

Atmos. Chem. Phys. Discuss., author comment AC2
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Reply on RC2

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-AC2>, 2022

I support publication. The manuscript is well written and the data is well presented.

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

There is one point which I think should be addressed, but overall, the manuscript more than meets the standards for publication in ACP.

The surface area of the particles that are examined in this study is a critical part of the analysis, and there are some subtleties to this that need to be explained more carefully.

If I am reading the manuscript correctly, all of the particles are from stage 6 of a MOUDI, which has a cut size of 0.56 micrometers. I realize of course that the cut size isn't a step function. But that cut size and the size of the particles listed in Table 3 are not consistent. For example, the last particle listed (Night 2 #6) has an area equivalent diameter of 11.96 microns. The MOUDI's largest cut size is 10 microns, if I'm using the sizes for the right model here. I could certainly understand a particle that large being on the first stage. But the sixth? This is only the most egregious example. Most of the other particles have sizes larger than the cut size that's listed in the manuscript.

As evident in our numerous previous publications using MOUDI, the theoretical cut-off size does not limit the size range of collected aerosol particles in an exact manner. The reasons for this are due to particle bounce and non-sphericity and varying density of the particles. To inhibit particle bounce it is typically suggested a silicon oil spray is applied on the substrates (Marple et al., 1991). Obviously, this would contaminate our particle samples. The cut-off sizes are derived for spherical particles with a specific aerodynamic particle diameter (and particle density). The collected (ambient) particles are clearly not perfectly spherical and uniform in density. This will further shift the cut-off curve of a given stage. Lastly, the sigmoidal cut-off curve for stage 6 extends the 100% collection efficiency close to 1 μm particle diameter (Marple et al., 1991). Thus, small variations in the aerodynamic diameter will shift the cut-off size significantly to larger particles.

Other effects that can change the particle sizes on a substrate include particle shattering that can occur for marine derived particles (e.g., Mouri and Okada, 1993;Pham et al., 2017) which would lead to the presence of smaller particles. If particles impact as liquid droplets, they might spread out. This may be observed as a halo surrounding the particle. We did not encounter such instances. Lastly if the sample is overloaded, particle may overlap. This was also not the case of the samples examined in this study.

In this sampling location, collection occurred over several hours and days. Hence there is the chance to encounter particle sizes larger than given by cut-off diameter due to particle bounce and non-sphericity of particles. For this reason, we always perform SEM analyses to derive particle sizes for a given particle sample and do not rely on the cut-off size of the specific stage.

We will add the following information to section "2.1 Particle Sampling":

Line 119: "Particle bounce, shattering, and non-sphericity of the ambient particles can lead to a much wider range in particle sizes collected on a stage with specific cut-off diameter (Marple et al., 1991;Knopf et al., 2014;Pham et al., 2017;Mouri and Okada, 1993). Hence, single-particle micro-spectroscopic analyses are used to determine the geometric particle sizes on the sample substrate."

This discrepancy or uncertainty can also be seen in the figures, for example Fig. 3. The size distributions are shown as a function of area equivalent diameter. In that figure, the axes extend only to 2 microns or so, but the distributions are all showing particles larger than the MOUDI cut size. (See for example, Day 1, STXM mixing state... the mode of the distribution is at about 1 micron.) These discrepancies are not as large, but they are still puzzling.

Please see our previous response. This is due to the combined effects of cut-off curve efficiency, particle bounce, shattering, and non-sphericity.

I realize that the MOUDI cut size and the area equivalent diameter derived from SEM measurements are not the same thing. But the authors do make an explicit point that these particles come from stage 6 of the MOUDI, and the cut size is specified. If you then go on to discuss particles much larger than the cut size, at least comment on it and perhaps provide some rationale for it.

We emphasize that particles examined in this study are from one stage only. For a complete description of the entire aerosol population, one would need to examine more particle samples acquired from different stages. Hence, the emphasis on the application of a single stage in this study. We are working on a manuscript that examines particles collected on substrates from different stages. Here, we analyze the particles on the substrate that were also used for the ice nucleation experiments. Thus, we do not claim that the particle population examined reflects the entire ambient particle population. Please see also our response to the first comment.

The larger issue is the derivation of the surface area of the particles. (This issue is

highlighted repeatedly in Knopf et al, 2020, which is cited in the manuscript.) Deriving the surface area of the particles from the SEM images (the area equivalent diameter) is problematic. Is the assumption that the particles are spherical, then using that to get a surface area once a diameter is derived? This is never stated.

