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Reply on RC1

Daniel A. Knopf et al.

Author comment on "Micro-spectroscopic and freezing characterization of ice-nucleating particles collected in the marine boundary layer in the eastern North Atlantic" by Daniel A. Knopf et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-61-AC1, 2022

This manuscript is well written. The experimental study of INPs from Graciosa is rare and invaluable. Though the data is limited to a single summer season based on a few samples, the result is well presented and worth it for the science community. The authors clearly address the necessity of future study, and this reviewer agrees with the addressed outlook. The study topic is relevant to the journal scope as ACP supports many INP-related papers. This reviewer supports the publication of this paper in ACP and has only several technical comments.

We thank the reviewer for taking the time to evaluate our manuscript and this general positive note.

P2L53-54: Later in this manuscript, the authors mention PCF and potential pre-activation. Then, in general, the ice formation pathway can be modulated by not only ambient conditions but also particle physical properties, correct? This point can be clarified here.

Considering the microscopic scale of ice nucleation, the reviewer makes a valid point. We will add this information and change the sentence accordingly:

"Furthermore, different ice formation pathways exist, which in turn depend on particle properties and ambient conditions such as temperature (T) and relative humidity (RH) (Marcolli, 2014;Pruppacher and Klett, 1997;Vali et al., 2015;Knopf et al., 2018)."

P3L75-77: The reviewer believes that the majority of past studies focus on IMF because IMF is the dominant ice nucleation path in the atmosphere. The authors might want to briefly explain how important (dominant) DIN is compared to IMF for the reader.

The reviewer is correct here. IMF represents the dominant ice nucleation path in the atmosphere and thus is mostly studied. DIN can become more important at lower temperatures and at water subsaturated conditions typical of upper

tropospheric conditions. We add the following information to this section:

"IMF is recognized as the dominant primary ice formation pathway in mixed-phase cloud regimes (Ansmann et al., 2009;de Boer et al., 2011;Westbrook and Illingworth, 2013) where supercooled droplets and ice crystals can coexist. DIN can contribute to ice crystal formation at lower temperatures and water subsaturated conditions representing cirrus cloud regimes, typical of the upper troposphere (DeMott, 2002;Heymsfield et al., 2017;Cziczo et al., 2013)."

P4L114: How low were ambient particle numbers? Does the ENA site offer the total aerosol particle concentration data?

When writing the manuscript we missed available total aerosol concentration data at the ENA site for particles larger than 10 nm reported by (Gallo et al., 2020). We now use hourly reported aerosol concentration over the collection periods of examined particle samples. This resulted in aerosol concentrations of 477, 493, 537, and 333 cm^{-3} for samples Day 1, Day2, Night 1, and Night 2, respectively. This is slightly greater than originally estimated 250 cm^{-3}.

We change the original sentence on line 113-115

"Since ambient particle numbers were low and sampling intervals for this ice nucleation study were limited, particle collection was conducted over several days intermittently."

to

"Since ambient particle numbers were low (between 330 and 540 cm^{-3}, Gallo et al. (2020)) and sampling intervals for this ice nucleation study were limited, particle collection was conducted over several days intermittently."

P4L119: Why this particular stage (D50 = 0.56 micron) was selected for sampling and subsequent analysis?

This stage has been chosen based on our previous experience to satisfy the necessary particle loading among the different applied analytical techniques. If the particle loading is too low, ice formation might not be detectable and CCSEM/EDX and STXM/NEXAFS analysis will not result in statistically significant data sets. If the particle loading is too high, one may lose the single particle characteristics. Hence, particle samples are first interrogated and then decided which cut-off diameter is chosen that can be used across different sampling periods and analytical techniques to allow for more consistent analyses.

We will add on line 123 this additional information:

"The particle samples for a given MOUDI stage were chosen in such a way to provide the optimal particle loading for ice nucleation experiments and application of single-particle analytical techniques across the different sampling periods to allow for more consistent analyses."

P4L129: Has the impact of precipitation been considered in the 10-day back trajectory? Heavy precipitation may have washed out aerosol particles in the given air mass (if they traveled near the surface)?

No, precipitation has not been considered as a potential loss mechanism of the boundary layer aerosol. In our case, though, long range transport from the free troposphere largely involves descending airmasses (Fig. S2) such that precipitation is not expected along them. Also, for a well-mixed boundary layer, one could expect that aerosol, e.g., stemming from the ocean emitted by bubble-bursting processes, are dispersed throughout the boundary layer within hours to a day. This would result in a replenishment of particles. As can be seen from Figs. 1 and S2, prior to arriving at the sampling site the airmasses often remained in the boundary layer for several days.

P5L151: It may be worth providing a reference (or brief description) of the k-means cluster method here for the reader who is not familiar with CCSEM/EDX.

We added as a reference our previous studies and two textbooks on this matter:

"More than 2000 particles were examined for each sample, though for identification of the major particle-type classes via k-means cluster analysis, the CCSEM/EDX data for all samples were taken together(Moffet et al., 2013;Seber, 1984;Spath, 1985;Tomlin et al., 2021;Tomlin et al., 2020)."

