall temperatures are meant? What other thermodynamic variables are available in the upper part of the chamber.

Replaced with “saturation conditions” (see also Table 1.)

Why not provide a list of all "features" in a supplemental table?

As stated in the text, an exponential fall of importance was observed and we present those within the first two e-foldings (see paragraph at end of Section 2 and Table 1). Presenting a full list of housekeeping variables beyond those (and used in the reduced model) has no bearing on the results and we believe it could actually create confusion

for the reader.

Page 7, line 22: Where the lamina is “initially” encased within the sheath flows? Results and Discussion

“initially” added as a qualifier

Page 8, line 3: Both walls at -20 C and with what uncertainty?

There is a misunderstanding here; there is no “-“ in the text. These were isothermal experiments at 20° C where this was performed intentionally so there would be no temperature difference. This point is relevant for latter experiments so we have added “Wall temperatures remained within ± 1 degree of the set point for all experiments.”

Page 8, line 7: Ice saturation ratio calculated in this case for average wall temperatures?

Clarified as “In Figure 5, flam is plotted against the lamina temperature and ice saturation ratio (Sice) calculated for walls at ice saturation and with temperatures corresponding to the measurement average value (Garimella et al., 2016).”

Page 8, line 18-19: The non-ideality in DeMott et al. was reported for a specific aerosol. Issues of response of aerosol to the chamber conditions is not discussed herein, and one can imagine that it is different for Snomax than for dust particles. Additionally, it could depend on particle hygroscopicity and so forth. Hence, that work was not an expansion on the work of Tobo et al. It regarded a different aerosol entirely, and a point made was that it was not clear if corrections translated to any aerosol. Since this is what is promoted in the present paper, you may wish to make this point.

We agree this statement was overly simplistic and have expanded this to “DeMott et al. (2015) noted the non-ideality, including due to particles spreading beyond the lamina, in the Colorado State University CFDC chamber. They proposed the use of a “calibration factor” (cf) = 3 by which the measured INP number could be multiplied to provide a corrected value. Previous studies, including Tobo et al. (2013), used cf = 1; this

corresponds to an assumption that all particles in a CFDC exist within the lamina. It should be noted particle properties, such as size, shape and hygroscopicity may have an effect on the correction factor and that the value found by DeMott et al. (2015) may not be universal even for that CFDC. The value of cf = 3 does correspond to a constant 33% of particles existing within the lamina, regardless of flow or thermodynamic state, for those experiments." which we believe is in keeping with the reviewer's suggestion here.

Page 9, line5: You could perhaps say more here. For example, that the cf could depend on instrument control factors, so would require RFR analysis for any given CFDC.

Suggested change made to "This suggests that cf could depend on various instrument control factors and would require RFR analysis for the various CFDC configurations."

Page 9, lines 7-9: Since homogeneous freezing is a clear rate process, you would expect a distribution of ice crystal sizes even in that case, no? This could depend on the exact temperature and the nucleation rate at that temperature. It will likely be monomodal, but I would not expect it to be monodisperse unless you can state the temperature and nucleation rate and show that all particles would be expected to freeze within a very short time after entry into the chamber. I think this paragraph needs some rewriting.

We start this response point by noting that this and the following four points all request an expansion of the ice growth calculation and the assumptions therein. We have expanded this section by several paragraphs and believe that this presentation is much more clear for the reader as a result. We are also compelled to point out that although the Reviewer initially raises important questions that were in need of clarification, the final points, especially that at "Page 10, lines 8-9", demonstrates a misunderstanding: In the initial manuscript we started this section with the qualification that this was a supporting argument, not our main point, and included multiple qualifying statements throughout. This remains true in the revised manuscript. It is not correct for the Re-

viewer to argue that we are trying to make points by assuming we know crystal sizes with high certainty; that is not and never was a central argument of this manuscript. We hope the review can proceed with this as context.

