Reply to referee #3: 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 numbered the reviewer comments for ease of cross-reference within the other reviews.

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(1) In this paper, authors measure the ice nucleation properties of various soot samples and further interpret these measurements by characterizing the particle properties and conclude that PCF kind of mechanism can explain the diverse INP properties observed for soot particles. My major concern is properties of realistic (emitted directly into the atmosphere through natural and anthropogenic processes) soot aerosol could be different than soot generated in the lab through dry-dispersion method, and this could affect the conclusions. Lab generated particles may not be atmospherically relevant particles. It is necessary to discuss how this connection can be made. An attempt is made in section 4, but not enough. The surface properties of soot samples from both sources are very different. Detailed discussion including these limitations needs to be explained and acknowledged. In addition, I have few following minor comments that I suggest to address before publication.

We thank the reviewer for his/her comments. Further, we agree with the reviewer's major comment, that the particle types investigated herein are not necessarily identical to atmospheric soot particles. In Section 2 we describe the sample and their (implicit laboratory) origin in great detail and state that these soot types cover *"a wide range of combustion aerosol physicochemical properties as proxies of atmospheric soot"* (p.4, l.3 in old manuscript), i.e. are taken only as surrogates of atmospheric particles.

We revised this statement to more carefully acknowledge the difference to realistic soot particles to page 4 line 3 in revised manuscript:

"Soot samples were chosen to represent a wide range of combustion aerosol physicochemical properties as proxies of atmospheric soot which could still differ from those particles studied here"

Additionally, to address the reviewer's concern we clarify the differences between the laboratory generated soot particles and atmospheric soot particles more clearly, by adding the following statement (page 24 line 2 in revised manuscript):

"This finding is important for instance for the fate of soot particles from aviation emissions, which are generally found to be even smaller than 100 nm in diameter (Moore et al., 2017, Yu et al., 2017). Such particles are often internally mixed with sulfuric acid (Kärcher, 2018) and can contain metallic compounds (Abegglen et al., 2016) or other residues such as lubrication oil (Yu et al., 2012) and organics (e.g.Yu et al., 2017). These factors can cause atmospheric soot particles to differ in physicochemical properties, e.g. contact angle (surface properties), from the particles types investigated here, which in turn influences their ice nucleation abilities. Still, there is increasing evidence [...]"

We added a reference for the change in particle wettability as the soot particles undergo atmospheric processing, i.e. interact with atmospheric gases on page 24 line 19 of the revised manuscript.

We added the following statement at the end of Section 4 (page 24 line 32):

"It is clear from this laboratory study that the physicochemical properties of soot aerosol determine their ice nucleation potential, with wettability being particularly important. At the same time our conclusions drawn here are limited by using bulk particle properties to explain ice nucleation taking place on individual particles (and at a molecular level). Further investigation of other factors, especially elaboration of a more quantitative pore size distribution and detailed chemical characterization of size selected particles, or at least individual particles, would be desirable to increase our understanding of soot ice nucleation abilities. Certainly, atmospheric soot particles can be more complex than the particle types investigated here. At the same time laboratory studies provide a more fundamental understanding of the properties relevant for ice nucleation"

(2) Page 2-3: Not all historical studies are discussed. It sounds like this is the first paper to study a majority of the soot samples (section 2.1 or Table 1). It may be best to discuss these studies briefly.

We agree with the reviewer and have revised the manuscript introduction (page 2, line 21-26) to include and discuss more previous studies on soot ice nucleation, namely:

Häusler et al. (2018), Ullrich et al. (2017), Gorbunov et al. (1998), Garten and Head (1964).

We hope that the added references in the introduction section on p.2-3 provide a sufficient background to put our work in context.

(3) Section 2.2: What is the size distribution of soot samples? What size was selected (page 6, line 9)? How was multiple charge correction applied?

We clarified the size distribution of the soot samples in the revised manuscript. Please see our reply to point (2) of reviewer #02.

Details of the mobility sizes and corresponding flow ratios of aerosol to sheath flow, as well as an exemplary size distributions of the size selected aerosol, where multiple charge correction was applied, are given in the SI Section S6 (Table S1 and Fig. S15). Note aerosol to sheath flow ratios in the DMA and SMPS system, with the higher aerosol to sheath flow generally yielding a wider size distribution (broader transfer function).