P6L187: the particle temperature - presuming the measured substrate surface temperature is equivalent to it?

Yes, this is the case. Melting points of thin films of organics and ice display a difference to the substrate temperature of less than 0.1 K (Knopf and Rigg, 2011). For applied ambient particles (~1 µm in size, smaller than the thin films), particle temperature can be assumed to be equal to substrate temperature. However, at this point of the text it is appropriate to use "substrate temperature", thus we change sentence to

"RH in the ice nucleation cell is derived by the substrate temperature and the measured dewpoint (Wang and Knopf, 2011)."

And add on line 190:

"The temperature accuracy of the cooling stage is independently verified by measuring the melting points of different organic compounds and ice indicating less than 0.1 K difference between substrate and particle temperature (Knopf and Rigg, 2011)."

P10L318: All identified INPs were in supermicron size because of the image resolution limit of the optical microscope for ice nucleation experiments, or is it the nature of INPs for the samples used in this study? The reviewer is aware that the authors cite some papers (e.g., Knopf et al., 2014). Regardless, this point can be perhaps briefly clarified in the manuscript.

Indeed, the INPs were all in the supermicrometer size regime. The INPs are examined using SEM applying re-localization of the ice crystal coordinates from the optical microscope. Line 318 provides this information:

"21 individual INPs were identified and analyzed by SEM/EDX. All identified INPs were in the supermicron size (Table 3)."

To make this point clearer we change the first sentence to

"21 individual INPs were identified and analyzed by SEM/EDX allowing for greater resolution compared to the OM.".

As other studies have observed, as discussed in our review (Knopf et al., 2018), larger ambient particles can serve as a significant source of INPs. The fact that all INPs are in the supermicrometer sized will be added to the "Atmospheric implications" and "Conclusions" sections:

Line 428: "Furthermore, all identified INPs belong to the supermicrometer size regime. INP measurements at a coastal marine boundary layer site also indicated that the greatest INP number concentrations are associated with the largest particles (Mason et al., 2015). These results further emphasize the need to examine supermicrometer-sized particles for their ability to serve as INPs."

Line 443: "All identified INPs belong to the supermicrometer size regime."

P11L346-347: How did the authors estimate ~250 cm^-3 of aerosol particle concentration? Taking particle density in the examined cross-section of the substrate and sampled air volume to estimate it in the unit volume of sampled air? This procedure can be clarified in the text. Did the estimate show any variation in different sampling periods (i.e., D1, D2, N1, and N2)?

As outlined above we have corrected this value using complementary on-site total particle concentration measurements for particles larger than 10 nm (Gallo et al., 2020). Since we have stated the range of particle number concentrations at an earlier place in the manuscript, we change the original sentences

"Complementary ambient particle size distribution (PSD) measurements are limited to the size range between 10 and 460 nm (Wang and Zheng, 2017). Considering this caveat, we can assume the presence of about 250 particles cm-3 as a rough average of particle concentrations during the campaign period. This yields IMF INP number concentrations of about 10 to 20 INP L-1 in accordance with the range of previous measurements of INP number concentrations (Knopf et al., 2021;DeMott et al., 2016;Mason et al., 2015;DeMott et al., 2010)."

To

"Applying mean total ambient particle concentrations for given sampling periods (Gallo et al., 2020) yields IMF INP number concentrations of about 15 to 40 INP L-1 in accordance with the range of previous measurements of INP number concentrations (Knopf et al., 2021;DeMott et al., 2016;Mason et al., 2015;DeMott et al., 2010)."

In Table 2, in the caption, we delete the superfluous statement

“at 240 and 221 K assuming ambient particle concentrations of 250 particles cm^{-3}.”

Table 2: >10,000 particles per mm^2 cross-section seems plenty. Were there any particles agglomerated upon impaction on substrates and miscounted as supermicron particles?

This is not an uncommon value for particle loading for this particle size range. Previously, we were able to work with particle loadings up to 1E6 particles per mm^2(China et al., 2017;Knopf et al., 2014;Wang et al., 2012). One cannot examine on a nanometer scale the entire substrate involved in the ice nucleation experiment by SEM. This would take too much time. However, randomly chosen examination areas (smaller than 1 mm^2 in size) did not show particle agglomeration by double impaction. Hence, even if agglomeration occurs, one can assume it not to be significant.

Figure S1. The ENA site is located right next to the airport and access road. Thus, there must have been some inclusions of particles from these sources on the authors’ samples. This point can be addressed in the supplement figure caption.

The location of the ENA site could be impacted by the airport and access road. However, the duration of local pollution from airport and access road is relatively short. In addition, these fresh emissions are dominated by nucleation/Aitken mode particles. Furthermore, these events are short compared to the multi-hours and multi-day sampling for presented particle samples. Hence, the airport and access road are not expected to influence the examined particle population and INPs significantly.

We add to the figure caption S1:

"Airport and access road could impact particle collection. However, the duration of local pollution from airport and access road is relatively short. In addition, these fresh emissions are dominated by nucleation/Aitken mode particles outside of the examined particle and INP sizes."

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