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Atmospheric Measurement Techniques Discussions

# *Interactive comment on* "Best practices for precipitation sample storage for offline studies of ice nucleation" *by* Charlotte M. Beall et al.

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The authors examine a procedural step in the process usually employed for determining the ice nucleating particle (INP) content of precipitation. The experiment they designed is well conceived and the study was thoroughly done. The data obtained is limited in extent and some clarifications are needed about details of the work but the indication for detectable differences among the storage methods seems clear. Importantly, the differences are not of such magnitude as to raise serious questions about results accumulated in past research. The results provide an indication that samples should be stored frozen in future work. The usefulness of the correction factors derived in the paper is doubtful. The authors performed a good experiment; the changes here suggested refer to the analyses of the results and to the clarification of some details of



the procedures.

GENERAL COMMENTS

The paper has two dimensions. One is the application of the results in handling of precipitation samples for analyses of ice nucleating particle (INP) content. The other is the possibility to make inferences about the nature of the INPs in terms of persistence, size and heat resistance. Ultimately, both are parts of the larger question of what can be learned about what is the role of INPs in precipitation formation in the atmosphere, and about what are the sources of those INPs. This paper set out to address a relatively modest part of the larger question but inevitably the results have to be examined in the larger context.

Measurements of INPs in precipitation collected at the ground has a long history (a useful list is found in the Supplement to this paper). These measurements have many caveats attached when making inferences about precipitation formation. The caveats relate to the assumption that INPs found in the precipitation were present at the formation of the cloud and the development of precipitation. Passive scavenging during the fall of already developed precipitation particles is known to contribute to the INP content but, as a first approximation, assumed to be negligible. This view is a reflection of the importance attached to INPs in initiating precipitation in many clouds, and is reinforced by their paucity.

Inferences based on analyses of the INP content of precipitation amount to 'reverse engineering' of the cloud processes. The samples obtained for analyses combine a vary large number of precipitation elements (drops and/or ice crystals) and the INPs are a very minor component of the overall mix of particulate and dissolved impurities. All this is well understood in principle but difficult to quantify.

Immersion-freezing is known from laboratory data to be more effective than other pathways of ice nucleation so drop-freezing assays of various types have gained prominence in this research, specially because INPs active at small supercooling can be

detected. Great care is generally taken in such work to avoid contamination in the process of collection and in the handling of the samples in the laboratory where the INP analyses are performed. The manner of storage of the samples between collection and analysis frequently has been assumed to be inconsequential, for the most part relying on the fact that INPs are insoluble particles. Also, inter-comparison of samples is frequently the goal and identical storage for all samples is assumed to be assurance for the absence of complications. The authors of this paper recognized that the aforementioned assumptions deserve scrutiny, so they designed and executed an experiment to examine what differences may result from four different storage methods. Their results show that storage is best done with the samples kept frozen.

Looking at the magnitude and the variability of the detected influences, my view is that the problem is not of major importance when compared to other uncertainties related to the use of these measurements. Putting it in another way, the results presented provide some assurance that the storage of rain samples between collection and analysis is not a limiting factor in extracting useful results on the INP content of precipitation, and that freezing of the samples is better than storage in liquid state. For snow and hail samples this is obvious, but aging of samples can't be excluded a priori even for those. All the above points are, of course, subject to more tests of storage effects with a greater variety of samples.

The authors raise relevant issues regarding possible influences, specially of freezing and of heat treatment, on INPs of different composition and size. At the moment these are useful speculations that would probably need to be examined with specifically designed experiments using INPs of known sizes and composition. Heat treatment effects are fairly well demonstrated to provide useful distinctions between organic and mineral INPs. Size-dependence of the effect of freezing is a new issue to my knowledge.

The following comments relate to how well the conclusions stated above are supported by data presented in the paper. Overall, the answer is positive, but there are simplifications and gaps that need to be recognized.



MAJOR POINTS

There is no indication in the paper of the kind of precipitation that was sampled. Presumably - vaguely deduced from the variations in the lengths of the sampling periods - a variety of precipitation types are included. Probably, some light rain to more showery situations were involved. Cases with all warm-rain processes and cases with ice origin may have been involved. This may justify the choice of 'precipitation' in the title rather than 'rain'. If all events were from clouds with no ice-phase, a change in the title would be warranted to indicate so. This point isn't very important to the main theme of the paper, but it could possibly make a difference for considerations of how the present results might apply to other situations. The main constraint mentioned in the paper and explicitly stated in the conclusions is that the results refer to coastal environments. This is not as helpful as could be, since precipitation and aerosol sources on the coasts may still include a very broad variety.

Separating measurement variability from actual changes is important. Figures 2-4 include indications of measurement reproducibility with the gray bars adjacent to the data point clusters. All of these bars are indicating values greater than unity. The caption to Fig. 2 says that the bars represent the 'average difference between replicates'. How is this to be interpreted? What conclusion can drawn from these data?

