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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 wish to thank Referee 1 for their comments and discussion. We summarize our responses and changes made to the manuscript below. Note that line numbers refer to the latest, marked-up version of the manuscript:

Referee: "1. The 15 samples used as the basis of this paper seems a reasonable number; how-ever, they are all from the same location and therefore likely have a similar mix of INP types. Do the researchers have access to more diverse samples? Would these results hold if the sample was e.g. collected from a boreal forest? A desert? (see also comment on the 'correction factor' in point 3). Given the expertise in the author list, it would seem that access to a variety of samples would be possible.

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Discussion paper

To emphasize this point : the title of this paper is ""Best practices for precipitation sample storage for offline studies of ice nucleation" – of universal importance. But in the Discussion "The aim of this study was to identify a storage protocol...in a coastal environment."– much more limited. The 'coastal' modifier is then repeatedly used but this isn't even universally coastal – it is a single coastal location. Either the authors should place the much more geographically restrictive information up front – title and abstract – or provide a larger diversity of samples. The latter, clearly, would be much more beneficial to the field as a whole."

We agree that a study with a greater diversity of samples and sites could be more broadly applicable, and perhaps provide greater insights. A focus on one location for demonstrating impacts of storage on precipitation samples allowed for a manageable study as one part of a PhD, and serves the purpose of highlighting that the lack of an existing standard storage protocol in the field is potentially problematic. These findings, thus, will serve as motivation for future efforts to quantify storage impacts on samples from a variety of environments, which will require either a series of field campaigns or a coordinated study between groups at different institutions/locations. To provide broader context for our dataset, we have updated Figure 1 following the assumptions of Petters and Wright, 2015 to estimate in-cloud INP concentrations from precipitation samples (i.e. 0.4 g condensed water content m-3). Figure 1 shows that the INPs observed here are comparable to spectra reported previously for a wide range of marine and coastal environments, including the Caribbean, Bering Sea, East Pacific and nascent sea spray aerosol (DeMott et al., 2016). As INP spectra in this temperature regime cluster distinctly by air mass type (e.g. Figure 1-10 in Kanji et al., 2017), Fig. 1 indicates that the air masses sampled in this study were likely primarily marine. Regarding the reviewer's point "[...] this isn't even universally coastal [. . .]", we agree that it remains to be seen how sensitivity to storage varies between sites with similar source types. This reinforces the need for future studies of the effects of storage, not only upon INPs in precipitation, but also with filter or impinger samples that are used in investigations globally.

We have made the following changes to explicitly state this assumption and reflect it consistently throughout the text:

Title: “Best practices for precipitation sample storage for offline studies of ice nucleation in marine and coastal environments”

Abstract, Line 25: “We provide the following recommendations for preservation of precipitation samples from coastal or marine environments intended for INP analysis. . .”

Introduction, Line 100: “Enhancements and losses of INPs according to storage protocol and treatment are reported, as well as recommendations for storage protocols that best preserve INPs in untreated, heated, and filtered precipitation samples from marine or coastal environments.”

Sec 3.1, Line 171: “ Following the assumptions in (Wright and Petters, 2015) to estimate in-cloud INP concentrations from precipitation samples (i.e. condensed water content of 0.4 g m-3 air), observations of INP concentrations in fresh precipitation samples are additionally compared to studies of field measurements conducted in marine and coastal environments. Figure 1 shows that atmospheric INP concentration estimates compare with INP concentrations observed in a range of marine and coastal environments, including the Caribbean, East Pacific, and Bering Sea, as well as laboratory-generated nascent sea spray aerosol (DeMott et al., 2016).”

Discussion, Line 282: “Additionally, the INP freezing temperatures and concentrations observed in this study compare with INPs observed in studies of marine and coastal environments (Fig. 1). As spectra in this regime (-5 to -20 °C and 10-5 to ∼10-1 per L air, respectively) cluster distinctly by source type (see Fig. 1-10 in Kanji et al., 2017), Fig. 1 indicates that the dominant sources to air masses sampled in this study were marine. Considering that data in this study compare well with marine and coastal INPs from a variety of marine-influenced air masses (DeMott et al., 2016, Yang et al., 2019), the findings herein are likely relevant to samples from other marine and coastal environments.”

