

## **Reply to referee #2: Interactive comment on “Ice nucleation abilities of soot particles determined with the Horizontal Ice Nucleation Chamber”**

**By Fabian Mahrt et al.**

Reviewer comments are reproduced in **bold** and our responses in normal typeface; extracts from the originally submitted manuscript are presented in *red italic*, and from the revised manuscript in *blue italic*.

We have renumbered the reviewer comments for ease of cross-reference within the other reviews.

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**This manuscript describes the ice nucleation activities of different types of laboratory generated soot particles using the horizontal ice nucleation chamber (HINC). They performed ice nucleation experiments for four different size (mobility diameter) selected particles using DMA. Furthermore, they investigated particle morphology using TEM, and DMA-CPMA; temperature induced mass loss using thermogravimetric analysis; and water uptake using dynamic vapor sorption measurements. They attempted to link all these measurements with the ice nucleation activities of different types of soot.**

- (1) Overall, the authors found that soot particles are not active in the mixed-phase cloud condition but some of the soot types are active in the cirrus cloud regime. The authors suggested that pore condensation and freezing (PCF) mechanism may be responsible for ice nucleation. Overall, the paper is clearly written and quite detailed. I appreciate all the details provided by the authors. Some suggested clarifications are listed below. I recommend this paper for publication after the comments outlined below are taken into account.

We thank the reviewer for their comments and address the concerns in the answers below and accordingly point out changes to the manuscript.

### **General comments:**

- (2) One of the main concerns is the size distribution of the particles investigated here. Even though the authors size selected the particles using DMA, but due to fractal morphology of soot the physical diameters are quite different than mobility diameter. Depending on the soot morphology and flow, the difference between geometric diameter and mobility diameter varies. I suggest to add the size distribution of soot particles if available. Authors provided SMPS size distribution for FS soot in the supplementary material but it will be useful to provide size distribution for all the soot types, especially for FW200 soot. If SMPS data is not available, then the authors can use TEM images to provide size distribution of soot particles (like they provided the size distribution of soot monomers). For example, looking at the TEM images of FW200 (the most effective INP investigated here), it seems like these particles are quite bigger in size compared to other soot particles investigated here. Authors should also discuss about the multiply charged particles in DMA.

We agree with the reviewer's point that selection of the mobility size can result in soot particles spanning a range of physical sizes. The reviewer further raises concerns that the FW200 sample could contain relatively larger particles compared to the other soots investigated, suggesting that this could contribute to its enhanced ice nucleation ability. We have added the SMPS size distributions of FW200 soot as suggested by the reviewer to the SI, Fig. S15.

As suggested by the reviewer we also made use of our TEM analysis and plotted the distribution of the area equivalent diameters derived from the projected areas, which reveals that the FW200 soot does not contain larger aggregates compared to the other soot types, but in fact is rather dominated by smaller aggregates. Furthermore this is supported by comparing the number size distributions from the SMPS of FS to FW200 (SI Fig. S15). Aware of the fact that the number of analyzed aggregates is limited, we added the following statement to the SI Sect. S8:

Page 17 line 14 of the revised SI:

*“In Fig. S19 we qualitatively show the distribution of area equivalent diameters calculated as:*

$$d_{Aeq} = \sqrt{\frac{4A_a}{\pi}}$$

*where  $A_a$  denotes the (2D) projected area of a soot particle derived from TEM analysis. For Fig. S19 we only analyzed TEM grids corresponding to particles that were selected at 400 nm mobility diameter within the DMA. The mode at small equivalent diameters ( $d_{Aeq} < 200$  nm) for the FW200 corresponds to small aggregates that are made of only a few ( $< 10$ ) primary particles. These are also visible in the exemplary images depicted in Fig. S18a1. We do not believe but cannot exclude whether these small particles are fragments being formed upon impaction of larger aggregates or result from other processes. From Fig. S19 there are strong indication to suggest that the most ice active FW200 soot does not contain a higher fraction of large particles relative to the other soot types, which could account for its enhanced ice nucleation ability.”*