We refer to the details of aerosol size selection a little bit further down in the main text on p.6, l.14 (initial manuscript):

"[…] where they were size selected based on their dry electrical mobility diameter, d_m (see Supplementary Information (SI) Table S1 for flow settings)."

For clarification that the SI also contains information on the electrical mobility size selected for ice nucleation experiments, we revised this statement to (page 7 line 2 in revised manuscript:

"[…] where they were size-selected based on their dry electrical mobility diameter, d_m (see Supplementary Information (SI) Table S1 for details of mobility sizes selected and associated flow settings within the DMA)."

We also added a cross-reference to the SI Section S6 in the manuscript on page 6 line 18 in the revised manuscript as well as to the caption of page 11, Fig. 2.

Our presented AF curves are not corrected for multiple-charged particles. We clarified this by adding the following statement to page 7 line 4 in the revised manuscript.

"The ice nucleation experiments presented below include multiple-charged particles, i.e. particles that are larger than the electrical mobility size selected. The amount of double-charged particles is approximately 6 and 12 % for the 100 and 200 nm particles respectively and 15 % for the case of selecting mobility diameters 300 and 400 nm (Wiedensohler, 1988)."

(4) Page 8: For ice crystal detection 1 um threshold was used. How it is ensured that soot particles are not larger than 1 um. Figure 5 shows the images of these soot samples, and it looks particles are greater than 1 um. Therefore, ice particles will grow larger than 1 um. Please clarify. The implications are briefly explained on page 9 (line 5), but details regarding how 'aerosol-correct' is needed.

The "aerosol correction" of the AF curves is applied to separate the signals from the particles from that corresponding to ice crystals. In Figure 1 below we illustrate the effect of this correction. Aerosol correction is applied when the size selected aerosol particles are detected in the OPC channel used for ice detection (in our case the 1 μm channel). This is the case in the example below, where an AF of approximately $8*10^{-2}$ is detected in the OPC for 70% < RH_w < 85%. In order to remove this bias and more clearly show the real ice signal, we calculated the mean AF value over the RH range, where no ice is detected (in this case 70-84%) and subtracted this value from every data point of the entire AF curve. This correction makes the ice signal more accessible, as it reduces the false AF signal from aerosol particles increasing our detection ability of ice crystals at these low AFs.

For clarification, we added the following statement to p.9, l.24 in the revised manuscript:

"In these cases the mean AF value detected by the OPC (channel) at low RH values, where no ice crystals are formed, was subtracted from each data point of the AF curve, correcting for any false signal in AF arising from large unactivated aerosol particles."

Such an aerosol correction was only applied to the 300 nm and 400 nm samples of the LB_OEC and LB_RC samples, but not to the other soot samples. For the other soot samples no counts were detected in the 1 μm OPC channel prior to ice formation. This is why we write on p. 9, l. 5 (initial manuscript):

"[…] to aerosol-correct some of the AF curves […]"

The reason why aerosol correction was only necessary for the lamp black soots might be related to their wider primary particle size distribution (Fig. S17), but we have no direct evidence to support this. Nevertheless, this gives us confidence that the majority of the soot particles are (optically) smaller than 1 μm, which is further supported by our new Fig. S18, showing the distribution of spherical equivalent diameters, as derived from TEM analysis. See our reply to (2) of reviewer #02.
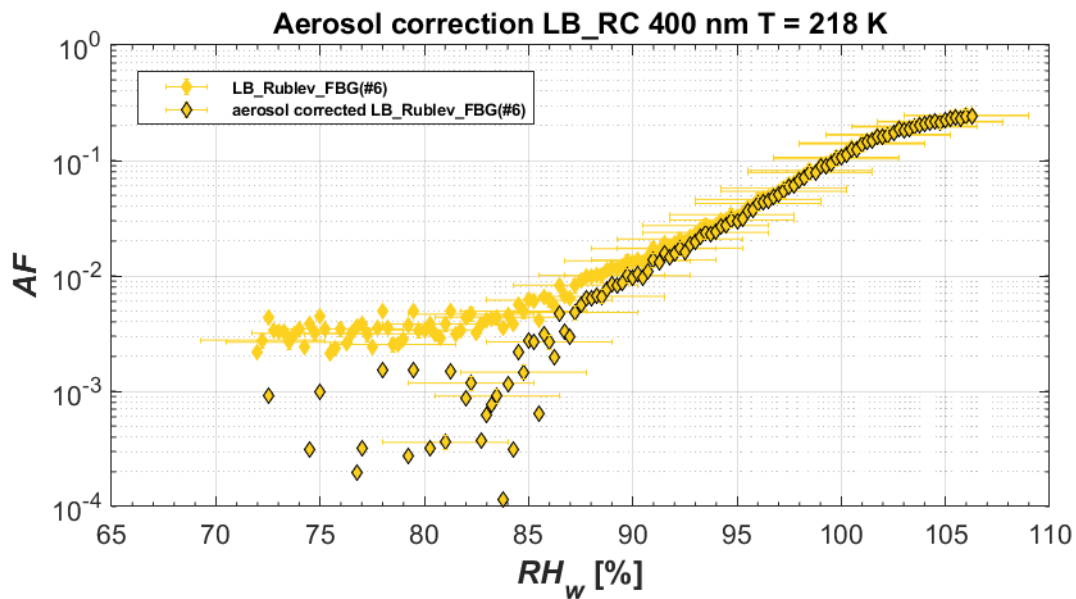
Figure 1: Exemplary AF curves of the LB_RC soot sample for 400 nm soot particles, which have been aerosol corrected (black border) and which have not been aerosol corrected (yellow outline), to illustrate the effect of the aerosol correction applied to our AF curves. AF curves shown correspond to the mean over six independent ice nucleation experiments, evaluated using the 1 μm channel of the OPC.