Regarding this specific point, we agree with the reviewer that the crystal size distribution should be quasi-monodisperse and monomondal since there is a variation in temperature within the aerosol sample layer even under ideal CFDC operation, which also leads to a variation in RHi. However, the particles should equilibrate with the internal chamber conditions within approximately the first second of entering the chamber and then freeze almost instantly due to the very high nucleation rate at these conditions. To clarify this in the text we have reworded this paragraph at the reviewer's suggestion to "Further evidence to support the spreading effect is provided by the size of the ice crystals measured at the output of a CFDC. Theoretically, a monodisperse population of an aerosol composition that only nucleates ice homogeneously should exhibit freezing almost the same time and location within a CFDC chamber. This is because particles should equilibrate with the internal chamber conditions within $\sim$1 second of entering the chamber and then freeze rapidly due to the resulting nucleation rate at these conditions (Koop et al., 2000). This should translate to a quasi-monodisperse ice crystal size distribution at the chamber output; the size of the crystals should be a function of the chamber RH and temperature and equivalent to the amount of vapor-deposited water under these conditions. Therefore, differences in crystal size should primarily be due to particles that leave the lamina and experience varying supersaturations and residence times in the chamber."

Page 9, lines 16-18: As above, would particles freeze instantly? Even considering their adjustment time in RH and T to chamber conditions that must amount to a second or more?

We agree, the time scale would be on the order of a second. We have added removed "immediately" from the text and added the clarification "In order to consider the effect spreading beyond the lamina, aerosol particles were assumed to nucleate ice upon

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entering the chamber since the -40° C lamina temperature was below that required for homogeneous ice nucleation. We note there is a short delay not directly accounted for in this calculation for thermal equilibration ($\sim$ 0.1 – 0.8 seconds at -40 °C assuming heat transfer coefficients for the NH4NO3 particles) and $\sim$1.0 seconds for the particles to travel to the ice coated region of the chamber (Stetzer et al., 2008). The combination of velocity profile and residence time from the pulse experiments (Figure 2) were then used to determine the location of the particles in the lamina and therefore the time they were exposed to variable supersaturation and the subsequent size to which they would grow."

Page 9, line 23: It is not intuitive in consideration of expected ice crystal growth rates that 4 micron ice particles are expected to be the product at -40 C. Is it due to the high supersaturation? What is the lamina residence time in ZINC? How large are particles assumed when they freeze? What is the condensation coefficient? What growth rate equation is used? Are spherical ice crystals assumed? There is much missing here in order to evaluate the statement made.

Note that this response also answers the first major point made in the initial review paragraph. In response we now include more information at this location as to the ice growth model : "The baseline crystal size was when all particles remained within the predicated lamina (i.e., within the dash lines in Figure 1). Ice crystal size was calculated per the formulation of Rogers and Yau, 1989). Crystals were assumed to be spherical due to the ice forming homogeneously from sub-micrometer diameter particles (Järvinen et al., 2016). The initial ice crystal size was assumed to be that of ammonium nitrate at the initial dry diameter, which may be a slight underestimation due to hygroscopic growth before freezing occurred. However, calculations with a doubling of the initial particle size had minimal impact on the final crystal size so this assumption was maintained for all calculations. An accommodation coefficient of 0.2 (Strotski et al., 2013) and the calculated residence time in the lamina ($\sim$10 seconds) were used to predict the crystal sizes. The calculations resulted in monodisperse ice crystals at $\sim$4

micrometers diameter (orange histogram)."

Page 10, lines 8-9: See questions above. How could one possibly know so well the sizes of ice crystals expected if you do not know the deposition coefficient for ice well enough to know what to specify? Are edge effects in the OPC the only explanation of ice crystals less than 3 microns in size? That size could represent a many second or more growth time at -40 C. And one must assume spherical ice crystals to claim to know the sizes very well.

We understand that reviewer has concerns about the ice growth model and we have – in addition to the changes outlined in the last four points – also added "It is important to note that the previous calculations are from a simple ice growth model and are used to illustrate that observed crystal size distributions are also consistent with particles spreading beyond the lamina." in this section. We request the Reviewer keep this in mind as we were not making statements or conclusions based on the level of certainty suggested in their point.

That said, we include the further qualifying statement regarding smaller crystals per the reviewer's comments as "In addition to spreading, there are other reasons that crystals smaller than the theoretical size might exist. These include uncertainty in shape, refractive index and crystals that are undersized by passing through the edge of the ZINC OPC (Stetzer et al., 2008). Furthermore, literature values of accommodation coefficient ranges between 0.2 and 1 (e.g.,Skrotzki et al., 2013). Here, 0.2 was used for these calculations. A value of 0.1 would result in $\sim$10% smaller crystals, which is still not sufficient to fully account for the smaller crystals < 2 micrometers diameter observed in the OPC."

