Summary of Author Responses to Reviewers

In summary, we have heeded the warnings of both reviewers. A chief concern was about relating the aerosol samples to major INP types in the model. We have always been open about the uncertainties inherent in assuming particular correspondences. To address this issue, we have now included more information characterizing the aerosol samples (lines 218-330), with fresh measurements in Sec. 2.2.2 with a new Table 2. We also compare in more detail the INP concentrations seen in the samples with a new Figure 6 in Sec. 3.1.1 (lines 450-580) and provide the statistical tests required in a new Appendix A (lines 1005-1035).

Specifically, the physico-chemical aerosol properties presented in the reviewed manuscript were considered too limited by both reviewers. In the revised manuscript we present many new measurements of additional relevant aerosol properties (see the renewed Table 1, lines 233-330). All aethalometer data from our sampling period had to be re-analysed, which has led to slightly different and more robust concentrations of black carbon. In addition, we have included (i) elemental concentrations inferred from particle induced X-ray emission studies of the remaining filter pieces, (ii) concentrations of supermicron primary biological particles when available and (iii) the chemical composition of the non-refractory particulate matter with diameters below 1 μm.

The added aerosol data support the initial classification of the samples and aid the discussion of potential differences in dominant types of ice nucleating particles within the sample ensemble.

Another concern was the need for more clarity in the explanations of the formulations applied. We now have done that by defining symbols more carefully and by giving a list of symbols in a new Table B1 in the Appendix B.

We have revised the figures for more clarity (new Figures 6-11). We have provided new Figures (e.g. Figures 5 and A1) to elucidate better the stochastic behavior, for instance with a new Figure 11b showing the fractional rate of change of the numbers of unfrozen drops.

With these changes, we hope that the paper is almost ready for publication.

Author Response

We are grateful to the reviewer for their comments on the manuscript, which have helped to improve it.

We have tried to improve the explanation of the mathematics with a new Appendix B with a list of symbols (lines 1045-1050).

Point-by-Point Comments

Reviewer: This study analyses the time-dependence of freezing exhibited by ambient aerosol samples collected in southern Sweden. Constant cooling and isothermal experiments were performed with a recently developed cold-stage. The time dependence was found to be comparable to that seen in previous studies. A representation of time dependence for incorporation into schemes of heterogeneous ice nucleation, which currently omit time dependence, is proposed. The relevance of time-dependence in heterogeneous ice nucleation and its implementation in freezing schemes of cloud models is a timely and important topic. Yet, the study has major weaknesses that need to be addressed before publication. Moreover, the manuscript is not written carefully. The language and formulations are often imprecise and unclear, which hampers the understanding.

Response: The reviewer's warning is well taken.

In response we have improved the language and formulations, with a more detailed definition of the mathematical symbols. These are listed in a new Appendix B (lines 1045-1050).

Reviewer: All the samples were collected at the Hyltemossa research station located in southern Sweden. The investigated samples were assigned to the following aerosol classes: marine dominated, mineral dust influenced, continental pristine, continental polluted, combustion dominated, and rural continental based on wind directions. In addition, BC content, PM1 and PM10 were determined. No attempt was made to further characterize the samples to confirm the assignments. The frozen fraction as a function of temperature shown in Fig. 6 and the INP concentration (Fig. 5) are all very similar and do not show the diversity found for INP samples collected at different locations. Also, the IN activity exhibited by the different samples are often opposite to expectations based on the class they were assigned to; e.g. the marine and the mineral dust samples were found to exhibit very similar INP concentrations, yet marine samples typically exhibit much lower INP concentrations than mineral dust samples.

Response: **We never claimed to cover all "the major relevant IN classes", so there is nothing to be abandoned.**

What we actually wrote in the reviewed manuscript was:

> *"Six ambient aerosol samples were collected representing aerosol conditions likely influenced by these types of INPs: marine, mineral dust, continental pristine, continental polluted, combustion-related and rural continental aerosol"*.

> *"A representation of time dependence for incorporation into schemes of heterogeneous ice nucleation that currently omit time dependence is proposed"*.

> *"In this study, we aimed at selecting samples likely to be dominated by different INP types at least of relevance to Northern Europe, and most likely of wider spatial-temporal relevance"*.

> *"In the present study we present empirical data about the time dependence of heterogeneous ice nucleation for six ambient environmental aerosol samples. Ambient environmental samples, representing a variety of aerosol types expected to be dominated by certain INP species, were investigated. As they were natural samples, they must be assumed to contain a complex composition, where multiple INP species may be active".*

The language here has always been cautious and we never claimed that our samples definitely characterise **all** major types of INPs.

