Referee #4, Gabor Vali
Received and published: 11 September 2015

[A0] For clarity and visual distinction, the referee comments or questions are listed here in black and are preceded by bracketed, italicized numbers (e.g. *[1]*). Authors' responses are offset in blue below each referee statement with matching numbers (e.g. *[A1]*). Page and line numbers refer to online ACPD version.

The problem addressed in this paper - the sizes of atmospheric ice nucleating particles - is important and is far from having been adequately resolved in previous studies.
The paper does leave the impression of a somewhat brief, preliminary study for exploring the potential of the relatively recent MOUDI-DFT technique. That is a legitimate goal and it has been successful. But there are some shortcomings that deserve to be mentioned. No ancillary data are presented, such as aerosol size distributions.
The aerosol were not brought to a standardized humidity so the sizing would be more consistently comparable. Possible aging of the samples was not cotrolled for. Other questions and suggestions are listed in the following sections. Some of the points are perhps marginal, as this paper focuses on the sizes of the INPs not on their concentration; nonetheless, the authors should discuss these problems and reflect on possible implications for the results. Some caveats would be in order and some changes should be included when the paper is revised.

We thank the referee for his helpful comments!

Technical issues:
Since the MOUDI-DFT method employed in this paper has been described in at least two previous publications, and is used here with no changes that would require special attention, the method is taken as established and few details are given. Nonetheless, there are some questions that can be esked regarding some aspects of the method.

[1] Background
Unless I missed it, it seems that the background level, or detection limit, has not been established. There is mention of sudden freezing at -25C (pg. 20531 line 14) and this may be an indication of the detection limit. But the background levels at other temperatures are still open to question. Tests with the intake air passed through an efficient fiter upstream of the sampler would have yielded blanks for establishing the background. This may have made the condensation of drops difficult but that could have been circumvented by some steps like higher supersaturation, producing drops meachanically, etc. None of this is simple, of course.

[A1] To address the referee's comments the average freezing temperature and standard deviation of the blanks as well as the warmest freezing temperatures of the blanks will be reported.

[2] Sample volume
The volume of the air sample that is evaluated for INP content by Eq. 1 is taken as the

ratio of the DFT view area to the area of the glass slip while the total volume is for the entire MOUDI sample. Isn't the ratio of glass slip to MOUDI disk missing here?

[A2] In Equation (1), the number of INPs found using the droplet freezing technique is first multiplied by the fraction of the total sample area to the analysed area ($A_{deposit}$/ A_{DFT}) and is then divided by the total volume of air sampled. $A_{deposit}$ is the area of the MOUDI disk that the referee is referring to above. To clarify this point, in the revised manuscript $A_{deposit}$ will be referred to as the total area of the sample deposit on the MOUDI impaction plate.

[3] INP content of drops

The assumption of equal drop sizes from Vali (1971) has been maintained in Eq. 1 in spite of the large range of droplet sizes (a factor 20 or more in volume) that form via condensation in these experiments. This can't be simply ignored.

The issue raised in the previous paragraph is linked to the question what is the relevant measure of INP content per drop in these experiments. The Vali (1971) proceedure is formulated for the case when all drops are derived from the same bulk sample of water with a random partitioning of INPs in the drops. In that case, all drops can be assumed to have the same probability of containing any type of INP. With the condensation method employed in these experiments the validity of this assumption needs to be examined carefully, considering what determines where the drops form on the plates and what particles they contain. If condensation is initiated on the INPs themselves, the question reduces to whether there is any dependence of the supersaturation required for condensation and the INP activity of that particle. This in turn depends on what kind of internal mixtures consitute the INPs. If the INPs become included into the drops as those drops grow from a condensation nucleus that is not an INP, than the assumption of random probability of INP content per drop seems to be fulfilled. The main point is that the authors should justify the use of the Vali (1971) formula for these experiments. It is not obvious how the original assumptions apply here. Additional possible problems relate to the adhesion of collected particles on the supporting surface. Perhaps the authors have looked into whether the drops move particles along the surface as they expand during condensation, or cover them up. The same question needs to be asked for the period of evaporation: are particles left behind as the drops shrink? There is a hint that perhaps this is the case in Fig 2(c) of Mason et al. (2015a) with particles(?) seen in circular patterns.

[A3] Droplet growth by water condensation in the DFT occurs in the same manner for samples containing particles and clean hydrophobic glass cover slips (no particles deposited and rinsed with ultrapure water). Therefore, water condenses uniformly on the cover slip, and these droplets then combine as they grow. Particles become incorporated into the droplets as this occurs. Analysis of the Ucluelet samples, with similar observations over the entire dataset, shows that only a small fraction (on average < 1%) of particles visible with the optical microscope remain outside of the droplets once they reach their final size.