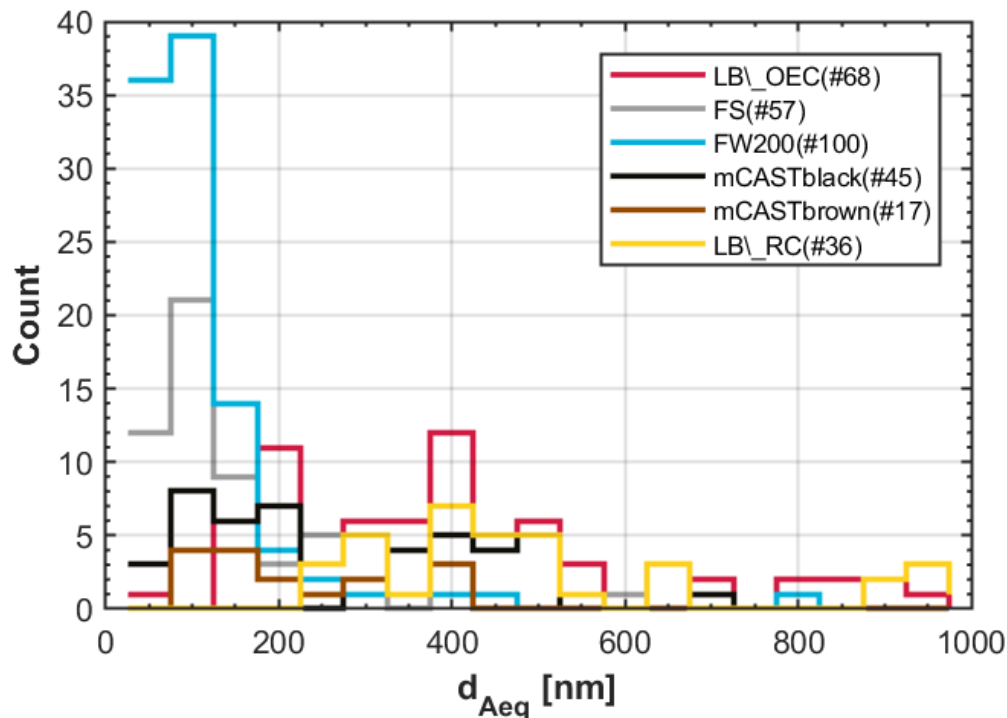


Figure 1: Distribution of area equivalent diameters (eq. 1) corresponding to 400 nm mobility diameter selected soot aggregates at an aerosol to sheath flow ratio of 1/7, derived from TEM analysis. The number in brackets indicates the number of aggregates sized for the corresponding soot type.

**(3) It seems like the differences in onset saturation ratio between 228K and 233 are significant for FW200 soot for both 300 nm and 400 nm size. Can you explain why?**

The answer to this question is stated on p.20, 23 (initial manuscript):

*“An exception are the results of  $T = 233\text{ K}$ , where the nucleation rate is likely too small for the volume of the pore water to freeze within the 16 s residence time of the particles in HINC (David et al., in prep.b).”*

In order to make this more explicit, we added a statement on p.21, l.22, in revised manuscript:

*“An exception are the results at  $T = 233\text{ K}$ , where the nucleation rate is possibly too small for the volume of the pore water to freeze within the 16 s residence time of the particles in HINC (David et al., in prep). This causes the significant increase in  $S_i$  required for ice to nucleate via homogeneous freezing of bulk solution droplets, as can clearly be seen for both 300 nm and 400 nm particles of the FW200 soot, depicted in Fig. 2c and d, respectively.”*

- (4) LB-RC soot nucleated ice in the cirrus cloud regime below homogeneous freezing and second most efficient INP investigated here for 300 nm size selected soot even though the surface area of LB\_RC soot is less than an order of magnitude lower compared to FW200 soot (Table B1). Why LB\_RC soot is relatively active even with low surface area? Overall size of the LB\_RC soot aggregate is smaller compared to FW soot but monomers of LB\_RC is too large (152 nm) compared to typically monomer size of soot in the atmosphere.**

The reviewer is right that the surface areas of the FW200 and the LB\_RC samples are significantly different (see Tab.1). However, we suggest that ice formation on soot particles does not take place via a (surface area) dependent deposition nucleation process, but instead a PCF mechanism prevails. The latter one being dependent on pore size and contact angle, but not directly on the surface area available on the INP. In other words, as long as the LB\_RC soot aggregates have pores with the right physicochemical properties, these particles will be able to form ice via PCF. Thus, assuming an identical pore size and contact angle distribution for FW200 and LB\_RC we would expect them to nucleate ice within our experiments at the same RH conditions at a given T, independent of the larger surface area of the FW200 sample.