The concentrations of INPs we report (the new Figure 6) for the marine sample are almost identical to the average concentrations reported for a number of Pacific Ocean samples (Mason et al., 2015) and very similar to concentrations reported by Si et al. (2018) for the Northern North Atlantic. In Arctic marine samples, lower INP concentrations have been reported (Irish et al., 2019). Overall, lower and higher INP concentrations than what we report have been observed in marine environments. So judging from the INP concentrations alone, there is nothing speaking against that sample potentially being dominated by marine INPs. There is no evidence of any problem.

This is all discussed with fresh text (lines 450-552).

It is likely that dust particles contribute significantly to the immersion freezing INP population at many different locations and in various environments where other types of INPs may be absent. Hence, dust particles may be the dominant immersion freezing INP type although present at low concentrations in remote pristine regions during some seasons. In our study, it is highly likely that a significant fraction of the PM in the dust dominated sample was comprised of Saharan dust, which had been transported for about a week in the atmosphere before collection in the boundary layer. Hence, we would not expect dust loadings or INP concentrations as high as could be expected in the dust plume and/or closer to the source region.

We have extended the supportive aerosol chemical analysis as suggested, and the results reported in the revised version of the manuscript do confirm elevated dust concentrations in the dust sample. Also,

the additional analysis confirmed that a significant fraction of the supermicron PM present in the marine sample could be associated with sea salt. In general, we find that the added aerosol properties support the sample classification.

In summary, the reviewer's warning is well taken. During revision of the manuscript we have added more analysis of the aerosol composition for each sample (lines 220-330) **and have included more cautious wording (e.g., line 18).**

Response: We have not been able to work with our cold stage since November 2021, due to major construction work in our lab. Hence, we are limited to data already obtained with the cold stage in this context.

The temperature of the cold stage has been measured with external thermocouples and a very good agreement was observed relative to the cold stage read out. So we do not expect any significant temperature biases, in addition to the one described in more detail below.

All data obtained during constant cooling ramps of 2.0 K/min (> 10 000 freezing incidents) have been analysed. We compared the freezing temperature of the outer 50% of droplets to the inner 50%, regarding the placement of drops in the array on the cold stage. We found that the subset of droplets present closer to the outer edge of the array on average appeared to be exposed to temperatures 0.20 K higher than the centrally placed droplets for these cooling ramps and temperatures within the range -20 to -15°C. The INP concentrations presented in the revised version of the manuscript has been corrected for that offset, which had only a minor influence on the reported results. We do not have sufficient cold stage data to tell to which extent the temperature offset would be reduced if a slower cooling rate (e.g., of 1.0 K/min) were applied, but it is likely. Also, we consider it likely that a temperature off-set for the isothermal operation would be less than 0.20 K for the droplets closer to the edge. Hence, it is likely that a fraction of the droplets during isothermal experiments had temperatures 0.1 to 0.2 K higher than was we report. We consider such minor offsets acceptable for this type of experimental work.

A fresh figure with freezing curves for ultra-pure water has been included in the revised manuscript. This new Figure 5 shows the frozen fraction observed for ultra-pure water during the constant cooling rate experiment (lines 441-443). It confirms the accuracy of our device, as the freezing then occurs mainly at temperatures colder than about -25 degC with a freezing temperature for 50% of drops frozen colder than -30 degC. This is near the homogeneous freezing temperature.

Response: "Stochastic" means that chance governs whether any active site on the solid aerosol particle nucleates ice so that there is a time-dependence of the population of such INPs. Our observations of time-dependence are consistent with that role of chance acting on active sites, each with a fixed freezing rate at any given temperature.

The goal of our paper is to measure the overall time-dependence of ambient aerosol samples and to provide an empirical framework for representing time-dependence in cloud models. Our aim is not chiefly to explain the underlying reason for the time-dependence, which would probably require additional experiments.

However, we can make some reasonable inferences about likely explanations. Regarding the freezing fraction spectrum among drops as a function of temperature during constant cooling experiments, a qualitatively similar spectrum was observed by Wright and Petters (2013, their Figure 5) as shown in our paper (our new Figure 6). They fitted their observed spectrum with a model based on a modified classical nucleation theory involving a statistical distribution of active sites of a wide range of efficiencies and multiple components. Moreover, observations by Wright and Petters (2013, their Figure 7) suggest an exponential decay of the freezing rate with time, which we also observe (our Figure 11). This all suggests that our results could be simulated by the same type of model based on multi-component multiple-component stochastic model of heterogeneous freezing nucleation, or even simply by assuming a variable amount of INP material per drop with a single component (Knopf et al. 2020).

It is difficult completely to rule out time-dependence arising from systematic changes in the freezing temperature of individual INPs over time. This could arise perhaps from morphological changes in the immersed solid material or immersed particles migrating with time towards the drop surface, where freezing is more likely.

However, as can be observed from Fig. 7, there is very high reproducibility of the frozen fraction vs temperature for repeated constant cooling ramps carried out on the same droplet population. It is also evident from Fig. 8, that the vast majority of studied droplets froze at almost identical temperatures between repeated cooling ramps (see the red error-bars).

