

Atmos. Chem. Phys. Discuss., referee comment RC2
<https://doi.org/10.5194/acp-2021-830-RC2>, 2021
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Comment on acp-2021-830

Anonymous Referee #2

Referee comment on "Time dependence of heterogeneous ice nucleation by ambient aerosols: laboratory observations and a formulation for models" by Jonas K. F. Jakobsson et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-830-RC2>, 2021

General Comments

This is quite a nice study, using a limited number of samples to study the time dependence of ambient ice nucleating particles freezing in the immersion freezing mode. In contrast to what I read in another review, I find the details about the experimental device (LUCS) and methods to be very good (and the authors responsible for it are to be lauded). The writing is also fairly clear, excepting poor introduction/definition of terms used in equations. The results demonstrate a relatively weak time dependence to freezing that is nevertheless consistent with prior studies using soil samples and cloud water. The consequent impact can be described by a temperature adjustment of say 2K in order to describe freezing at longer time scales. One does wonder to what extent temperature control of the drops and where an INP may be floating in individual drops may influence these results. This is not discussed. In any case, the corrections in comparison to very short time scales range up to at most about a factor of 2. It is interesting that this is well within the bounds of the agreement of many immersion freezing methods when compared together. This is not spoken about either, but should be mentioned, the reason being that it emphasizes the utility of such measurements, regardless of whether used in a deterministic manner or with an approach as suggested here to describe the modest time dependence. While much effort is expended on analyzing cooling ramps and isothermal data on six samples, the least convincing aspect of the study is that these six cases can be clearly identified and taken as sufficiently representative and attributable to the types of aerosols identified for comparison. There are reasons that there should be variability amongst those types, and season could matter for different types as well. I recognize that numerous caveats were added in regard to the inability to know INP composition, but they are ultimately ignored in fashioning a parameterization that differs for the different types. Consequently, in suggesting that these results could be used as representative of INP types present in the noted aerosol scenarios (e.g., mineral, or organics) moving forward, when in fact the differences between them are modest (note Fig. 5 and Fig. 10, with insignificant differences apparent), is questionable. In reality, it seems unnecessary, unless one is only intent on using the referenced parameterizations instead of simply pointing out how deeper insights could be gained in the future using these methods in places where certain aerosol scenarios are clearly more dominant. This is not meant as a severe judgment on a study that has been needed for a long time. Needed and useful, especially for pointing out that corrections to INP data for time dependence is small, and

results do not change greatly in repeated experiments, challenging some other recent studies (not noted, but oddly referenced at one point for the exponential decay of freezing rates – which those authors seem to attribute to experimental artifacts) that suggest that immersion freezing nucleation is largely purely stochastic for ambient INPs. It should be emphasized more that the present results appear to reject that hypothesis. One other factor that I felt needed to be brought out in discussing Westbrook and Illingworth is the extreme population (extraordinarily high INP concentrations) required by that study to exist for their hypothesis of long freezing time constants to explain ice formation in clouds. Considering all other existing measurements of INP concentrations in the ambient atmosphere, and results such as presented in this paper on time dependence of freezing, the numbers required by that conjecture are not within the realm of possibility. I kept expecting the discussion to come back to this point, but clearly the authors have in mind to do full model simulations to invalidate the earlier hypothesis. That is a bit disappointing, because it leaves the readers hanging. In the end, the study is demonstrative of what could be done, with great effort obviously, if many more cases are identified or if done in environments that are more clearly dominated by certain INP types. I have an assortment of related and other specific comments added to this, which I do below in order of appearance. My recommendation is that this paper needs revision in places before being accepted for publication.

Specific Comments

Abstract

Line 13: It should read “six” ambient samples, to be explicit.

Introduction

Line 53: The first ice in any mixed phase cloud does not have to be from activation of INPs if sedimentation occurs from higher levels that may reflect homogeneous freezing conditions.

Lines 61: Only spot I saw where ice nuclei is used in preference to ice nucleating particles.