Discussion, Line 297: “If correspondence within 1 order of magnitude (or 2-3 °C) is desired, uncertainties associated with storage should also be considered in studies using samples from coastal or marine environments. Thus, uncertainty distributions provided in Tables 5-7 can be used to evaluate observed INP concentrations and responses to treatments in the context of potential changes due to storage. However, the degree to which INP sensitivity to storage varies by INP source (e.g. with soil-derived INP populations) remains to be tested.”

Conclusions, Line 370: “Based on all observations in this study, we provide the following recommendations for precipitation samples collected in coastal and marine environments for offline INP analyses...”

Referee: “2. Follow on. : At what time of year / conditions were the samples collected? Are these from the same or similar events? What is the diversity of conditions (season, meteorological, etc.)”

A summary of the meteorological conditions associated with each sample have been added to Table 1, and the following changes have been made to the text: Sec. 2.1, Line 117: “Satellite composites from the National Weather Service Weather Prediction Center’s North American Surface Analysis Products were used for synoptic weather analysis to generally characterize each rain event (see Table 1). Atmospheric river (AR) events were identified using the AR Reanalysis Database described in (Guan and Waliser, 2015) and (Guan et al., 2018).”

Sec. 3.1 Line 165: “Figure 1 shows INP concentrations of 15 coastal rain samples, collected in a variety of meteorological conditions including scattered, low coastal rainclouds, frontal rain, and atmospheric river events (see Table 1).”

Referee: “3. Starting in the Abstract and continuing through the paper : “...non-heat-labile INPs being generally less sensitive to storage regime...” “Non-heat-labile INPs were generally less sensitive” This seems to be an assumption; the experiment determines abundances of heat or non-head labile INPs before and after but can not

directly say something was changed or not. The authors should indicate that, based on abundances, they assume that the storage process is responsible for the change but not absolutely attribute it. As an example, a constant abundance could mean that no change was caused by storage or that there were roughly equal rates of enhancement and deactivation; the measurements made would not be able to differential this, correct?"

The referee makes a good point that there are other potential causes of changes in INPs that should be discussed. Sample handling procedures, for example, could cause apparent differences in INP concentrations, or contamination in storage containers. However, we are able to distinguish changes due to sample handling and changes due to storage by considering the differences between sample replicates. The following changes to the text have been made:

Sec 3.2, line 218: "Replicate samples were processed for each storage protocol so that impacts of sample handling can be distinguished from storage impacts. For example, if settling occurs in bulk rain samples that are then divided into smaller volumes prior to storage, INP concentrations may differ between replicates of the bulk sample. . Thus, it is assumed that INP concentration changes that are greater than differences between replicates (grey bars in Figs 2-4) can be attributed to storage impacts. We also assume that stored:fresh INP concentration ratios of 1:1 indicate insensitivity to storage, although it is possible that enhancements and losses of equal magnitude could also result in a 1:1 concentration ratio."

Referee: If the assumption that heat labile INPs are more sensitive to storage, I don't believe the authors can offer (again, point made in Abstract and continuing through paper):"correction factors are provided so that INP measurements obtained from stored samples may be used to estimate concentrations in fresh samples"– wouldn't said correction factor necessarily be a function of the ratio of non- to heat labile INPs? Therefore the correction factor would not be universal but a function of the INP mix?

Due to referee #2's point that many of the correction factors are within measurement uncertainty for droplet assay techniques, we have updated Tables 5-7 with average changes in INP concentration and 95% confidence intervals that can be used to estimate uncertainty associated with storage in samples from marine and coastal environments (see response to point #1 above). Emissions of heat-labile particles can be increased in bloom-enhanced conditions, although it is variable (McCluskey et al., 2018), and considering bloom timescales (e.g. 10 days), bloom-enhanced marine sources would not have dominated air-masses sampled in a precipitation study.

The following changes have been made to the text to reflect this update:

Abstract: Finally, the estimated uncertainties associated with the 4 storage protocols are provided for untreated, heat-treated and filtered samples for INPs between -9 and -17 °C. Conclusion, Line 398: "2. Estimates of uncertainty attributed to storage impacts and 95% confidence intervals for INP measurements obtained from stored samples are provided (see Tables 5-7)."