The singular model would be a good approximation for our observations since the degree of time-dependence seen is quite limited. We were aware of potential changes in freezing patterns over time and after performed freezing cycles. The impact of exposure to isothermal conditions for 10 hours is merely a change of freezing temperature by 2 or 3 K for most drops.

We do observe some pronounced variability in freezing temperature for a minor subset of droplets. In future work, it would be interesting to check when and how that variability occurs. Is it a systematic change/jump in freezing temperature – which shows reproducibility – or did we observe more 'random' variability in such cases?

In summary, our observations are qualitatively consistent with the stochastic theory from Marcolli et al. (2007) or Wright and Petters (2013) or Knopf et al. (2020). However, the degree of time-dependence we see is weaker. It is beyond the scope of our paper to analyse the theoretical reasons for the time-dependence we observed. Text has been added to clarify (lines 610-635).

Reviewer: The relevant literature is not sufficiently taken into consideration in the introduction and in the discussion of the results (see specific comments).

Response: In the revised paper, the literature is now discussed more fully with inclusion of the references suggested in the reviews (lines 63-70, 103-108, and 126-130).

Reviewer: Line 41: the "many possible pathways" should be specified in the text.

Response: This has been done (lines 46-49).

Reviewer: Field and Heymsfield (2015) is not listed in the reference list. Moreover, more references should be given to support this statement, e.g. DeMott et al. (2010); Mülmenstädt et al. (2015).

Response: This has been done (line 43).

Reviewer: Lines 53-58: The discussion of the different types of atmospherically relevant INPs includes only two references. This is not sufficient.

Response: Many further references have been added (lines 60-70). Also, the description of INPs potentially associated with combustion emissions has been extended for support of the more extensive chemical aerosol analysis presented in the revised manuscript.

Reviewer: Lines 61–62: this statement is too general.

Response: We have added text to that sentence so as to explain what is meant (lines 73-76).

Reviewer: Line 93: here again, more than just one study should be referenced, e.g. add Vali (2008; 2014).

Response: Done, we have also cited Vali (1994) here (line 107).

Reviewer: There have not been many studies on temperature dependence but more than mentioned here. Older studies have been reviewed in Vali (2008) and Westbrook and Illingworth (2013). More recent laboratory studies have been performed by Herbert et al. (2014), Beydoun et al. (2016), Alpert and Knopf (2016), and Kaufmann et al. (2017). Moreover, there have also been recent modeling studies on the time dependence of immersion freezing, namely by Vali and Snider (2019) and Fan et al. (2019). These references should be included and discussed.

Response: We presume here that the reviewer meant to write "time dependence" instead of "temperature dependence".   These references have been added as required (lines 126-130 and 155-158).

Response: Yes, that follows from the definition of PM1 and PM10.

Response: Yes. It is now corrected.

Response: The parameterization from Fletcher (1962) represents and average over different types of airmasses. The Fletcher parameterization is extremely often used as reference when these types of data are presented also in several recent publications. Hence, we find it useful to include here as a reference as well.

As stated above, we do not agree with the reviewer, that any given type of sample (e.g., marine or dust dominated) is associated with a specific INP concentration. In reality, the associated INP concentrations of a given type of sample typically spans several orders of magnitude in concentration.

Finally, we have included references (e.g., Si et al., Irish et al., Mason et al.) in the text to indicate that the observed concentrations of INPs are comparable to what has been reported in the literature (lines 495-500).

Response: Statistical tests have been performed as required for the freezing behaviour at -15 degC for all possible permutations of pairs (two-sample F tests) among the six samples. Some pairs of samples statistically differ from each other; other pairs are similar.

A new Appendix A in the paper now summarises the results.

Furthermore, random errors are included in the new Figure 6 showing the INP spectra.

Response: These variations of 0.3 K refer to repeated experiments of freezing for any given population of drops. The text now clarifies this (line 551), (see also lines 560, with a new Table 2).

Reviewer: Lines 357–360: The values given here should become part of a table, in which also the largest and smallest standard deviations could be listed.

Response: This has been done with a new Table 2.

Reviewer: Line 360: Vali et al. (2008) is not in the reference list.

Response: This has been added.

Reviewer: Lines 362–369: It should be stated which fraction of the droplets remains unfrozen, e.g. as an additional column in Table 4. The difference for most drops was stated to be "about 1–2 K". How was this value calculated?

Response: This extra column in the new Table 3 (previously Table 4) has been included.

The statement that for most drops the difference was "about 1–2 K" is a comment on Figure 8 and not a formal calculation. It should be regarded as data commentary (lines 566 and 578).