Page 10, line 14: Does a perfect immersion freezing nuclei imply that they are fully dilute at a condition of a water activity of 1? Most CCN are not activated at 100 percent RH, but immersion freezing can happen before activation if the temperature is cold enough. I think it may have to be stated as a highly idealized and possibly unrealistic

example.

We agree with the reviewer and this was the reason we described Figure 8 as “idealized” and then used the term “perfect” (quotes here in original text) and called out the assumption they activated at exactly 100% in the initial manuscript. We have now further qualified this as “The aerosol population is assumed to be idealized “perfect” immersion mode INP that form ice crystals immediately upon exposure at water saturation (Sliq=1)”

Page 11, lines 2-3: A number of 10 percent of aerosols freezing in ambient air is taken as realistic for ambient atmospheric conditions? Under what conditions? Again, I think one can say this is for demonstration purposes, not meant to simulate a real case except one that might be found in a laboratory or at very low temperatures such as for cirrus parcels.

As with the preceding point, we believe the reviewer might have missed the qualifications that these plots were meant to be idealized representations, not atmospheric examples, in the original text. To make this more clear we have further qualified this line with “Figure 9 expands on Figure 8 by considering another idealized case, but one more applicable to measurement of an ambient aerosol population. In this case only 10% of the particles are perfect immersion mode INP, whereas the rest are cloud condensation nuclei (CCN) that activate at exactly Sliq=1.”

Page 11, line 12: “of droplets”

Corrected

Page 11, line 16: perhaps “we propose due to the primary importance of the particle spreading effect.” Otherwise you are interpreting another study that discussed multiple processes potentially at play.

Suggested wording change made.

Conclusions

Page 11: A general comment noted in the above summary comments. It was surprising that no actual ice nucleation data are shown in this paper to support that the spreading effect is realized in the same manner as reported by DeMott et al. (2015).

Regarding ZINC data from previous workshops (ICIS 2007, DeMott et al., 2011) we prefer not to use these data as the experiments were performed with a goal to observe only the onset RH of activation. In addition, ZINC was still under development during the workshop conducted in 2007 as such it may be pre-mature to use those data for a comparison.

However, for this work, we present another experiment with a complete activation spectrum (see Figure 1 below) in ZINC taken at 233 K for homogeneous freezing of 400 nm (dry diameter) NH4NO3 particles. For these conditions, we don't have to compare to another immersion freezing device since the particle freezing efficiency is not of concern given that homogeneous freezing should render all particles frozen for Sliq$\geq$0.99 (Koop et al., 2000)

For approximately these conditions (233 K and Sliq 1.02) we have reported that $\sim$ 25% of the particles escape the lamina in ZINC (see caption Figure 2). As is predicted from the curves shown in Figure 8, the deviation from a step function form of the curve is indicative of particles escaping the lamina, thus broadening the Sliq range at which complete activation (100% of particles freezing) is observed. In the figure below (new figure in revised version (Figure 9)), the range of Sliq that the aerosol particles in the lamina are exposed to is shown by the shaded region. Within this range $\sim$ 70% of the particles freeze homogeneously in ZINC, consistent with the pulse tests in Figure 2 of the manuscript, considering counting uncertainties of $\sim$14% arising from the CPC and OPC. However, in order to observe 100% of particles freezing, one must increase Sliq to 1.05 in ZINC suggesting that $\sim$30% of the particles escape the lamina in this case. We have now added this explanation to the revised manuscript on page 13 lines 3-12.

Fraction of 400 nm (dry diameter) NH4NO3 particles freezing homogenously as a func-

tion of Sliq in ZINC at -40 °C. According to Koop et al. (2000), 400 nm salt particles at -40 °C should freeze homogenously at Sliq $\sim$ 0.99. Shaded region indicates the range and uncertainty of Sliq that the aerosol in the lamina are exposed to.

Page 12: Regarding the comment about instrument geometry, you may wish to say what you mean. For example, some instruments are parallel plate, with lamina edges, while others are cylindrical in design.