Legend Table 5: Table 5. Estimate of uncertainty associated with storage impacts for INPs with activation temperatures between -9 and -17 °C measured in stored, untreated precipitation samples. Confidence intervals were derived from the log-normal distribution of changes observed in INP concentrations due to storage (see Fig. 2 and details in Sect. 3.2). Temperature intervals where datapoints were too few to derive confidence intervals are indicated with "NA". Changes in INP concentration corresponding to enhancements or losses greater than 1 order of magnitude (losses <= -90% or enhancements >= +900%) in bold.

Legend Table 6: Table 6. Estimate of uncertainty associated with storage impacts for INPs with activation temperatures between -9 and -17 °C measured in stored, heat-treated precipitation samples. Confidence intervals were derived from the log-normal distribution of changes observed in INP concentrations due to storage (see Fig. 3 and details in Sect. 3.2). Changes in INP concentration corresponding to enhancements

or losses greater than 1 order of magnitude (losses <= -90% or enhancements >= +900%) in bold.

Legend Table 7: Table 7. Estimate of uncertainty associated with storage impacts for INPs with activation temperatures between -11 and -19 °C measured in stored, filtered precipitation samples. Confidence intervals were derived from the log-normal distribution of changes observed in INP concentrations due to storage (see Fig. 2 and details in Sect. 3.2). Temperature intervals where datapoints were too few to derive confidence intervals are indicated with "NA". Changes in INP concentration corresponding to enhancements or losses greater than 1 order of magnitude (losses <= -90% or enhancements >= +900%) in bold.

Referee: "5. Introduction "Measurements of INPs suspended in precipitation are commonly made offline using a droplet freezing assay technique, and many studies report results from samples stored prior to processing. Storage protocols vary widely, including total storage time, time between collection and storage, and temperature fluctuations between collection, shipment and storage (if these details are provided at all), yet generally samples are stored between + 4âŮęC and -20âŮęC (see Table S1)." – These two sentences follow on a paragraph on INP in clouds. They are disparate concepts and should represent two new paragraphs: (1) how are off-line INP measurements made (they are not only by drop freezing assay – that is only the technique used here)? and (2) there should be a more complete description of storage used by previous researchers, not just a statement that it varies widely / table reference."

This paragraph has been updated with the suggested structure and content.

Introduction, Paragraph beginning Line 56: A number of online (real-time) and offline (processed post-collection) techniques exist for measurement of INPs for each ice nucleation mechanism, including condensation, deposition, immersion and contact freezing. However, as some simulations have shown that immersion mode freezing is the dominant mode of primary freezing in the atmosphere between 1000 and 200 hPa

(Hoose et al, 2010), most techniques target immersion freezing. Despite the lack of time resolution, offline techniques enable measurement of INPs at modest supercooling (e.g. up to -5 °C) and temperature regimes where concentrations typically fall below detection limits of online instruments (DeMott et al., 2017). Offline instruments capable of immersion mode INP measurement include a number of droplet assays, in which sample suspensions are distributed among an array of droplets that are then cooled and frozen (e.g. Budke and Koop, 2015, Harrison et al., 2018, Hill et al., 2014, Whale et al., 2015) as well as other systems in which water is condensed onto particles collected on substrates prior to cooling and freezing (e.g. Mason et al., 2015). As they are designed for analysis of liquid suspensions, droplet freezing assay techniques are commonly used for measurement of INPs suspended in precipitation (e.g. Creamean et al., 2019, Rangel-Alvarado et al., 2015, Michaud et al., 2015, Stopelli et al., 2014, Wright et al., 2014).

Many studies report results from samples stored prior to processing. Storage protocols vary widely, including total storage time, time between collection and storage, and temperature fluctuations between collection, shipment and storage (if these details are provided at all, see summary Table S1). Storage temperatures range from -80 °C (Vali et al., 1971) to +4 °C (e.g. Petters and Wright, 2015, Failor et al., 2017, Joyce et al., 2019), yet generally samples are stored between +4 °C and -20 °C. Reported storage intervals range between hours (Schnell et al. 1977; Christner et al., 2008) to 48 years (Vasebi et al. 2019).