Reviewer: Lines 376–378: The differences between individual isothermal experiments cannot be seen properly in Fig. 8, because all the isothermal experiments are shown as blue data points. Please choose different colors for different isothermal experiments. Moreover, the larger diversity between isothermal compared to constant cooling experiments should be discussed/explained.

Response: Figure 9 (previously Fig. 8) has been replotted as required.

The diversity between the isothermal experiments is larger compared to the constant cooling rate experiments as the dependence on temperature is much larger than that on time. This makes the constant cooling rate experiments appear much more predictable and thus repeatable than the isothermal experiments, which show a more stochastic behavior and more diversity.

Text has been added to clarify (lines 587-588).

Reviewer: Line 381 and throughout the manuscript: There seems to be a confusion between "freezing fraction" and "frozen fraction", which seem to be used synonymously. Yet, the frozen fraction means the fraction frozen at a given time, while the freezing fraction designates the fraction of drops that froze within a set time interval. As it seems, the authors mean "frozen fraction" most of the time.

Response: The terminology is now changed everywhere as required.

Response: Thank you for the suggestion.

We are inclined to keep the figure as it is, since it encapsulates the essence of the measured time-dependence in one simple picture.   The purpose of this Table 3 is to provide many more measurements for extra information. Table 3 includes much more information than what is shown in the new Figure 10.

The formula defining chi is included in the text as required (line 593).

Response: The plotted fractional freezing rate (now Figure 11) was evaluated numerically with a finite difference scheme to approximate the derivative, using consecutive values of freezing fraction in each time series of measurements. The text is modified to clarify (line 604).

Response: We now add text to clarify (lines 624-627).

By "active", we really meant more efficient (a higher nucleation efficiency).

We now realise it may have been better to plot the fractional change of the unfrozen fraction for analysis of the stochasticity. So we have added a new Figure 11b showing this.

This sentence is about isothermal experiments, so the temperature dependence of the efficiency of INPs is not so relevant here. Anyway we now include mention of this temperature and also clarify the concept of slow and fast INPs.

Response: We agree that temperature dependence is crucially important generally.

But this Section 3.2.1 is entitled "**Isothermal time series and relaxation time**". This is not the point in the paper where we consider temperature-dependence.

The model (Eq (1)) provided at this specific point in the paper is not intended as a model of ice nucleation generally for all temperatures. Of course, later in the paper we will show how to create such a model. Perhaps the word "model" has connotations in the experimental community that we never intended.

To avoid confusion, this Eq (1) is renamed as an "empirical isothermal formulation" (instead of "model"), (line 641), to convey the fact that it treats the measurements in isothermal experiments at a single fixed temperature. There are no temperature fluctuations of any significance during each isothermal experiment.

Reviewer: e.g., what would be the time dependence of freezing in an air parcel that was supercooled by 1 K before reaching the isothermal period? Vali (1994) found that this depletes the INPs that are active at the isothermal temperature. The proposed approach should also be discussed in view of the findings of Vali and Snider (2015).

Response: See the preceding comment. We will propose a general model of atmospheric ice nucleation with time- and temperature-dependence later in the paper, not here.

Here, with Eq (1), we are only trying to understand the observations at constant temperature.

Reviewer: Line 419–421: Again, this argumentation insinuates that less active sites activate more slowly than the more active ones.

Response: That is what Herbert et al. (2014) found: INPs that are less efficient display more time-dependence and activate more slowly.

Reviewer: Yet, the nucleation rates of sites are highly temperature dependent.

Response: Yes, absolutely. We never denied that. Right here, with Eq (1), our focus is not on temperature-dependence. This section 3.2.1 is about the isothermal experiments.

Reviewer: Line 440, Eq. 4: How is the time dependence of the INP concentration calculated?

Response: There was a typing error in Eq (4). On the RHS the only time-dependence represented is via DeltaT, the temperature shift, which is informed by our lab data empirically.

Reviewer How can the temperature shift approach be combined with temperature fluctuations observed in air parcels?

Response: Those temperature fluctuations in air parcels are predicted by any cloud model that resolves the parcels. Our approach is designed to be implemented in the IN scheme of such a cloud model.

The dependence of IN activity on the ambient air temperature is already represented in the unmodified empirical parameterization (Phillips *et al.* 2008, 2013). The time-dependence of INPs is represented as a higher order perturbation, with the time-dependence of the temperature-shift being assumed to be the same at all temperatures.

The lack of sensitivity of this time-dependence of the temperature shift with respect to temperature is suggested by results from Herbert et al. (2014, their Figure 2).

Response: Done (Table 5, line 716).

Response: The grammar has been improved (line 726).

Response: Done (Table 5, line 734).

Response: We were referring only to the qualitative pattern of the degree of time-dependence among the six samples. The text is now clarified (line 736).

Response: Done (line 740). This sentence was intended to explain the previous sentence.

Response: Done (line 746).