We have also investigated binning the measurements based on droplet size and residual inclusion area, using 2–4 bins, to see how this would influence our results.

The samples used in the binning analysis are those from the CSU intercomparison study noted in the Mason et al (2015a) instrument paper. We found in 98% of the samples the INP number concentration found using the binned data was within the experimental uncertainty of the unbinned data. This information will be added to the revised manuscript to address the referee's comments.

[4] Cooling rate

The reported cooling rate in the freezing experiments is -10C min^{-1}. Thermal lags throughout the system, specially within the drops but also within the stage, could be a problem with such rapid cooling. Has that been considered? How uniform was the rate of cooling throughout an experiment?

[A4] The possibility of a thermal lag using a cooling rate of -10 ºC min^{-1} was investigated in detail previously using a similar droplet freezing technique (Koop et al., 1998), and the thermal lag in that study was shown to be small at a cooling rate of 10 ºC min^{-1} (the correction was 0.2 ºC at -33 ºC). In addition we tested the possibility of a thermal lag by investigating the freezing of pure water droplets using a cooling rate of -5 and -10 ºCmin^{-1} (unpublished results). The median freezing temperature determined with the two cooling rates of -5 and -10 ºC min^{-1} were -36.3 ± 1.5 and -36.7 ± 2.0 ºC, respectively, with uncertainty given as the standard deviation.

To determine the stability of the cooling rate we cooled the freezing cell from -5 ºC to -37 ºC three times using the set cooling rate of -10 ºCmin^{-1}. The average cooling rate was found to be -9.8 ± 0.4 ºC based on the three experiments. In Figure 1 of this document (see below) we have plotted the cooling rate from three experiments over the temperature range of -5 to -37 ºC measured at a frequency of 1 Hz.

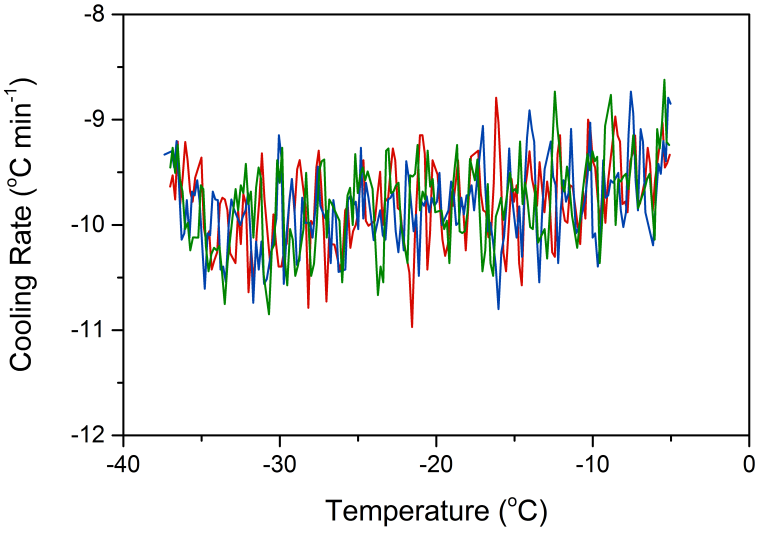

Fig 1. The cooling rate of three experiments over the temperature range of -5 to -37 ºC measured at a frequency of 1 Hz.

[5] Correction factors
Two corrections factors are included in Eq. (1). The first one, f_{nu} is explained in some detail in the referenced paper (Mason et al. 2015a). The second one, f_{ne} is less clear as the referenced paper (Koop et al. 1997) doesn't show this quantity directly and here it is applied to a formula (Vali 1971) that is differently derived. This requires some explanation. Numerical values for the correction factors should be given.

> ***[A5]*** Values of these correction factors will be added to the Supplement. In addition, Equation 1 will be separated into 2 equations; similar to our earlier paper that describes the DFT-MOUDI technique (Mason et al. 2015a). The correction factors should be clearer when 2 equations are included. In addition, the Koop correction will be discussed in more detail in the revised manuscript.

Results:
[6] Were the overall average and median concentrations reported calculated with weighting by the number of samples for each location? In light of the sample numbers varying from 1 to 34, giving equal weight to each results in some distortion of the data.

> ***[A6]*** In our analysis the overall average and median concentrations were calculated by giving each location (i.e. sampling site) equal weight. We felt that weighting by the sample number would skew the average toward the sites of Amphitrite Point, Saclay, and Alert while largely ignoring the remaining locations. This information will be included in the revised manuscript for clarity.

[7] On page 20534 long-range transport is stated to preferentially reduce the numbers of large particles. That is not an obvious result for INPs, specially since the mixture of components that make up the INPs is unknown.

