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Comment on acp-2021-830

Anonymous Referee #1

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-RC1, 2021

Review of "Time-dependence of Heterogeneous Ice Nucleation by Ambient Aerosols: Laboratory Observations and a Formulation for Models" by Jakobsson et al.

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.

Major comments:

1. 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. Thus, the claim that the collected samples cover the major relevant INP classes needs to be abandoned, unless it were to be supported through chemical characterization (e.g. elemental analysis).

2. As it seems, the cold stage used in this study has not been described before. Therefore, its performance needs to be characterized properly. What is the precision and accuracy of the temperature measurement? Is there a freezing bias depending on the location of the drop on the substrate? What is the freezing curve of pure water?

3. A time dependence is inferred without specifying whether it complies with the assumption of stochastic ice nucleation. The reason of the time dependence should be discussed. It should be analyzed to what degree the time dependence is indeed stochastic, i.e. stemming from identical INPs freezing at a certain rate, or whether distinct nucleation sites exhibit gradual shifts or sudden jumps in freezing temperature as e.g. shown in Vali (2008), Wright and Petters (2013) or Kaufmann et al. (2017).

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

Specific comments:

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

Line 44: Field and Heimsfield (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).

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

Lines 61–62: this statement is too general.

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

Lines 96–105: 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.

Lines 178–179: Do you mean the particle size range between PM1 and PM10?

Line 305: should it be “arise” instead of “rise”?

Lines 314–326: Here, the INP concentrations are just compared with Fletcher (1962), without mentioning where the samples from Fletcher (1962) were collected. Typical INP concentrations of the claimed aerosol classes should be added and used for comparison.

Lines 331–332: statistical tests should be performed to analyze whether the investigated samples are statistically different.

Lines 347–349: do these variations in freezing temperature refer to the instrumental precision or characterize the samples?

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.

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

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?

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.

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.

Line 381–385, Fig. 9 and Table 4: The information provided in Fig. 9 is given more precisely as part of Table 4. This figure can therefore be removed. Moreover, the formula to calculate the data of Fig. 9 should be explicitly given.

Line 386 and Fig. 10: The analysis is unclear, also because freezing and frozen fraction are mixed up. The quantities in the formula should be properly defined. Did you really take the derivative or not just evaluate time intervals?

Lines 391–392: What is meant in this sentence by more and less active INPs? Typically, the ice nucleation rate of an INP increases with decreasing temperature. Yet, this sentence does not mention any temperature dependence and seems to imply that there are fast and slow nucleating INPs independent of temperature. The concept of slow and fast INPs needs to be clarified.

Lines 394–405: Here, a time dependence of INP activation is proposed without taking the temperature dependence into account. Yet, models need to combine both, and cover also situations of temperature fluctuations: 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).

Line 419–421: Again, this argumentation insinuates that less active sites activate more slowly than the more active ones. Yet, the nucleation rates of sites are highly temperature dependent.

Line 440, Eq. 4: How is the time dependence of the INP concentration calculated? How can the temperature shift approach be combined with temperature fluctuations observed in air parcels?

Line 467–468: This listing of temperature information should be put in a table.

Lines 478–480: This sentence needs to be formulated better.

Line 486: Again, a table would be more appropriate.

Lines 488–489: How did you establish the consistency?

Lines 493–495: this sentence should be formulated better.

Lines 499–500: this sentence should be formulated better.

Line 507: it is Budke and Koop, 2015.

Line 524–525: A further explanation of the time dependence would be non-stochastic changes in IN activity that have been found e.g. in refreeze experiments by Vali (2008), Wright and Petters (2013) or Kaufmann et al. (2017). An estimate of the contribution of such changes compared to stochastic freezing would be interesting.

Lines 532–537: Here, the possibility of several INPs present in the same drop is discussed as a risk. Yet, it is a fact that there are multiple INPs present in microliter drops, albeit with different characteristic freezing temperatures. Also in cooling experiments, several INPs compete in ice nucleation. To judge how many INPs have similar characteristic ice nucleation temperatures and might compete within a drop, samples with different degrees of dilution should be compared. The authors should consider performing experiments with more diluted samples for comparison.

Lines 541–552: Here again the temperature range of activity needs to be specified. This discussion does not make sense without specifying the temperature.

Lines 549–552: CCN are mostly liquid and do not contain any INP. Thus, having several INPs in one cloud droplet is highly unlikely.

Lines 564–644: this needs to be explained better.

Lines 574–590: The use of Q needs to be explained better.

Line 714: Knopf et al. (2021) has been published in the meantime.

Line 831: do you mean "quartz" instead of "quarts"?

Figure 5: The formula that was used to calculate the INP concentrations should be stated or referenced. The different aerosol classes exhibit quite similar INP concentrations as a function of temperature. Therefore, statistical tests need to be performed to test whether the aerosol classes are statistically different. Moreover, each droplet population could be shown as separate line in Fig. 5, as it is done in the freezing spectra in Fig. 6, to judge visually whether the different aerosol classes are different. Finally, the INP concentrations should be compared with typical INP concentrations of the aerosol classes they should represent.

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.

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).

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

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?

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

Table 1: The line numbers are shifted to the right.

Line 982: what do you mean by "much more limited"?

References:

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