Dear Allan Bertram!

Below is the point to point answer for the manuscript on "Intercomparing different devices for the investigation of ice nucleating particles using Snomax® as test substance" by H. Wex et al. .

One review was very positive and did not require any changes.

The response to the second review, which was also uploaded at the discussion page of the manuscript, is also given below. Likewise, the respective changes made in the text are given in bold letters in the .pdf-file of the revised manuscript, which I submit simultaneously to this file.

Greetings from

Heike Wex

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**G. Vali (Referee)**

Dear Gabor Vali!

Thank you very much for taking the time to act as referee for our manuscript and thank you also for the positive comments and remarks. Below, we give our respective responses. Your remarks and suggestions are given in blue, italic print. Our answers are given in plain text, and **new text that was added to the manuscript is given as bold letters**.

*The experiments described in this paper make valuable contributions. It is a good exploration both of the specific material tested (Snowmax) and of the degree of agreement that can be achieved among different measuring systems. The authors are to be congratulated on the organization of the cooperative effort and on the cohesive analyses of the results. Some points are raised in the following for the authors' consideration with the aim of clarifying some aspects of the data presentation and interpretation.*

*22327/2 In a round robin tournament all teams play all other teams, so the use of this term is not strictly valid here, but it is suggestive of the intentions of the organizers.*

The term "round robin like tests" was chosen as it has been used in other scientific comparison studies before, and the German translation ("Ringversuch") seemed to fit. But as it seems to not be such a good choice of wording, we now use "**intercomparison**" instead.

*22330/20-22 The logic of these two sentences is elusive. Minimal time-dependence is not related to the shape of the spectrum (frequency) of INM of different activities.*

Thank you for pointing this out. The new results that are now available on the time dependence of ice nucleation by Snomax (Budke & Koop, 2014) are used now, in this context, i.e., we motivate the use of a time independent treatment based on this work as follows (new text in bold):

"This indicates that the group III protein complexes responsible for inducing the observed ice nucleation are all comparably similar in their ice nucleation ability. **Furthermore, it was recently shown that ice nucleation by Snomax shows only a very small time dependence at cooling rates comparable to the current intercomparison (Budke & Koop, 2014),** and hence a time-independent treatment of the freezing process seems justifiable."

*22331/3 It would be helpful to point out that in this study ice nucleating ability is expressed per unit mass of material, not per unit surface area as is done in some other studies with solid materials. This is due to the two complicating factors discussed later: changes in particle size due to dispersion as dry particles, and the unknown shapes of the particles. Are there other reasons?*

The main reason for expressing the ice nucleating ability per unit mass of material is based on the following result from Hartmann et al. (2013): The number of ice nucleation active macromolecules (INM) scaled with the volume of the examined particles, and therefore also with the mass of Snomax present in a droplet.

We interpret this as being indicative for the fact that the Snomax particle dissolves / goes into suspension as soon as a droplet is activated on it, hence bringing material which would otherwise be "hidden" in its interior in contact with water, making it available to induce freezing. Therefore, differently than for insoluble particles (e.g., from mineral dust), all of the material of a particle, i.e., all of the mass, adds to ice nucleation activity, and the ice nucleation activity should scale with particle mass.

A clarifying sentence was added above Eq. (1):

"It was clearly shown in Hartmann et al. (2013), that the number of ice nucleation active macromolecules (INM) (i.e., the protein complexes) scaled with the volume of the examined particles, and therefore also with the mass of Snomax present in a droplet. **Therefore, in the here presented study, the ice nucleation ability will be expressed per unit mass of Snomax.** For similar cases, ... "

*Eq.(1) is written with the implied assumption that all drops have identical values of $V_d$ and $C_m$. Stating this would help the later discussion.*

The following was added to the text, following Eq. (1): "... in our study the suspension-methods AL, BINARY, and the WT. **For each suspension-method, the examined droplets all had an identical size, and during each individual experiment, all droplets had the same Snomax concentration (and different concentrations in different experimental runs).**"

*Eq. (2) and (3) are written for size-selected samples, i.e. same $d_p$*

This was clarified in the text, following Eq. (3):"... particle-methods (i.e., AIDA, FINCH, LACIS and PINC) shown in Fig. 1. **Please note that Eqs. (2) and (3) are valid for size selected particles, i.e., for cases where, during one experiment, particles of the same $d_p$ are used, or for which, alternatively, a mass mean $d_p$ can be determined.**"

*22332/7-> "INM" is used in places where it really refers to Snowmax particles as they exist and are distributed into droplets before the freezing experiment. This is confusing. Perhaps the author would consider using SP to refer to the dry particles.*

In the location of the text which you mention here, INM is the correct wording, whereas replacing it by Snomax particle would be wrong. The remainder of the text was checked accordingly.