Response: Corrected.

Response: We do not completely agree with this notion.

In reality, repeatability of measured freezing spectra before and after the isothermal experiments, as reported in the paper, implies that there is little systematic shift in freezing temperatures of individual INPs. We do not see signs of such non-stochastic changes in IN activity in our data for the vast majority of drops we observe.

The weaker repeatability of freezing for a minority of drops requires further investigation (see the few wider error-bars in the new Fig. 8).

Our observation here further reinforces the need for the experimental community to study ambient aerosol samples, instead of surrogate samples from the ground or artificially manufactured aerosol material, when seeking conclusions about atmospheric ice nucleation.

A change of focus is needed we believe in the community. We have added text to convey this in the concluding section (lines 931 and 967).

Response: The reviewer is correct in this comment, and we have considered experiments with diluted samples to further investigate this phenomenon. Unfortunately, under the scope of this study we were limited both in experimental time and in the amount of available sample to perform these experiments. Thus, we have prioritized to keep the measurement procedure, including sample preparation, consistent for all samples in this study.

Also, as stated in lines 787-790, we have made calculations which imply that further dilution of the samples may have a significant impact on the number of observed freezing events during the isothermal phase of the experiments. This could potentially further weaken the counting statistics which is already a challenging.

Studying more dilute samples would involve isothermal experiments at colder temperatures with the potential to investigate the INPs active at lower temperatures. With our apparatus – we may not be able to carry out isothermal experiments at much lower temperatures – before the background may start to bias observations.   Also, these isothermal experiments are extremely time consuming – already representing months of full time lab-work.

Response: Done (lines 787-790).

Response: We agree. The sentence is now deleted.

Response: This has been done (lines 830, 840-861). The definition of "cold cloud" is delineated precisely.

We have re-written some of the maths so as to make clearer the numerical technique for including the time-dependence in a cloud model. We have now included a new Appendix B with a list of symbols for extra clarity.

Response: This change is now made.

Response: Yes, this is now corrected.

Response: The INP concentrations were obtained as described by Vali (1971), and that has been specified in the text. The new Figure 6 (previously figure 5) showing the INP spectra easily becomes hard to read. In the revised manuscript, we have only made use of the first constant cooling ramps for

each of the five different droplet populations investigated for each sample (in total 500 droplets). The random errors representing the variability between these data have been included in the revised figure.

As described in more detail above statistical tests have been performed and we do not agree to the idea that a well-defined INP concentration is linked specific aerosol types. The limited data set we present in the revised manuscript with several additional aerosol properties included clearly shows that similar INP spectra can be observed for significantly different aerosol classes.

Also, we do not find evidence supporting the reviewer's point of view here in the literature, as described in more detail above.

Reviewer: Figure 6: The differences in frozen fraction between aerosol classes are small and difficult to judge the way the frozen fraction is plotted. The figure could be improved by narrowing the temperature range to -5°C to - 25°C (as it is done in Fig. 13) and by adding gridlines to the panels.

Response: This is now done in the new Figure 7.

Reviewer: Figure 7: It might be helpful to add dots for the drops that did not freeze during the isothermal experiments. They could be put at the bottom of the panel (at -25°C).

Response: It is not possible to do this since the temperatures at which those drops froze were not observed. They generally did not freeze at -25 degC.

Line 884: what is meant by "minimum of 4 cooling cycles"?

Response: Some of the experiments involved multiple cooling and heating cycles. For the new Figure 8 we used at least 4 such cycles per sample.

Reviewer: Figure 8: These plots are again difficult to read. The frozen fraction for each experiment should increase continuously but the blue data points just scatter, most probably because they stem from isothermal experiments performed with different droplet populations. In this case, they should be shown in different colors or symbols so that different experiments can be discriminated. Were the data points taken at defined time intervals?

 Response: Corrected in the new Figure 9 with different shades of dots for different drop populations.

Reviewer: Figure 9: the information provided by this figure is also given in Table 4. It can be removed.

Response: We prefer to keep this new Figure 10 as it encapsulates the essence of the time-dependence in a vivid way.

Response: Corrected.

Response: We meant "much scarcer". We have now clarified the caption of the new Table 3 to explain this.

Replies to Reviewer 2

Author response

We are grateful to the reviewer for their effort in scrutinizing the manuscript.

We have included the extra statistical analysis required with a new Appendix A. We now characterize the chemical composition of the aerosol samples in more detail (lines 218-326), justifying the classification we have given. Table 1 and Sec. 2.2.2 have been greatly extended.

Point-by-point Responses

Reviewer: 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.

Response: We are grateful to the reviewer for the encouragement and we agree that the time-dependence observed is rather limited.

We have improved the definition of the maths symbols to make the paper more accessible to the modeling community. There is now a list of all maths symbols in a new Appendix B.