Finally, it is true that larger OPC channels could have been used for analysis, which is e.g. done by Lacher et al. (2017) when considering MPCs where different hydrometeor types are separated by optical particle size. However, this comes at the cost of detecting the ice nucleation at higher RH, as particles need to grow larger, especially for the cold temperatures investigated here.

(5) Page 22, line 31-: If the soot properties of combustion aerosols are different than labgenerated, how it is possible that ice nucleation properties of 100 nm will be similar? The sentence saying '. . .it is unlikely that such small soot particles . . ..' is not true.

We agree, and therefore have clarified this in the manuscript by stating that 100 nm particles with properties similar to the ones investigated here will not act as INP in the MPC regime. However, this could be different for combustion aerosols emitted in the atmosphere.

We have now modified the sentence to acknowledge that (see page 23 line 32 in revised manuscript):

"Since none of the investigated soot types was ice nucleation active when particles of 100 nm mobility diameter were selected, it is unlikely that such small soot particles with properties similar to those investigated here will act as INP unless they are internally mixed with other ice active material."

(6) Section 4: Discussions such as comparison of residence time (timescales) within HINC and aircraft plume is irrelevant. Soot properties in both cases are not similar. Also, the assumption regarding cloud formation cycles is not supported.

We agree that a comparison of timescales between aircraft plume and chamber residence time is irrelevant. We therefore deleted the following statement from the manuscript, p.23, l.10 (initial manuscript):

"However, ice nucleation in aircraft plumes happens rapidly as contrail formation becomes visible within approximately one wingspan behind the air plane due to the high local supersaturations. This corresponds to timescales of a few seconds after particle emission (Schumann and Heymsfield, 2017; Schumann, 2012) similar to the residence time in HINC and the high saturation ratios achieved towards the end of our RH scans."

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We note that atmospheric soot particles can undergo multiple cloud formation cycles (e.g. Huang et al., 1994). Involvement of a soot particle to form a cloud droplet or an ice crystal resulting in altered physicochemical properties of the residual aerosol particle, is broadly referred to as "cloud processing". For instance, China et al. (2015) have recently shown that such processing can lead to a compaction of the soot aerosol, with implication for its optical properties. However, a change in particle morphology likely also alters the surface and hence pore distribution of the aggregate. From our conclusion of a PCF mechanism triggering ice nucleation, this would ultimately also affect/change the ice nucleation ability of the aerosol. It is thus our purpose to clearly state that the ice nucleation results as presented, are only valid for the first ice nucleation process (first cloud cycle) these particles are exposed to, but not necessarily any further ice nucleation cycles. At the same time once ice has been nucleated on a soot particle, the ice within the pores can be preserved even within environments that are subsaturated with respect to ice, due to the lower saturation vapor pressure over the concave surface within the cavity. Such "ice pockets" can then trigger detectable, macroscopic ice formation (growth) at lower RH, compared to the ice nucleation results presented herein.

We have clarified the statement regarding cloud formation page 24 line 21 in revised manuscript and reply to point (32) of reviewer #01.

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