For all particle-methods, each examined droplet was activated on a Snomax particle, but there are Snomax particles (generated from the Snomax suspension which was sprayed from an atomizer) which consisted of biological ("Snomax") material, but did not contain an INM. (Besides fragments of cell membranes with INM, Snomax also contains a lot of additional material, e.g., non ice active cell constituents and nutrition remnants).

This is related to your remark concerning 22332/19-20, and we tried to clarify this by adding a sentence which we cite at your respective remark below.

*22332/14 Eq. (4) is just a repetition of Eq. (1) with different symbols. The value of $\lambda$ is given by the product $n_m \cdot C_m \cdot V_d$. The validity of these equations is constrained to $\lambda < 1$ (cf. Vali, 1971); the restriction of use of these equations to fractions less than unity (below the plateau region) follows from that. This makes much of the discussion regarding Fig. 9 and most of section 5.1 somewhat superfluous. Not incorrect, but not necessary if the f 1 region is excluded by definition. As pointed out in 5.1, the Poisson distribution is only confirmed for $\lambda < 1$.*

Indeed there is a limitation to the range of $\lambda$ - values for which the Poisson distribution is confirmed.

But Eq. (1) and Eq. (4) differ: Eq. (1) displays the temperature dependency of the frozen fractions f_ice, while Eq. (4) is formulated for a constant value of f*_ice (i.e., for f_ice in the plateau region), and as such only has information about this f*_ice. In fact, Eq. (4) is the limit for Eq. (1) towards lower temperatures, valid at and below temperatures for which a plateau of f*_ice < 1 has formed.

Also, for the particle-methods applied in the present study, the size of the examined droplets is often unknown. Hence, for these methods, a description using the parameters $C_m$ and $V_d$ is not feasible, leading to the necessity of formulating Eq. (3).

Eq. (4), as given, allows for the unified description of both, suspension- and particle-methods. This unified description then leads to data from both types of methods shown together in Fig. 9, together with the description and discussion in Sec. 5.1. Measurements which show a plateau region at f*_ice < 1 are important, as these can be used to obtain the number of INM per mass (in this case per Snomax mass), which is not possible if f*_ice = 1 is reached. Therefore we feel that the discussion around Fig. 9 and Sec. 5.1 are important. In that light we hope you can agree with us to not change the respective equations, figure or text.

*22332/16 fraction of particles, not number*

Thank you, has been changed.

*22332/19-20 The significance of this sentence is worth spelling out. I understand it to mean that the plateau is not due to having more than one INM per droplet but because all SP become active (INM) near -10 or -12°C. Of course this fact is collaborated by the plateau observed in the suspension measurements (Fig. 10.).*

The plateau in general occurs because, as you say, all droplets with INM in them become ice active near -10 or -12°C. A plateau with f*_ice < 1 occurs, when there are droplets that contain no INM. This can happen when for suspension-methods either suspensions with correspondingly low concentrations are examined, or in case of particle-methods, for particles of the respective sizes. (As it turned out, in the case of Snomax, typical particle sizes that can be selected by a DMA are such that in general f*_ice < 1 occurs, i.e., even for the largest selected particle sizes, only some particles have an INM (a fragment of cell membrane with an INM on them), while other particles only consist of non ice active biological material.)
This is stated now explicitly, following the sentence you mention here:

"For the present study, it was possible for most instruments to run experiments such that a plateau with f*_ice < 1 could be observed for at least one data set**. This occurs when there are droplets that contain no INM, which can occur for suspensions with correspondingly low concentrations or for particles of respective sizes which might consist of biological material without containing an INM.**"

