<u>Reply to referee #1: Interactive comment on "Ice nucleation abilities of soot particles determined with the Horizontal Ice Nucleation Chamber"</u>

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.

(1) In the manuscript, the ice nucleation activity of 6 different soot samples is examined with the CFDC-type ice nucleation chamber HINC at the ETH (Zurich). Additionally, a thorough analysis of physical properties of the soot particles is presented. All data are jointly discussed. It is concluded that the examined soot particles do not act as ice nucleating particles in the mixed cloud regime. In the cirrus cloud regime, some soot types were more ice active than others, which was traced back to pore condensation and freezing. The manuscript is well written. Data is nicely presented. The overall message is clear. Sometimes I felt that the information was a bit too much, but then it is all interesting and well researched, so I will not suggest so shorten anything. Below, I give a number of (mostly small) remarks / suggestions for improvements. The number of remarks makes me choose "major revisions", but it should all be easily done. Overall I recommend this manuscript for publication in ACP once these suggestions will have been addressed.

We thank the reviewer for carefully reading the manuscript and the overall constructive comments on it. We appreciate the detail of the comments provided and hope that the responses below satisfactorily address the reviewer concerns.

Specific comments:

(2) page 2, line 8: Vali et al. (2015) do not introduce any research or their own, but rather summarize knowledge, thus this citation here is a bit misleading. They don't show that soot particles can act as INPs. I suggest removing this citation here.

We have removed this reference, as suggested (page 2 line 8 in revised manuscript).

(3) page 4, line 25: You claim that your sample "LB_RC" is "directly comparable to the lamp black soot purchased from OEC, due to their very similar physical properties" – however, the BET surface areas of these two soot samples is an order of magnitude apart, so I suggest to delete this statement about their comparability, or adjust it accordingly.

We are grateful for the reviewer to have realized this. There is a typo in the numeric value given for the surface area of LB_RC on p.4, I.24:

"Its specific surface area was measured to be 233 m^2g^{-1} "

We changed it to (page 4 line 24 in revised manuscript):

"Its specific surface area was measured to be 23 m²g⁻¹"

This is also in accordance with the value reported in Tab.1.

(4) page 5, Table 1: It would be interesting to know how many particles were counted in the TEM analysis. This could be given in an additional line.

We believe you are referring to the number of primary particles counted to derive the mean primary particle diameter indicated in Tab. 1. The corresponding figure and number is shown in Fig. S17. We have now added information to Tab. 1 to show the number of particles counted.

(5) page 6, line 8: What were these filters used for? It would be nice to get this information here in the text.

We primarily used the mCAST filters to obtain bulk soot aerosols of the mCAST samples for TGA, DVS and BET analysis. We agree with the reviewer that the use of the filters should be more clearly specified in the main text. We therefore deleted the following statement on p.26 I.1.

"For the miniCAST samples, not available in powder form, soot was collected on 47 mm diameter quartz fiber filters (Tissuquartz Filters, Type 2500QAT-UP, Pall Inc.), using a 47 mm aluminum in-line filter holder. The filter holder was mounted at a distance of 10 cm downstream of the miniCAST exhaust pipe, using an air-cooled stainless-steel pipe. Soot aerosols were then carefully removed from the filter with a metal spatula prior to TGA analysis."

And instead extended the statement on page 6 line 11 in the revised manuscript to read:

"mCAST samples collected for analysis were directly sampled from the miniCAST outlet, upstream of the VKL10, on 47 mm diameter quartz fiber filters (Tissuquartz Filters, Type 2500QAT-UP, Pall Inc.), using a 47 mm aluminum in-line filter holder. The filter holder was mounted at a distance of 10 cm downstream of the miniCAST exhaust pipe, using an air-cooled stainless-steel pipe and connected to a vacuum pump, operated at a constant flow rate of 20 Lmin⁻¹. Soot aerosols were then carefully removed from the filters with a metal spatula for bulk particle analysis as specified in Sect. 2.4."

(6) page 6, line 10: Does this mean that the mini-CAST samples on the filters were sampled BEFORE this additional coagulation took place? Please give the answer to this question in the text.

Yes, collection on quartz fibre filters took place upstream of the mixing chamber (where coagulation occurred). This is now clarified on page 6 line 11 in the revised manuscript. We also added the filter collection stage to Fig. 1 for clarity.

(7) page 6, line 18 and 19: You use HINCNE and HINCNE (i.e., once is in italic, the other isn't). Be consistent throughout the text. My personal preference is the one with italic letters.