The larger surface area of the FW200 is believed to result from the smaller monomer size (Fig. S17).

We have described the difference in surface area of the soots in context of deposition nucleation and PCF on p.11, l.32-p.13, l.7 (old manuscript).

We have revised the following statement to clarify the independence from particle surface area:

p.12, l.3: *“This suggests a homogeneous freezing mechanism for the FW200 particles below water saturation.”*

To (page 12 line 24 in revised manuscript):

*“This suggests a homogeneous freezing mechanism for the FW200 particles below water saturation, most likely not directly related to the particle surface area.”*

In addition, we have added a statement (page 25 line 15 revised manuscript) for clarification. See our reply to question (33) of reviewer #01.

The monomer size stated for the LB\_RC corresponds to our TEM data (see Fig. S17). We agree that this is rather large compared to atmospheric soot particles. See our reply to point (1) of reviewer #03. Besides, the LB\_RC sample is very heterogeneous in primary particle size, as shown in our Fig. 5, resulting in the rather large mean primary particle size (152 nm) reported. This does not preclude LB\_RC aggregates with smaller primary particles to nucleate ice via PCF.

- (5) Overall, the discussion of soot aggregate porosity is rather qualitative and they tried to make a link with PCF freezing. Perhaps authors can use the BET surface area**

**measurements to make conclusions or make an attempt to provide more quantitative information on the porosity.**

We acknowledge the point raised by the author that the presented porosity is rather qualitative and mainly based on our BET and DVS data. Deriving a pore size distribution requires some a priori assumptions to be made on the particle system that is probed, for instance the pore structure (Dubinin and Stoeckli, 1980). Next, different adsorbents are used to probe these different pore types/structures (Popovitcheva et al., 2000). The uncertainty associated with the resulting (bulk) pore distribution for a complex fractal aerosol such as soot, where a variety of different pore structures are likely present, along with the instrumental cost/requirements are beyond the scope of this paper. To really control the pore size and structure, experiments with carbon nanotubes (Alstadt et al., 2017) or synthesized mesoporous particles (David et al., submitted) would be needed, but these are less atmospherically relevant and focus on a different research question.

**Minor comments:**

- (1) Page2, line6: typically in the atmosphere primary particle diameter of soot particles ranges from 15-60 nm. Several hundreds of nanometer sounds too large to me.**

We agree that most of the atmospheric soot particles have primary particle diameters below 100 nm and that significantly larger primary particles are an extreme case, but still found for some of our particles, as shown in Fig. S17. Nevertheless, we tuned down “several hundred” so that this introductory statement covers the case for the majority of the soot aerosols.

Accordingly, we changed p.2, l.6:

“The primary particle diameter itself can vary from around 10 nm to several hundred nanometers, depending on the combustion source.”

To (page 2 line 5 in revised manuscript)

“The primary particle diameter itself can vary from around 10 nm to several tens of nanometers, depending on the combustion source.”

- (2) Page 13, line 34: please provide the number of aggregates and monomers analyzed.**

We revised the sentence and added the number of aggregates and monomers to be more explicit as follows on page 15 line 9 of the revised manuscript:

*“This is further supported by the size distribution of primary particles shown in SI Fig. S17, for which between 10 to 50 aggregates and a minimum of 122 primary particles have been evaluated for each soot type.”*

- (3) Page 14, line 1: “the most ice active FW200 soot shows particularly densely clustered aggregates” – why the DMA-CPMA derived fractal dimension is low then compared to other soot investigated? May be it’s related to coating that added to mass. For example, FS particles seem more coated and has higher Dfm compared to other soot samples.**

It should be noted that the TEM images only show a 2D projection of the particles. Thus the FW200 particles could be more branched/fractal than they appear on the TEM images shown, which would be in-line with our DMA-CPMA derived fractal dimension.