> ***[A7]*** To address the referee's comments, the discussion on long-range transport will be deleted. Specifically, lines 18-27 on page 20534 will be deleted.

[8] There are many facets of the results obtained in this work and the authors have selected meaningful diagrams to present those results. Yet, it would have been useful to see the results also in the form of temperature versus concentration. That would also be a good way to compare present results with other published works.

> ***[A8]*** To address the referee's comments in the revised manuscript a spectrum of INP concentration vs. temperature for each location will be added to the Supplement.

[9] Results from the Colby site lie at the upper ends of the data both in concentration and in size. It is stated that sampling was during and following combine operations. The range of variability in concentrations and in sizes for these 3 samples is no different from other sites. Is this relative uniformity related to having combine operations in the area, if not directly near the site, throughout the sampling periods? On page 20258 it is indicated that sampling was 3-10 m from the fields. Isn't that an error and kilometers were meant?

[A9] It is possible that additional combine activities in the region also contributed to the measured INP population. However, we don't have information that can confirm this possibility.

The stated proximity of 3–10 m is correct. Equipment was set up in a mobile laboratory parked next to the fields.

[10] There is interesting aspect of the data that the authors might want to explore. The question arises: are the INPs of different sizes of the same composition and have the same surface properties? If so, the probability of a nucleating site being found on any size particle would be the same. A rough estimate of the relative proportions indicated in Fig. 3 of the paper for two sizes indicates a negative answer to the question. Using a ratio of about 1.3 for INPs greater than 1μm to 2.5μm and using those as nominal sizes whose surface areas would differ by a factor of 6.25, the indication is that the larger particles have a much lower probability per unit surface area to contain an ice nucleus. That would be something to ponder. This calculation could be made more precise and extended to the full range of sizes covered by the sampling. There are broad implications of this type of analyses so presentation of the results in this form would make a valuable addition to the paper.

[A10] We assume here that the referee is suggesting that we calculate ice-nucleation active surface site density (n_s) values as a function of size. We certainly agree these calculations would be very interesting. To carry out these types of calculations we would need the size distribution of the particle population at each site, measured at the same times as the INP measurements. Unfortunately, this data was not measured at all sites (e.g. UBC), and for the cases were this information was measured, accessing this data and then carryout out these calculations would require a large amount of work. We hope the Editor agrees that these calculations are not required for the current publication. However, we will pursue these types of calculations in future publications where we intend to report INP values from these sites in more detail.

[11] It is pointed out in the paper that the size range of INPs examined is restricted to > 0.1μm aerodynamic size and that further studies are needed to examine the contributions of smaller size particles to INP populations. An additional aspect of INP sizing would be worth mentioning. The size distributions of atmospheric particles undergo many changes due to capturing, scavenging and other processes. Few particles are of single composition. The measurements here reported refer to sizes of internally mixed particles and also of aggregates. Thus, small INPs may be detected at larger sizes if they adhere to other particles. This may take place already at the origin (soil especially) but also during atmospheric transport. A difficult issue, no doubt, but one that need to be recognized.

[A11] This is a good point raised by the referee. The last paragraph of the Summary and Conclusions section will be rewritten to address the referee's comment. Specifically the last paragraph will be revised to the following:

"One caveat to this study is that our measurements were confined to aerosol particle sizes greater than either 0.10 or 0.18 μm. If there were a significant contribution from INPs of smaller sizes (Vali, 1966; Schnell and Vali, 1973; Pummer et al., 2012; Augustin et al., 2013; Fröhlich-Nowoisky et al., 2015; O'Sullivan et al., 2015; Tong et al., 2015; Wilson et al., 2015), and these smaller sizes did not coagulate or get scavenged by larger particles, the values presented here would represent upper limits to the contribution of supermicron and coarse mode particles to the total INP population. Additional studies exploring the relative atmospheric abundance of INPs < 0.10 μm are necessary (Hader et al., 2014). Future studies of the size distribution of INPs should also include measurements of particle mixing state to determine if particles are internally or externally mixed at the locations where the size distribution of INPs are being measured."

Supplement:
[12] It is good to have the authors' analyses of the works cited for comparison of size determinations. It helps to illustrate the sparsity of data on this important point.

All but one of the works cited employed aerosol samplers. The exception is the Vali (1966) report which is based on size discrimination by filtering of liquid samples. It would be helpful to readers to point out this difference and its possible implications, namely that soluble components of the INP get removed and particle might break up when immersed in water. Both of these factors introduce a bias in the comparison of sizes, with corresponding aerosol sizes likely to have been considerably larger than the size found in water. Coagulation of particles in the liquid would add a bias in the opposite directions but is less likely to have been a factor.

[A12] These points will be noted in section S1.1 of the Supplement where the Vali (1966) measurements are discussed. Thank you for the suggestion.