Reviewer: 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.

Response: These are key questions and we now include discussion of possible systematic reasons for time-dependence (lines 541-547).

However, as we point out in the fresh text, the high degree of repeatability of the freezing temperature of each drop indicates that such systematic reasons for time-dependence are not significant.

Reviewer: 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.

Response: Yes, we agree that the degree of time-dependence we detect is so limited that its effect, when represented in cloud models by adapting IN schemes derived from field probes (e.g. CFDC), may be dwarfed by the instrumental errors of those probes.

We agree that our study confirms the utility of measurements of IN with the CFDC and other similar field probes. We add text to stress this with a new paragraph in the concluding section (lines 942-950).

Reviewer: 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.

Response: We agree that this is a limitation of our study. However, there are reasons for believing that there is little effect on the time-dependent temperature shift arising from the type of INP composition. Herbert et al. (2014) found that this temperature shift was invariant when comparing contrasting INP types with high and low nucleation efficiencies. This invariance was explained theoretically.

If the degree of time-dependence is not dramatically sensitive to INP type (e.g. Figure 10), then there is no problem arising from uncertainty in the assumptions of which INP type are represented by which of our aerosol samples when the scheme is applied in a model.

In this revision of the paper we have substantially extended the amount of presented physico-chemical aerosol properties in the revised Table 1 (lines 220-330). So there is more evidence provided now for the contrasting aerosol conditions represented by sampling with much extra text (especially in Sec. 2.2.2).

Reviewer: 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.

Response: Well, we think there are some differences in the degree of time-dependence between the samples. "Time will tell" which INP types these differences reflect, future research will reveal this.

Reviewer: 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.

Response: There seems to be the potential for some confusion here about terminology.

If by "stochastic" one means that the fractional freezing rate of unfrozen drops remains constant with time such that the unfrozen fraction declines exponentially, then yes we disagree with that. But also Knopf et al. (2020) and Wright and Petter (2013) failed to observe such "pure" simple stochasticity.

If by "stochastic" one means that there is a wide PDF of nucleating efficiencies and of amounts of immersed solid material among the INPs of drops (e.g. Marcolli et al. 2007; Knopf et al. 2020), then we find qualitative agreement with that perspective.

By the way, we have more closely inspected our own published results and those of Knopf et al. and Wright and Petters, and we now find that the fractional freezing rate declines steadily, but not exactly exponentially over a constant relaxation time-scale. The decline is only exponential in the sense of a relaxation time-scale that dilates with time.   We are more cautious the use of the term "exponential" now.

Reviewer: 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.

Response: **We agree with the apparent inconsistency with the results from Westbrook and Illingworth (2013) and have added text to explain (lines 942-950).**

The processes occurring in natural long-lived layer-clouds are complex. There are fluctuations of temperature and humidity from in-cloud turbulence and there may be secondary ice production that may amplify or damp the effects from extra activity of INPs.

There may have been cells of weak embedded convection with outflow feeding the layer-cloud observed by Westbrook and Illingworth. Such ascent may have replenished the INPs continuously. They report there were some such cells present away from their target area, but it is difficult to see how they could prove that the cloudy region they studied were unaffected by these far upshear.

So it is difficult a priori to be completely certain whether the Westbrook-Illingworth hypothesis is inconsistent with our results. Another paper may investigate this.

Reviewer: **Abstract**

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

Response: Done.

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.

Response: Agreed. We have qualified what we wrote and now say: *"The first ice in any mixed phase cloud is from activation of INPs, if its top is below the level of homogeneous-freezing (about -36 °C depending on drop size; Pruppacher and Klett 1997)"*.

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

Response: Corrected.

Reviewer: 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.

Response: **We now mention this with new text (lines 942-950).**

The purpose of the paper is not to prove or disprove the Westbrook and Illingworth argument. In view of the complexity of cloud-microphysical processes, potentially with secondary ice production (sublimational breakup), a detailed simulation of such a cloud is needed to do that.

Since they claimed the cloud was precipitating, then secondary ice production is possible.   What they wrote is "*The only established ice multiplication mechanism is rime-splintering which occurs exclusively between −3 and −8 ◦C (Pruppacher and Klett, 1997). Since our supercooled cloud did not span this temperature range, and since riming of the crystals themselves was minimal …, we do not believe that multiplication occurred in this cloud layer."*

We now know that ice multiplication by ice-ice collisions or by fragmentation of freezing drizzle or by sublimational breakup is possible. Rime-splintering is not the only possibility.

Since their cloud was observed over land and there were efforts to exclude embedded convection from the analysis, there might have been undetected pockets of ascent that drove turbulence mixing fresh IN into the cloud.

There are many possible explanations other than time-dependence for the Westbrook and Illingworth observations of the long-lived layer-cloud. Theirs was only a hypothesis and it awaits investigation with a detailed model. Our paper provides a tool enabling this.

