Comment on the quantitative evaluation of background noise in drop freezing experiments

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I'd like to expand on the important topic discussed in this paper by Polen et al. The paper focuses on the factors influencing the background noise in drop freezing experiments due, among other factors, to the imperfect purity of the water used to suspend INPs for testing. In this Comment, I wish to show how the background noise can be **quantitatively** accounted for. The method is not new and, perhaps, it has been already applied by some researchers, but I am not aware of a specific exposition of it in the literature. The method is described here in some detail and its use is demonstrated with a specific example.

The paper by Polen *et al.* contains much important practical information regarding the problem of the 'background noise' unavoidably present in drop freezing experiments on heterogeneous ice nucleation[1]. Background noise in such experiments arises from several sources. The two most important and inescapable ones are (1) the fact that there is no absolutely pure water in which to suspend the INPs to be evaluated, and (2) the fact that the drops are in contact with some supporting surface. These are systematic influences which affect equally all drops in an experimental run. Additional potential systematic noise factors are: INPs in the air, other gas, or liquid covering the drops, mechanical disturbances, electrical fields, and the spread of ice from one frozen sample to another. Other items may have to be added to this list, but as far as we know now, the two main factors far outweigh the others.

Evaluation and quantitative correction for noise is the battleground of experimentalists. The first step in the battle is to keep the noise (interference) low. This is the main point addressed by Polen *et al.* as the title of their paper indicates. The second front is the evaluation and quantitative treatment of the noise. In the case of the drop freezing experiments, the solution to this second problem is approached by the use of background tests, a point well emphasized in the paper. To resume briefly, in situations where the

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[1] The generic description as 'drop' freezing is applied in the paper and in this comment to stand for any manner in which a bulk sample is divided in numerous small sub-samples in order to observe the distribution of INPs of various activity. The resulting distribution is called the spectrum of INP activity.

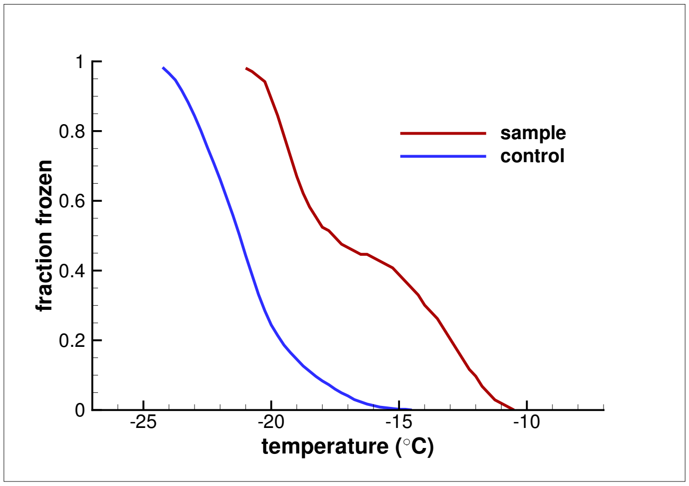

Figure 1: Fraction of sample drops and control drops frozen as a function of temperature.

sample is a laboratory preparation, i.e. the material to be tested is added to purified water, the background can be evaluated by testing the purified water in exactly the same manner as the INP-bearing sample is. This can be done either in separate tests, or by simultaneously observing drops of the purified water and those already containing the sample in the same run. For testing for the INP content of water samples like rain, snow, etc., determination of the background consists of parallel tests with the most highly purified water available[2]. This provides an assessment of the noise level arising from the supporting surface(s) and other factors, and it is assumed that the measured INP content exceeding this level is a true part of the sample. Non-systematic effects, like frost spreading on the supporting surface, have to eliminated because they cannot be corrected for with noise subtraction.

As already implied in the foregoing, the basic assumption in drop freezing experiments is that the observed INP content is the sum of the background and of the sample. There are limits to the validity of this assumption, such as possible dissolution of some potential INPs in the sample of solid material, but this possibility is covered by referring to the tests as probing for INPs active in ”immersion freezing”. In general, the very nature of the drop freezing tests is based on the additive assumption, since INPs are counted and the results are given as normalized values of the number concentration or total surface area of INPs.

Consider the results shown in Figure 1 for an experiment with a sample of soil suspension and with a control sample with the distilled water. The same drop volumes were

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[2] It is unlikely to be necessary, but it may be useful to simulate the ionic composition of the rain or snow sample just in case the sample to be tested is has some chemical properties that may have some interaction with the supporting surface.

used for both. As can be seen, there is substantial overlap between the temperature ranges of the obseerved freezing events for the sample and for the control. This appears to be alarming as an indication of lack of purity of the distilled water, i.e. a high background INP content. This may be thought to invalidate the portion of the data in the region of overlap, or the temptation may arise to subtract the fraction frozen for the control from the fraction frozen for the sample. This would be an error.