Now included “(i.e., parallel plate, cylindrical, etc.)”

Page 12, lines 4-6: There was little exposition given to the idea that small scale flow features at the point of aerosol injection and sheathing are responsible for the observed spreading of particles outside of the lamina. Fluid dynamics simulations might be advised in the future.

This was suggested in the initial manuscript and remains in the revised version “. . .drawing comparisons to computational fluid dynamics simulations to complement the RFR statistical modeling. . .”

Perhaps you should say that the only reason for non-ideality explored here was related to sample injection methods.

This is incorrect. The RFR points to this being the case since the location of the most important factors were in this area. A different RFR result would have caused us to consider different reasons / chamber features. As such this would not be a correct statement / qualification.

A full analysis might also include particle compositional variability as well, since many INPs are thought to be relatively hydrophobic. One might also ask how the noted behaviors impact "deposition" nucleation?

We agree and have now added “consider other freezing regimes such as depositional nucleation of ice” to the list of future work / suggestions.

Page 12, lines 11-14 and beyond: I suggest some revision to the statement here. CFDCs have needed to be operated at higher RH than expected values to inspect immersion freezing. However, an RH value of say 102 percent is not non-physical for Cu clouds, and 106 percent may not be either in wave clouds or very strong elevated convection. Of course, this discussion might be easily resolved by saying the super-saturations are higher than expected for immersion freezing of most particles, rather than stating realism for the atmosphere. Furthermore, S-liq = 1 is not the threshold for immersion freezing. It can be higher or lower in dependence on particle hygroscopic properties, particle size, and temperature, and data in the literature demonstrate this.

We believe the reviewer might have missed the wording in this section. We have not discussed atmospheric cloud supersaturation. Instead, we made reference to droplet nucleation in e.g. CCN instruments where 1.02 and great are unrealistic supersaturations "By contrast, CCN instruments routinely activate essentially all particles into droplets at 1.01 – 1.02.". This is a valid comparison and it is the one that was stated in the initial, and remains in the revised, manuscript.

Page 12, line 13: INP number concentrations.

Corrected

Table 1. Please explain some terms better. For example: 1) Lamina saturation at TC3 means using the temperature difference across walls at this elevation to calculate the saturation profile there? Likewise TC4, etc...?

Table caption now revised to "List of the ten most important features from the RFR. TC corresponds to Thermocouple and H to heater where numbers correspond to locations described in Garimella et al. (2016). Saturation is calculated at specific locations using temperature measurements and assuming walls exist at ice saturation per the method outlined in Garimella et al. (2016). The features are predominantly located in the top and middle sections of the chamber."

2) What does total volume flow at mass flow controllers mean? Where else do you know it?

This is “total volume flow”; MFC now eliminated for clarity.

3) Probably need to explain the heater concept, since some CFDCs do not heat their coolant.

Within the caption now included “(supplemental heating is used to maintain wall isothermality in the SPIN chamber)”

Figure 1. If you were to draw the sample to scale, would it represent such a small fraction of the flow cross-section?

This figure starts with the statement “Schematic representation of an idealized CFDC” – exact dimensions are not meant to be represented.

Figure 3 caption: Don’t particles also migrate to higher and lower temperatures?

Reworded to “some particles have migrated into the sheath and are therefore exposed to higher and lower temperatures and supersaturation lower than the maximum.”

Figure 4 and caption. Why such a narrow range of total flow, or if constant, why does it vary so much? Why would that be important and why would it even vary? There is a need to state conditions for which these data are collected, that it is for 1-sec pulses, etc.

Flow was varied slightly around the nominal value “varied around a nominal value of 9.8 slpm.” added to text. The pulse length was explicitly stated in the text; we do not believe it should be repeated here.

Figure 9 caption: S-liq > 1.07 is the droplet breakthrough point for what SPIN temperature, or is it uniform? Also, I do not really get what is shown in panel b as a “composite of black and blue traces” from panel a. Why not just say that what is observed by an OPC is shown in panel b?

This has been corrected to “to a “droplet breakthrough” point”; we did not mean to imply a specific instrument or condition. We have also reworded the main text to make this clear. Also corrected (see Reviewer 2) is red, not black. Now further explained with “as is the case for an OPC”.

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