*22332/24 It should perhaps be made a little clearer to the reader that the uncertainty derived here is an error range estimate, quite different than probability of allocation of particles considered in the preceding paragraph. The caption in Fig. 2 refers to 'theoretical considerations' - while this is true, it is simpler to say that the standard deviations reflect predicted uncertainties due to limited sample sizes.*

We tried to make this clearer, loosely following the wording you suggest above:

"Depending on the number of droplets examined in a particular experiment, an additional uncertainty in the measurements appears for those experiments where f*_ice < 1, based on the fact that a comparably small number of INM is Poisson distributed to all particles/droplets. This is shown exemplarily for four different values of f*_ice < 1 and a range of droplet numbers in Fig. 2, **where the standard deviations represent theoretically predicted uncertainties which are due to the examination of only a limited number of droplets**."

*22344/1 The emphasis in this section is well placed. The two temperatures at which sudden rises in concentration are observed indicate the frequent occurrence of two types of sites with different characteristic temperatures. This type of sudden rise in not common, most materials exhibit gradual rises in the frequency of sites of different characteristic temperatures. The value of omega defined by Vali (2014) here observed is about 4.5, well above the values shown in Table 1 of Vali (2014) for heterogeneous* *nucleation. If the results were displayed in a differential rather than cumulative spectral form (Vali, 1971 and 2014) the presence of two peaks in activity would be visually apparent.*

Thank you for pointing this out. The method of differential spectra has been used by some of the co-authors of this manuscript before (Augustin et al., 2013), where it was very useful as the plateaus did not show up as clearly as in the case of the present study. As the plateaus are rather well visible in our Snomax data-set, we wonder if you would prefer us to use the differential method here, too, or if at least we should mention it. For the time being, nothing was changed.

*22347/26 True, as long as the manufacturer doesn't change the manner of production of Snowmax. Also, if the material currently available is as tolerant to handling and generation, etc., perhaps there is no need for the caution expressed in the last sentence of the Abstract.*

This is correct, however, we prefer to keep the note of caution in the abstract and the text, as e.g. issues as the manner of production are something which we cannot influence at all.

*22348/7-8 ". . . plateau value below 1. . ." is not well expressed*

You are right, and we tried to improve this. The new text now is:

"The range in which the strong increase is observed is important when temperature accuracy is examined. However, **also temperature ranges were observed in which no additional ice nucleation was observed, i.e., in which $n_m$ was rather constant (around -6°C and below -12°C). When $f_{ice}$ measured in these temperature ranges is below 1, then these measurements, made for Snomax or other substances,** can give information about the counting accuracy of the instrument or about instrumental issues. **To obtain the respective measurements with values of $f_{ice}$ below 1,** either sufficiently low concentrated suspensions have to be used for suspension-methods, or a respectively small particle size for the particle methods has to be chosen, **where, however, in our study all particle sizes which could possibly be chosen with a DMA were sufficiently small**."

*22348/10-22 Doesn't the presence of the plateau in the particle-method measurements argue against it being an artifact in the suspension-method measurements? If so, the argument here presented is misplaced and needless. While the mentioned limitations do in fact exist they were not a factor in this experiment.*

There might be a misunderstanding here. In the BINARY data-set, for temperatures below -20°C, $f_{ice}$ (if it was still below 1) and $n_m$ did increase, and that was different from a plateau seen in the LACIS and PINC data-sets. The respective BINARY data were not shown, because it was obvious from measurements with "pure" water that this increase either comes from impurities in the water or from interactions of the droplets with the substrate. Values of $n_m$ derived from these data at the most dilute Snomax concentrations were orders of magnitude larger than those from the Snomax particles. Moreover, these $n_m$ values did scale with the dilution factor, clearly indicating that the ice nucleation was not caused by Snomax but rather by the water. Hence, it did not influence the Snomax measurements, and may become more of an issue when INP active at lower temperatures are examined (e.g. mineral dust particles). Hence we feel that it is important to make readers of the text aware of this existing limitation, particularly as it seems to become more of a limitation (in terms of lowest temperature that can be reached) the larger the examined droplets are. This way we hope to avoid surprises for scientists who might decide to build a freezing array, by discussing these potential limitations here so clearly (a first important decision is the droplet size one wants to examine). We did add more clearly the hint that the respective BINARY data are not shown and did not influence the Snomax results:

"In our study, measurements in the plateau region below −20°C revealed a **clear** increase in $f_{ice}$ for the BINARY data sets **obtained for the four lowest concentrations. This increase occurred** well above the homogeneous nucleation temperature of −38°C, where an increase is unavoidable. **These BIANRY data were not displayed here, neither were they included in the analysis of the ice nucleation behavior of Snomax. The observed increase** was either caused by impurities in the water **used for dilution** or by the **substrate surface itself, as evidenced by the fact that the respective $n_m$ values did scale with the dilution factor, i.e. a reduction of Snomax concentration by a factor of 10 resulted in an increase in the observed $n_m$ values by a factor of about 10.**"

*22352/18 -> It is surprising that the authors use a time-dependent parameterization which is tailored to LACIS's short exposure time and the SBM with a relatively arbitrary time. The analyses in this paper are* *based on the singular approximation (22330/15) and the time-dependence found by Budke and Koop (2014) is acknowledged to be small and is neglected in the analysis. A function for $n_m$ versus T alone (as is shown in the right-hand side of Eq. (6) is an adequate representation of the results.*

We compare two different parameterizations existing in literature to the data shown in this study, and both of them fit the data presented in this study well, although they originated "only" from LACIS data. This in itself is an interesting result, as indeed exposure times in LACIS are really short. The small time-dependence reported in Budke and Koop (2014) might be advantageous for this agreement.

We are able to reformulate one of the parameterizations (the first one you mention above) in such a way (see Eq. (6)) that a time-independent description is now available. Eq. (6), which you refer to as adequate, is just a reformulation of the parameterization given in Hartmann et al. (2013) (H13 from here on), taking into account the LACIS residence time and thus omitting the time-dependence from the equation. (This is similar as if H13 would have been formulated time-independent right away.) Therefore, as mentioned in the manuscript, the red curve in Fig. 12 really represents Eq. (6) (i.e., H13 without the time-dependence) and therefore has to be shown, as it represents, as you state it, the "adequate representation of the results". To avoid misunderstanding, the caption of Fig. 12 was changed as follows:

"... together with fits obtained from **a time-independent variant of** the parameterization given in Hartmann et al. (2013) (red curve**, see Eq. (6)**) ..."

Showing also the SBM is based on an attempt to satisfy the need of different modeling groups. The past showed us that some modelers use models with time independent descriptions, while others have time dependent descriptions implemented (often based on Classical Nucleation Theory) and cannot easily change this. Therefore, although a time dependent description is not really necessary for the Snomax we examine here, we feel that it can be useful for some of our readers to see that the SBM and the respective contact angle distribution yield results in agreement to the findings of the present paper. The residence time used in the SBM (10 s) is roughly a mean value for the methods used in our study, but due to the weak time dependence, a wide range of residence times would have yielded very similar results (the time dependence modeled with the SBM is similar to that found experimentally in Budke and Koop, 2014). This was mentioned in the text: "... a change of the nucleation time of a factor of 10 shifts the freezing curve by roughly only 0.3 K (and a factor of 100 by 0.6 K etc.) ...".

Based on the explanations given above, we hope you can agree to keep these parts of the manuscript.

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Literature:

Augustin, S., H. Wex, D. Niedermeier, B. Pummer, H. Grothe, S. Hartmann, L. Tomsche, T. Clauss, J. Voigtländer, K. Ignatius, and F. Stratmann (2013), Immersion freezing of birch pollen washing water, Atmos. Chem. Phys., 13, 10989–11003, doi:10.5194/acp-13-10989-2013.

Budke, C., and T. Koop (2014), BINARY: An optical freezing array for assessing temperature and time dependence of heterogeneous ice nucleation, Atmos. Meas. Tech. Discuss., 7, 9137-9172.

Hartmann, S., S. Augustin, T. Clauss, H. Wex, T. Santl Temkiv, J. Voigtländer, D. Niedermeier, and F. Stratmann (2013), Immersion freezing of ice nucleating active protein complexes, Atmos. Chem. Phys., 13, 5751-5766, doi:10.5194/acp-13-5751-2013.