Response: References are now included (line 114).

Response: Knopf *et al.* (2020) write that "*We demonstrate that IF* [immersion freezing] *can be consistently described by a stochastic nucleation process accounting for uncertainties in the INP surface area*" immersed in each drop.   They get adequate agreement in isothermal experiments with illite for up to half an hour or so.

We have clarified the citation in the text (lines 140-142).

Response: The reason that we do not treat our samples merely as randomly selected "examples" is that the goal of the paper is to provide a way to include time-dependence in the INP schemes of cloud models that are based on field probe measurements. That is why we took great care to select the samples in such as way as to typify the airmass types as representatively as we could.

We initially decided which airmass types we would target, then we selected a subset of measurement days that conformed in terms of physico-chemistry and back-trajectories with the corresponding classification criteria of each target.

Response: We used the minimal pore size that was deemed possible to achieve 24 h sampling.

Studies of sampling efficiency have been carried out by others. The types of filters we used generally collect >90% of the particles present in the mobility size range from 20 to 300 nm - often with a collection efficiency >95% by number (Zikova et al., 2015). Hence, we cannot exclude that a tiny fraction of small INPs could had made it through the filter pores during sampling. However, the aim of our study was not to report accurate ambient INP concentrations, so we do not consider this an issue with respect to any of the main results reported.

This is now clarified in the text (line 203).

Response: The flowrates and sampled volume were recorded in 5 min intervals by the sequential sampler. The sequential sampler stopped automatically when the pressure drop exceeded the instruments capacity to maintain the set flowrate of 1 m^3/h. So yes, in a sense, the instrument stopped because of overloading in some cases. But this was quite rare.

Response: We fully agree to those considerations.

We find it highly useful to classify the samples based on their physico-chemical aerosol characteristics – which are presented in more detail in the revised manuscript (lines 220-320). We can tell, that the relative ratios between potential ambient INPs vary significantly within the sample ensemble. We believe that we already have made it clear, that in our study, it is not possible to directly identify the types of active INPs.

However, it is highly unlikely that the active INP populations were identical between these samples, which is discussed in more detail in the revised manuscript (a new Appendix A compares the samples statistically for ice nucleating properties).

Response: Additional information about the HYSPLIT operation has been included in the revised manuscript (lines 227-232, and a new Figure 1).

It is evident from the aerosol data presented in Table 1, that regional to long-range atmospheric transport has a huge impact on the aerosol properties at the Hyltemossa site. It is well known that friction in the very lowest parts of the planetary boundary layer (PBL) inhibits efficient horizontal transport. Horizontal transportation is more pronounced at somewhat higher altitudes in the PBL. Hence, a location 500 m above ground level is very often chosen for airmass back-trajectory modeling related to ground based aerosol measurements (e.g. Waked et al., (2018) and references therein).

It cannot be excluded that atmospheric circulation in the free troposphere can be of relevance to some aerosol parameters detected close to the ground level. Therefore we have also analysed airmass back trajectories arriving over Hyltemossa at an altitude of 2000 m AGL (above ground level).

In the revised Figure 1, we now present HYSPLIT 120h air mass back trajectories arriving at Hyltemossa 50 m (dashed lines) and 2000 m (dotted lines) above the ground. As can be observed from this Figure, the atmospheric circulation did not appear to vary greatly with altitude in the lower troposphere during the sampling periods.

Reviewer: 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.

Response: As stated further above, it was not possible for us to identify specific active INPs in these samples.

In the revised manuscript (lines 220-320), we present more extensive physico-chemical aerosol properties of more direct relevance to the potential INP population. Based on those supportive measurements, it appears highly likely that the relative abundance of different potential INP classes vary significantly between the samples. That is discussed in more detail in the revised version of the manuscript.

Reviewer: 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.

Response: We are grateful to the reviewer for this excellent suggestion for future work and we now cite this reference by Testa et al. (2021) at the end of the concluding section (line 968).

We have included data related to minerals, BC, organics and supermicron primary biological particles when available in the revised version of Table 1. We have modified the discussion about potential INPs accordingly.

Response: We thank the reviewer for this helpful suggestion and will use MERRA-2 in any similar future observations.

Response: The sterile cryogenic vials are small, sterilized polypropylene vials designed for the storage of biological material, human or animal cells, etc. at temperatures down to –196 °C. They are delivered sterilized by gamma radiation and are certified RNase-, DNase-, pyrogen- and DNA-free. The vials are flushed with ultrapure water before use and never opened outside of the laminar airflow benches. The vials were used during the "ultra clean water"- background measurements that are now included in the manuscript as Figure 5, and are thus included in these background measurements. (The vials are supplied by VWR, product number: 479-1237).