Lines 72-73: There is a fine point here that is not stated with regard to Westbrook and Illingworth’s argument. This is that the action of a stochastic process over many hours would require an INP population unlike any ever measured. It already seems a nonstarter, but this study provides insight.

Lines 93-94: A reference seems appropriate to support this point

Line 115: This is a curious reference for a paper that ultimately finds results in complete disagreement with single parameter CNT. Is it meant to point out that this is the case for certain INPs, such as illite?

Line 130: "...here is an inevitable cost from lack of identification of the precise chemical species initiating the ice in observed samples." I appreciated these caveats, so then I wondered why the selected samples were not treated only as examples, rather than suggesting they are meaningfully representative of specific aerosol types. There are ways to get at INP composition, even via immersion freezing methods, they simply are not used herein (see below).

Methods

Lines 159-160: I am curious about the selection of filter pore size. I understand that larger pores allow high flow. Was face velocity and collection efficiency considered to estimate if there were undercollection of particles at 0.4 microns and smaller?

Line 161: What does it literally mean that not all filters were able to achieve a full 24-hour sampling? This is an unusual statement. The pump stopped because of overloading of the filter? The flow rate changed and you did not record it over time to get an accurate volume? If flow rates were not recorded, then this should be stated as an uncertainty for INP concentrations.

Line 168: There is a difference between marking the samples to reflect different aerosol types and what will dominate as INPs, right? Sometimes the dominant composition is irrelevant if one particular type acts with higher efficiency. I think you aimed to select episodes that represented potentially different dominant aerosol types, assuming that these might reflect different abundances of INPs of different types. Ideally, you need a single type that is not influenced by trace amounts of another type, but there is literature to show that a little mineral dust sometimes overwhelms a marine INP population. Hence, the approach has a great deal of uncertainty associated with it. This of course is the nature of ambient sampling, and why some attempt to parse out influences of the different aerosol types present through more detailed approaches.

Line 174: You need to say more about how the HYSPLIT model was set up, and it should be referenced appropriately. I especially did not understand why the trajectories were set to end at 500 m, instead of somewhere closer to the surface site. Did you test different levels for this end point location?

Lines 188-189: But can you say that soil dust does not dominate also in the "combustion-

dominated" sample, or any particular continental sample for that matter? You are a bit blind without knowing anything about the nature of the INPs contained in the air at any time.

Section 2.2.2 overall: I will say that I otherwise appreciated the honesty and accuracy in statements made in this section about how certain (not very) one could be about the assumed total aerosol composition as representing INPs. Then why title it "Sample classification according to likely dominant composition of INPs"? Again, you are referring to what you think is the dominant aerosol type. There is no guarantee that the total aerosol type abundance will be reflected by a dominant INP of that type. It depends on individual efficiencies and what all types are there, which I think the authors understand. I suggest that in the future it could be beneficial to analyze for general INP types using methods in the literature (e.g., Testa et al., 2021, J. Geophys. Res, doi: 10.1029/2021JD035186). There are ways to get at inorganics that would include minerals and black carbon, for example.

Section 2.2.2 also: Have you considered testing your assumption using aerosol reanalyses, such as MERRA-2?

Section 2.2.3: What is a sterile cryogenic vial? That is, what do you mean by sterile? Was it tested for INPs released by pure water?

Lines 306-308: No freezing, meaning zero wells frozen? In general, I felt that the testing of water, field blank filters rinsed in water, and any other handling protocols need a little better documentation, especially for temperature ramps. Surely there is a background in the device. There were no frozen wells for DI in similar ramps, nor for the field blanks?

Results

Lines 319-326: These generalizations are fine. At such a sampling site, even these characterized types must have seasonality, no? Perhaps in the conclusions you should note that using these 6 samples to characterize different source types might be a stretch until an annual cycle is explored or means are derived to more carefully distinguish influences and assured impacts on INPs.