We now also report the uncertainties of the derived fractal dimensions (see our reply to point (5) of reviewer #02). Considering the standard error of the fractal dimensions, the FW200 and FS sample are very similar.

- (4) Page 14, lines 5-10: “. . .soot particles with smaller spherules are more likely to nucleate ice via a PCF mechanism”- I didn’t follow this part. How did you come to this conclusion?**

In case of a relatively smaller primary particle diameter an aggregate of a given mobility size is composed of a larger number of primary spherules (monomers) compared to a soot type

with a relatively larger primary particle diameter. In the aggregate with the higher number density of primary particles (smaller primary particle diameter) the chances for pores are higher and therefore the probability of ice formation via PCF is higher.

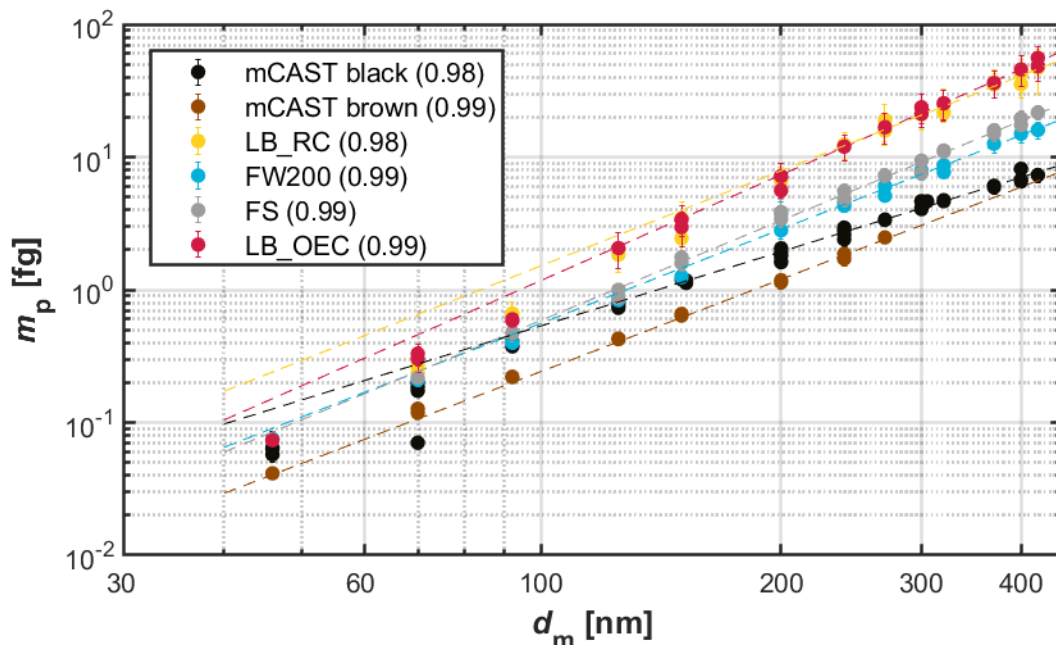
This is supported by our ice nucleation results (Fig. 3) and the primary particle size distribution (Fig. S17). The step-like AF curves of the FW200 reflects very homogeneous pore properties of this sample, which is supported by the narrow primary particle size distribution and also suggest a narrow distribution of contact angles on this sample. Other soot samples that nucleate ice via PCF have more heterogeneous distributions of primary particle sizes (pores) and/or contact angles (also see reply to point (30) of reviewer #01).

This point is already explained in the original manuscript (p.14 | 3-10) and we revised the statement further down in the text (page 16 line 1 in the revised manuscript) to read:

*“Nevertheless, it is likely that the clear difference in primary particle size determines and/or strongly influences overall aggregate porosity. Soot aggregates of a given mobility size are composed of an increasing number of carbon spherules for decreasing primary particle sizes. As the number of spherules increases, the propensity for pores in an aggregate also increases due to the potential for pores between sintered spherules and/or through intra-aggregate cavities between the branches of the aggregate. As such, soot particles with smaller spherules are more likely to nucleate ice via a PCF mechanism due to the higher concentration of pores, resulting from the increased number of primary particles in these aggregates.”*

**Figure 4: perhaps the authors can consider to plot using log-log scale, then show the power fit. Then it will be easier to read the fractal dimension.**

This is a very good idea. We replotted the figure using log-log scale and also included the fit lines along with the  $R^2$  of the fits in the legend.