A simple and direct subtraction of the noise level from the signal is available in terms of the differential nucleus spectra defined in Vali (1971, V71). Time-dependence is not considered and is a minor factor in any case (cf. V71 and numerous recent publications). With the sample and the control data taken with the same cooling rate the importance of time is further reduced. The differential spectra offer a clear and intuitive way of achieving the noise subtraction whether it is done in terms of number concentration or surface area. These spectra express the number of INPs per unit volume of water, or per particle surface area. For simplicity, the example is presented here in terms of the number of INPs per unit volume per temperature interval. As given by Eq. 1 in V71:

$$k(T) = -1/(V\Delta T) * ln(1 - \Delta T/N(T))$$

where T stands for temperature in °C, N is the number of drops not frozen and V is the volume of the drops. It is to be remembered that this expression is the result of considering that a freezing event in the interval ΔT is the result of a drop containing *at least* one INP active in that temperature interval. For relatively small ΔT-values and for large N this approximation to having a *single* INP per drop responsible for the observed freezing event is very good (and can be quantified). Under these circustances it is entirely appropriate to take $k_{\text{corrected}}(T) = k_{\text{sample}}(T) - k_{\text{control}}(T)$.

For the data shown in Fig.1, the results in terms of $k(T)$ are shown in Fig. 2. As can be seen the actual correction is small over most of the temperature range of the sample except in the region of the dip of the spectrum where the ratio $k_{sample}/k_{control}$ becomes small, almost becoming equal near -17°C. The corrected value is lower than the control in that region. Here, acceptance of the corrected value may well be questioned and the question would have to be examined considering the probable errors in both the the soil sample and the control in terms of the sample sizes involved, namely the ΔN_i values for each ΔT_i in the region of interest. In fact, that evaluation should be done for all parts of the spectrum but for the majority of points in this example the significance of the corrected spectrum appears to be assured by the small values of the corrections. For the sake of brevity, this statistical evaluation is not entered into here. It is worth noting that the relatively minor correction seen in Fig. 2 is in contrast with the impression given by Fig. 1 for a possibly more important impact of the background due to the distilled water used.

The differential spectrum is used in the foregoing discussion because it is the most straightforward for the purpose, specially in the potential to evaluate statistical errors

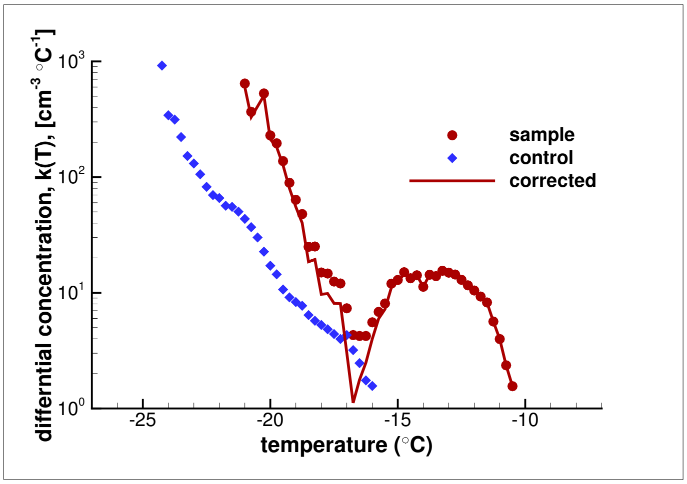

Figure 2: Differential spectra for the two data sets shown in Fig. 1. The line labelled 'corrected' represents $k_{\text{corrected}}$.

for each temperature interval. The cumulative spectra, $K(T)$ in V71, is an integral of the differential spectrum and correction for background noise (distilled water INPs) can be also made in terms of K(T). It may be noted that in Section 3 of the paper under discussion the cumulative spectra are introduced as c_{IN} in their Eq. 1, with N_{unfrozen} designating the fraction, not the number of unfrozen drops as in this comment. This equation is the same as Eq. 13 in V71.

In summary, measurements of INP content by drop-freezing experiments can be evaluated with quantitative corrections for the INPs that may be introduced with the water carrying the sample to be tested, or whatever other systematic factor contributes to the background freezing events. Such corrections increase confidence in the results, and in extreme cases indicate when the results cannot be trusted due to high background levels. If needed, statistical confidence levels can be computed. It should be noted that the ultimate reliability of results derived from drop freezing experments is determoned in many cases – above and beyond the corrections for background influences – by difficult to control time-varying variables. Time varying factors are, for example, aging of the sample itself, problems of controlling particle sizes precisely from experiment to experiment, the settling of particles in the storage containers, and more. These problems nonewithstanding, drop freezing experiments have many uses; the paper by Polen *et al.*, as well as this comment, may help to further increase scientific gains from these experiments.