Lines 331-332: Given this, I do not think that you can make the statement that it is "highly likely" that these six identified types differ significantly. You have not proven that. They all look quite similar within some bounds (again, differences in both Fig. 5 and Fig. 10 are minimal). Are they representative of INP in general for the region? That seems likely. If you have the aerosol data and can make such calculations, could you not normalize all of these events (except the dust one where there is no data) by total aerosol surface area to see if that separates them at all? I understand that what you would want

is speciated surface area, but total could be informative.

Figure 5: Should you not actually show the variability you are referring to in the caption, e.g., with error bars?

Line 340. I became confused already earlier in the paper as to whether or not repeated cycling involving heating and cooling were used. This fact should be moved forward in the methods.

Lines 366-367: "...because the probability of any drop freezing during any isothermal experiment decreases with decreasing normal freezing temperature below the isothermal temperature." I did not understand this at all. This is not intuitive without some additional explanation.

Figure 8: Question of clarification. The "freezing fraction" here is on the basis of the droplet population, correct? Or on the basis of the final number frozen? This figure is difficult to read due to the use of a logarithmic scale on the x-axis. What do these look like with time on a linear scale of say hours starting from time zero? That would seem to be a starting point, before plotting them this way.

Figure 9: I especially cannot understand this figure. Should not the end total ice fraction be larger than the initial ice fraction in all cases? Why would this ratio be less than 1? Or does 0.5 mean a 50% increase and so on? If so, the y-axis needs redefinition.

Figure 10 and discussion around it: This is an interesting figure that suggests to me that the INPs generally have similar freezing behaviors that are describable in nearly a chemical kinetic fashion (e.g., DeMott et al., 1983, *J. Clim. Appl. Meteor.*, doi:10.1175/1520-0450(1983)022<1190:AAOCKT>2.0.CO;2). I wondered though what N and N_{ice} exactly are. They are the same? These are not defined anywhere, either in the manuscript or the caption. Are they the total number of drops? Or the total number frozen after xx hours? If looking at the change in freezing rate, it seems like the reference should be the total INP population, not the drop number that may or may not reflect an INP per drop. I think that the relevant value is $N_{ice, infinity}$, in Eq. (1), but it is unclear how this is determined or estimated. I think this is finally stated later, perhaps at line 408. Hence, the introduction of these things is a bit out of order.

Figure 10 caption: "Occasional negative rates are not plotted." How do you get a fractional freezing rate that is negative?

Line 399: Now $N_{ice}(t)$ is a frozen fraction? This is very confusing. Frozen fraction or

number terms need careful definition before they are used. N normally refers to number, but I sense it is being used for both number and fraction in this paper.

Line 534: That there are multiple INPs in each drop is a risk? This is a fact of the method, at least for cooling ramps that extend over the mixed-phase regime. It is accounted for in most immersion freezing analyses, ala Vali (1971).

Lines 571 to 572: I do not trust that you can make such correspondences at all. The study is not sufficiently detailed to do so. You do not even know if sources are organic or inorganic, for sure.

Line 590: Possibly. It remains to be seen how useful the approach will be. But this is where we are left hanging. If the total INP number is not so much greater than measured deterministically with a small temperature shift, aren't the conjectures of Wetsbrook and Illingworth invalid already?

Line 644-645: It may enable it, but odd to highlight a single study without proving it. Can we expect that robust simulations will be achieved? I suggest that the emphasis on saying that single events can be used to target certain aerosol types be removed from this paper, and postulated instead in the next one that seems in preparation.

Data availability: No statement was made. Will the data be made available somewhere? This is important.

Editorial notes

Line 24: decline, rather than declines.

Line 124: do you really need the word "Background", which is not really quantifiable. Just say you collected aerosol data?

Line 137: I would omit "assumed to be likely". It does not help qualify that there is no way to be certain about influences, considering limited information on aerosol compositions.

Line 616: "for what we have inferred to be representative of mineral..."