Accordingly, we added the following statement to the caption of Fig. 4:

*“Error bars correspond to standard deviations of the individual measurements and dashed lines to the power law fits using eq. A4. The values in parenthesis give the  $R^2$  of the fit.”*

**(5) Table B4: please provide the error for pre-factor and fractal dimension.**

We have added the standard error of the fit values for the pre-factor and the fractal dimension to the table, and added the following statement to the caption of Table A4 (former B4).

*“The value in brackets indicates the standard error.”*

- (6) It is interesting that FW200 soot samples show significant mass loss from TGA experiments and also show highest ice nucleation ability. Significant mass loss below 200°C suggest that there were volatile material. I didn't follow why authors refer this observation as presence of hydrophilic sites? Why there were condense water?**

As correctly pointed out by the reviewer, the significant mass loss of the FW200 sample in the TGA (Fig. 6) indicates the presence of *“highly volatile compounds”* (p.16, l.21, revised manuscript). This term encompasses any material that volatilizes at temperatures below 200 °C. Now the question arises, whether the observed mass loss is due to *“adsorbed/condensed water and/or low molecular weight organic substances”* (p.16, l.24, revised manuscript). We interpret the majority of the mass loss of the FW200 sample to be associated through evaporation of adsorbed water but do not fully exclude the presence of any other highly volatile material. This conclusion is drawn by combining our TGA results with our ice nucleation and DVS experiments. We refer to the FW200 sample having hydrophilic sites, as it demonstrates the highest water uptake in the DVS already at very low  $RH_w$  (< 30%).

To include the simultaneous presence of OM, we changed the sentence on p.19, l.25 (initial manuscript):

*“[...] attribute the water uptake of FW200 to pores present on the soot aggregates, and not only due to absorption of water vapor by hydrophilic OM.”*

To (page 20 line 24, revised manuscript)

*“[...] attribute the water uptake of FW200 to pores present on the soot aggregates, and not only due to absorption of water vapor by hydrophilic OM, which is also present, as suggested by our TGA results.”*

**May be I missed something how the experiments were performed. Also, I'm surprise by the amount of mass loss. It suggest that there were quite a bit of volatile material in the soot sample. Information about the chemical composition of soot samples would have been helpful.**

Chemical composition data is unfortunately not available within the auxiliary measurements performed within the presented study, except what is given within the discussion/interpretation of the TGA data in Section 3.4. However, we acknowledge the point made by the referee and believe that using more detailed chemical data (along with physical properties as for instance presented herein) will help to further our understanding of soot ice nucleation in further studies, as we suggest in the added statement (page 24 line 32 in the revised manuscript), given in the reply to point (1) of reviewer #03.

- (7) Page 23, line 15: May be add some examples of atmospheric processing of soot after long-range transport when soot particles become more compact (change contact angle) or coated with other materials.**

We agree that it is a good idea to add a brief description of possible processing mechanism.

Therefore, we changed the sentence from:

*“During this time the soot aggregates undergo atmospheric processing, for instance in the form of multiple cloud formation cycles.”*

To (page 24 line 15, revised manuscript)

*“During this time the soot aggregates undergo atmospheric processing, encompassing any chemical and/or physical change of the particle properties (e.g. Zhang et al., 2008), for instance through photochemical processes (Li et al., 2018) or by acquiring of a coating due to condensation of semivolatile species or compaction of the soot agglomerate. Such processing can alter the physicochemical properties, such as fractal dimension or hygroscopicity (contact angle). Of particular interest here is the cloud processing of soot particles, i.e. the change in*

*physicochemical properties as the particles are involved in cloud microphysical processes such as cloud droplet or ice crystal formation.”*

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