This is a very good point raised by the reviewer. We agree to clearly communicate the assumptions underlying the particle surface area employed in the analysis of the data.

Indeed, despite the use of SEM, the surface area available for ice nucleation given in Table 2 can be considered to be an estimate. However, it is still the most feasible approach considering the large numbers of different particle types and morphologies that are probed during the analyses. The equivalent area diameter represents the diameter of a circle that would equal the same projected surface area as the imaged particle. We then assume (half-) spherical particles to estimate the total particle surface area available in the ice nucleation experiments. On a nanoscale, this clearly will not reflect the actual particle surface area.

We will add this information on line 155:

“The equivalent circle diameter represents the diameter of a circle that would equal the same projected surface area as the imaged particle.”

On line 156, we add:

“Estimation of particle surface area applies an equivalent circle diameter and relies on the assumption that the particles are spherical. The collected particles are in most cases not spherical. Furthermore, nanoscale morphology, like nanopores, cavities, and cracks, is not considered in this analysis.”

And if that is, in fact, what is assumed, it almost certainly wrong. The SEM only “sees” the top of the particle. You can’t access the third dimension. There’s been work in recent years showing that dust, for example, is rarely spherical. See Huang et al, 2020 for example. I know that the INPs detailed here are not dust, but the point is still valid. None of the particles in panel A of Fig. 5, for example, look spherical to me.

The reviewer is correct in this point. When analyzing 1000s of particles by CCSEM/EDX and avoiding beam damage (including possible volatilization of organic matter), one cannot apply higher resolution and/or shift the sampling plane to assess the third dimension.

The implications for the freezing kinetics could be twofold: If we overestimate the particle surface area by assuming particle sphericity, then derived J_{het} values would represent lower limits and ice formation in the atmosphere may proceed more efficiently. Considering the presence of nanopores, cracks and cavities on the order of nanometers, we likely underestimate the actual particle surface area. In this case, our derived J_{het} values would represent upper limits. However, one should keep in mind that the statistical uncertainty of nucleation is about +1 order of magnitude and about -3 orders of magnitude. This uncertainty range might cover the uncertainty in surface area by neglecting nanoscale features and three dimensionality.

We will add this discussion on line 360:

“As outlined above, particle surface area is derived assuming that the particles are spherical and neglecting nanoscale morphological features. If the particle surface area is overestimated, derived J_{het} values would represent lower limits. Taking into account nanoscale morphology, which was not achievable in this study, might yield greater particle surface area. This in turn, would indicate the underestimation of the actual particle surface area. Hence, derived J_{het} values would represent upper limits. However, the statistical uncertainty of nucleation spans several orders of magnitude and, thus, likely accounts for the uncertainty in particle surface area.”

I am not asking the authors to resolve these issues. I am asking that they more explicitly outline how the particle surface area is derived and discuss (at least) some of the uncertainties that may arise from that method. (I think quantifying the uncertainty may be beyond what's possible for this study.)

We hope our responses above are satisfactory. We now mention the assumption of particle sphericity and the potential uncertainties related to this. Considering the nature of the particles containing organic matter, which is more prone to beam damage, and the number of particles examined, the reviewer is correct that a high-resolution determination of the particle surface area is not possible in this study. Understanding the nature of the INPs in relation to the particle population was the primary goal of this study. Decreasing the uncertainty in surface area significantly for these large particle samples would require a significantly greater effort which is unlikely to change the conclusions made.

Minor points

Table 2, heading to column 6: ‘or’ should ‘of’?

Yes, this is a typo. It should be “of”. This is corrected.

Figure 4: the blue open circle at ~ 231 K... The open symbol indicates that this is immersion freezing, but it is well below the water saturation line. Is this a particle that deliquesced, then froze from solution?

This is correct. Previous work by Molina, Koop, our group, and others have shown that immersion freezing can proceed in subsaturated (with respect to water) conditions. One can envision that a hygroscopic coating was present (e.g., NaCl) that could result in an aqueous solution from which ice formed (e.g., deliquescence of NaCl at low temperatures; see, e.g., Wagner et al., 2018). Another scenario could include a partially deliquesced amorphous solid organic particles (or solid organic coating) that served as INP. See e.g., Berkemeier et al., 2014 and Knopf et al., 2018.

Reference:

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