Referee: “6. Discussion, last paragraph starts “Significant enhancements in INP concentrations occurred less frequently than losses. Again, changes in the total particle size distribution could explain some of the observed INP concentration enhancements.” – an important conclusion. However, the paragraph then changes topics to the impact of freezing on IN-active (biological) molecules. This is neither consistent with the topic of the paragraph nor is it part of the research outlined in the paper. Lines 259-269, as currently constituted, should be removed.”

These lines have been removed from the last paragraph of the Discussion.

Abstract ": : :likely and an additional uncertainty in INP concentrations: : :" remove and?

Corrected. Abstract, Line 25: "We provide the following recommendations for preservation of precipitation samples from coastal or marine environments intended for INP analysis: that samples be stored at -20 °C to minimize storage artifacts, that changes due to storage are likely an additional uncertainty in INP concentrations. . ."

"Significant insights have been obtained: : :" 'highly uncertain" : please eliminate nonobjective terms like 'significant' (throughout paper) – these are reader dependent, not quantitative.

These terms have been removed from the paper, except for instances referring to Fisher's Exact Test. A statement to clarify this has been added to the Results section 3.2.

Sec. 3.2, Line 229: "The term "significant" henceforth is intended to describe INP losses or enhancements that correspond to frozen well fractions that are determined to be significantly different from corresponding fresh sample frozen well fractions, according to Fisher's Exact Test (i.e. filled markers in Figs. 2-4)."

Introduction, Line 78: "The understanding of storage effects on INPs suspended in precipitation is limited (Petters and Wright, 2015). . ."

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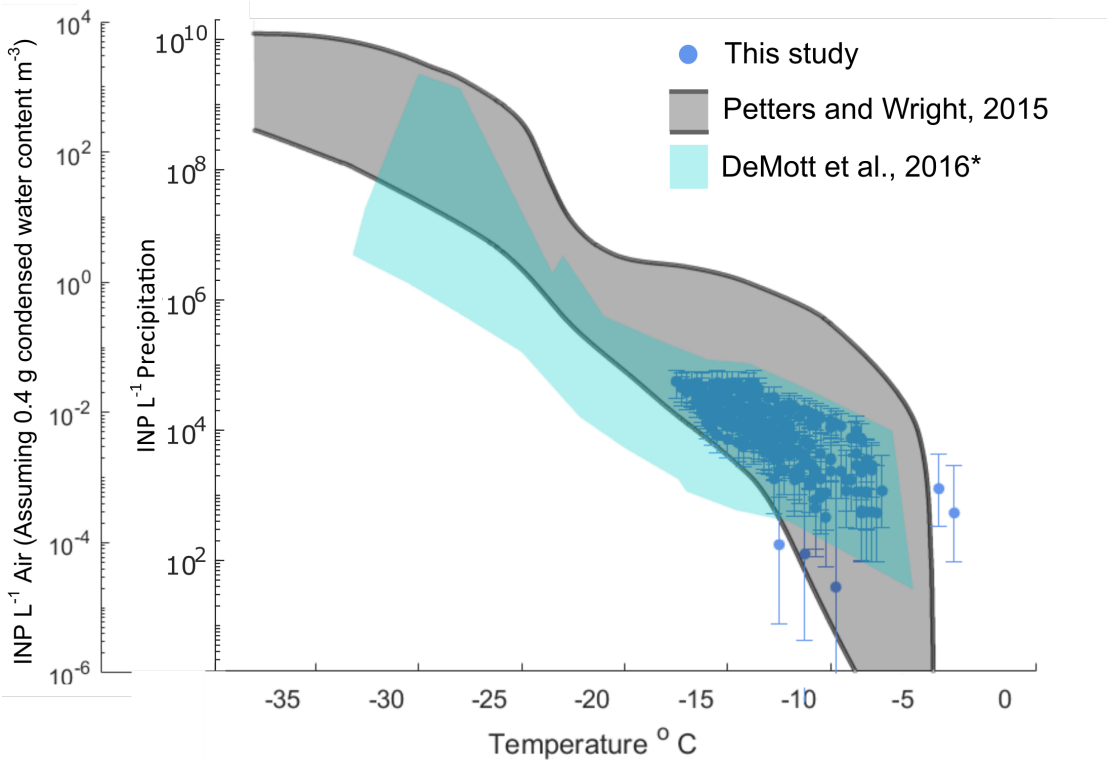

Fig. 1. Figure1

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