Considering the effects of heat treatment and of filtering in conjunction with storage methods is useful since these are applied in many studies of INP composition and source. A lingering uncertainty in the paper about whether these treatments were applied to the fresh sample before division and storage, or just prior to INP measurement, is disconcerting. The discussion in lines following 218 seem to indicate that filtering was done before freezing for storage. It would be good to have the sequence better described. The overall effects of the treatments are given as, on the average, 59% of INPs were found resistant to heat and 69% passed the filters. These numbers are overly vague, as dependence of temperature can be expected as well as variations from sample to sample. While such detail will not alter the data, it is relevant to pos-

sible explanations of the results. On the level of internal consistency in the paper, it is worth asking how justified is the statement underlying conclusion 6 (line 280). Significantly greater losses are said to occur in storage for filtered samples. This is not really evident from a comparison of Fig. 2 with Fig. 4, or from the figures in Table 5 versus Table 7. Greater variability (larger 95% range) is found only for 'refrigeration' and 'freezing', while 'room temperature' and 'flash freezing' have narrower ranges and smaller standard deviations in Table 7 than in Table 5. Perhaps the claimed effect was clear for selected samples but not for the combined sample set.

Tables 5-7 have some technical problems (see comment below on lines 185-189), but taking the data as is, most notable is the large range of variations for the corrections factors. Not just the 95% range, but even 50% spread: for the last line in Table 5, the 50% range is roughly 0.78 to 2.8. Experiments seldom lead to more accurate INP concentrations due to limitations in sample sizes (number of drops or vials). This reinforces the point that the results should be viewed as indications of the uncertainties associated with aging of samples during storage and not as correction factors that can usefully improve measured INP data in other studies. This argument is further supported by the potential for differences in the aging effects for precipitation at different times and locations. The current data provide help in weighing the importance of aging versus other sources of uncertainties in a given experimental design

MINOR POINTS:

How was the sample division done for different treatments? While this can be expected to be a step without risk of introducing discrepancies among the samples, it is not without such a possibility. Thus, the manner it was done should be described, as well as any tests done to assure that this step doesn't lead to artifacts.

Line 85 mentions samples getting divided into 24 bottles during collection. What is the relationship between this and the division of the samples for different treatments? Figure 1 shows points near -5°C for one sample. This should be of special interest but



the paper doesn't mention it. Was the sample unusable?

Perhaps Fig.1 could be made less congested by showing only the interval 0°C to -20°C. Is there more than one point included in Figs. 2-4 for a sample from the same rain event and time period? Unfortunately, one can't determine from the figures how many data points are shown for each temperature. More than the number of rain events? The number of points differs for different temperatures. Is this because of limits in the temperature range of freezing events?

It would have been useful to identify by precipitation sample each data point in Figs 2-4, at least for the outliers. This would clarify, for example, if all the points with lowest values in Fig 2(a) are for the same sample or not, and if the same sample has the lowest points in Fig 2(b) and 2(c).

Line 73: Were heat treatment and filtering applied before division for different storage temperatures, or just before INP analysis? One can assume it is the former, but the paper leaves it unspecified. Lines 101-102 still don't make clear what was done. Line 179 seems to indicate that filtration was done before storage.

Line 100: reference to 'section above' seems incorrect

Line 171: Is the ratio cited independent of the INP activity temperature?

Line 138: ' ... binned by 2°C increments .. ' seems odd for cumulative data. More likely, values are 'determined (or calculated) at successive 2°C intervals'. If that is not the case, please explain. The word 'binned' appears in numerous places in the text.

Line 140: What does 'significant' refer to here? Maybe the authors meant 'measured'.

Line 141: The cumulative values at any point are calculated by accounting for all freezing events (all frozen sample wells) at temperatures higher than the value at which the concentrations is evaluated, not just those of the preceding value at 2°C higher temperature. Also, in line 146, 'each' should be replaced by 'all', and line 147 should be rephrased and clarified.

Line 157: ' .. containing data from at least two sets of replicate samples ...' seems to say that data points shown include replicates from the same rain event. This is brought up again in lines 187-188 and in the caption to Fig. 2.

Lines 160-161: 'well counts' and 'well fractions' are not the same - please clarify.

Line 161: ' ... at each of the 5 temperatures ..' should probably be left out

Line 163: Here it says that all stored samples showed significant changes whereas only a few points are shaded in Fig. 2.

Line 179: The reference to Sect. 2.3 for detail is incorrect.

Lines 185-189: Tables 5-7 indicate the range of impacts that may be expected on the basis of the data presented in this paper. The correction factors here given appear to have been derived combining data from all temperatures for given storage and treatment type. This has an inherent multiplicity problem as data at successively lower temperatures include all data from higher temperatures. Thus, a value for, say, -11°C is also incorporated into the values at -13°C, -15°C etc. so that the ratio at -11°C is given multiple, though uneven, weights when combining all the values for -11°C and lower into calculating a mean and standard deviation for the given treatment. Also, all data were included in calculating the values in Tables 5-7, not just the cases for which the differences observed were shown to be statistically significant. One may wonder what the results would be of only those cases were included.

Line 192: What is meant by 'in situ' collection? Similarly, in line 241 'in situ dust' is vague.

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