Response: We have included a new figure (Figure 5) in the manuscript to show the instrument freezing background for the instrument of ultrapure water, using the same procedure as the constant cooling rate experiments, including the transfer of water "sample" by the sterile cryogenic vials. During the experiments mentioned in Sec. 2.4.2 no freezing events were observed during 2h experiments at the isothermal temperatures (see also lines 432-437).

Response: Yes, and that discussion has been modified in the revised manuscript accordingly. There is now a reference to Schneider et al. (2021) so as to depict seasonality of aerosol loadings (line 471).

Reviewer: 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).

Response: We have addressed this issue in Appendix A with statistical tests for the difference in active INPs at -15 degC. None of the six samples are perfectly unique, each is statistically indistinguishable from at least one other sample. But most pairs of samples are statistically different from each other.

Reviewer: 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.

Response: Additional aerosol data are presented in the revised manuscript (lines 220-330, a new Table 1), and the discussion of likely INPs has been modified accordingly. With those changes, we do not see the purpose of normalizing the INP spectra to an estimated total aerosol particle surface.

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

Response: This is now done in the new Figure 6.

Reviewer: 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.

Response: Done. It is now moved to section 2.4.3.

Reviewer: 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.

Response: Extra explanation with more precise language is now provided:

> *"The practically sigmoidal-like distribution of normal freezing temperatures (Fig. 8) arises because the average probability of any drop freezing per unit time during any isothermal experiment must, when comparing all such drops, decrease with decreasing normal freezing temperature below the isothermal temperature among them. For a given drop, this probability is governed by the immersed surface area of INP material and its composition. These underlying*

quantities also follow a statistical distribution among drops. Drops with the most depression of the normal freezing temperature below the isothermal temperature would be expected to contain less, or less efficient, INP material than most that freeze, causing these rare drops to freeze only on unusually long time-scales in the isothermal experiment."

Reviewer: 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.

Response: This new Figure 9 has been modified to include a linear time scale as required.

Reviewer: 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.

Response: Yes, this was a typing error. The label has been corrected on the new Figure 10. It should have been "eventual fractional increase in frozen fraction" or just "chi".

Reviewer: 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).

Response: This is an excellent point and we now cite the DeMott paper for this in the discussion around the new Fig. 11 (line 615).

Reviewer: I wondered though what N and Nice 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 Nice,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.

Response: N_ice was the number of drops frozen as a function of time, t, since the start of the experiment at 0 degC normalized by the total number of drops. We have corrected the introduction of these definitions. We have now changed the terminology with "f" now used instead of "N" for frozen fractions throughout the paper.

Response: What we meant was that our numerical estimate using a finite difference scheme occasionally yielded unrealistic negative values of the freezing rate.

Response: No, N_ice(t) was always a frozen fraction.

To clarify this, we have changed the terminology to "f" for fraction everywhere and now define all symbols in a new Appendix B.

Response: Yes, the reviewer is correct that this was poorly phrased. As we are using environmental samples, all drops will of course contain an ensemble of different INPs. 'Risk' here refers to the risk that we have a masking effect of more effective INPs activating before we can get information about less active INPs.

We have updated the manuscript to clarify this (line 782). In the next paragraph (line 787) we explain why we do not think this is a real problem for our experiments.

Response: We never claimed to make any such correspondences with certainty.

What we wrote was fine:

> "*From the classification of our samples (section 2.2) from the Hyltemossa field station, some likely correspondences may be hypothesized*".

The paper's goal is chiefly to advance models in light of fresh lab results. Modellers do not have the luxury of waiting until perfectly representative observations become available before representing a potentially critical process in the model. When imperfect or incomplete data exists that allows a rudimentary representation of the target process in a model, then to ignore this may introduce more bias into the simulations than to include it. We think that is the situation here.

Regarding Figure 6, there is no evidence of any problem with the INP concentrations we measured in each type of airmass, as we argue (Sec. 3.1.1).   There is commonality with some other published

studies (e.g. Si et al., Irish et al.) showing observations of INPs in marine environment, as we explain in the results section (e.g. lines 470-500).

Reviewer: 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 Westbrook and Illingworth invalid already?

Response: See the above comment on this hypothesis. To be sure, we need to simulate with a cloud model since there are so many nonlinear feedbacks and other processes occurring. We include new text to discuss this hypothesis in the concluding section (lines 935-940).

Reviewer: 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.

Response: To avoid emphasizing a single event unduly we have added an extra reference to studies simulating long-lived cold clouds (line 976).

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

Response: Yes, the availability of data is now stated (line 1001).   We will archive data on public '*ftp-servers'.*

Editorial notes

Reviewer: Line 24: decline, rather than declines.

Response: Corrected as required.

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

Response: Corrected.

Reviewer: 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.

Response: Done.

During revision, we have augmented the information on aerosol composition (see Table 1).

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

Response: Corrected as required.