We have changed this to italics *NE* and *ST*, respectively. We also changed this in the caption of Fig. S16 to italics.

(8) page 7, line 7-9: It is not so clear to me if you really can assure that the aerosol flow through the DMA is stable – did you check the exhaust air from the mixing chamber regularly? Was it constant? And were the flows in the DMA stable?

Yes, the flow through the DMA column was stable. The DMA output flow was regularly checked between experiments with a flow meter mounted inline between the DMA outlet and the flow splitter depicted in Fig. 1 and deviations were found to be well below 10% over a period of 3h. Besides the pressure within the mixing chamber was continuously monitored using a pressure sensor. We refer to this on page 7 line 7 of the original manuscript:

"The over-pressure was regulated with a needle-valve controlled exhaust, mounted to the mixing volume."

But we further clarify this now on page 7 line 19 of the revised manuscript

"The over-pressure was regulated with a needle-valve controlled exhaust, mounted to the mixing volume, where the pressure was continuously monitored using a pressure sensor."

We also added on page 7 line 21 of the revised manuscript

"In addition, a stable correct flow through the DMA was ensured by checking the flow between the DMA and the flow splitter over regular intervals of approximately 3 h."

(9) page 7, line 22: The phrase "Cloud particles can be formed" is not correct. Ice may or may not form, as you say, and water droplets will only form at RH_w > 100% and therewith at much higher humidities. Therefore, it would be better to say "Ice crystals may be formed".

We intended to use the term cloud particles to encompass both ice crystals and cloud droplets. You are right that the sentence as written is incomplete and with that incorrect, as it only holds for T < 273 K (no ice saturation for higher T). As in our experiments both ice crystals and cloud droplets can be formed at the respective RH conditions we would like to make the reader aware of this possibility at this stage, also it is more detailed when discussing the WDS (p.8 I.10). We thus revised the sentence on p.7 I.22 from:

"Cloud particles can be formed within the chamber by exposing the injected aerosol particles to RH conditions $RH_i > 100$ %, where the subscript I denotes evaluation with respect to ice."

To (page 8 line 1 in the revised manuscript)

"Ice particles can be formed within the chamber by exposing the injected aerosol particles to conditions of $RH_i > 100$ %, where the subscript i denotes evaluation with respect to ice, and cloud droplets can be formed for conditions of $RH_w > 100$ %, where the subscript w denotes evaluation with respect to water."

(10) page 8, line 1-2: "The residence time is the sum of a nucleation and water droplet or ice crystal growth time in the chamber." – This is strangely formulated. Please reformulate. Maybe "The residence time is the sum of the times..."

"The residence time is the sum of a nucleation and water droplet or ice crystal growth time in the chamber."

Is now changed to (page 8 line 18 in the revised manuscript):

"Assuming a perfectly parabolic velocity profile across the chamber, the aerosol particles are assumed to travel at the maximal velocity at the center of the profile, which is used to derive the particle residence time in the chamber, i.e. the time it takes a particle to cross the chamber. The residence time can be divided into the time it takes to nucleate an ice crystal (or activate a water droplet) and the subsequent growth time of the particle within the chamber."

(11) page 8, line 14-15: How long does it take, until the particles reach the destined temperature after entering HINC? If both sheath and aerosol flow are at laboratory temperature upon entering HINC, there will certainly be a non-negligible delay. This needs to be mentioned and shortly discussed.

The reviewer raises a valid point here. The time needed to equilibrate the aerosol and sheath flow from room temperature to the temperature conditions within HINC is on the order of 0.3-2 seconds (depending on temperature) before steady state is achieved, as detailed in Kanji and Abbatt (2009), and thus only a small fraction of the residence time used here. However, we note that the sheath flow has a longer residence time in the chamber before it joins the aerosol flow. The sheath flow enters HINC upstream of the aerosol flow and as such has approximately 8-9 seconds in HINC before meeting the aerosol flow, thus should already be equilibrated to the chamber conditions (T and RH). Furthermore, the aerosol flow also traverses through the injector inside HINC before joining the sheath flow at the injector exit. Thus when the aerosol flow meets the sheath flow at the centre temperature of HINC, only the aerosol flow (~1/10th of the total flow) needs to equilibrate to the HINC RH conditions which should be instantaneous given the aerosol would be temperature conditioned in the injector.

We included a discussion of this point on (page 8 line 12 in the revised manuscript)::

"Both F_{AP} and F_{sheath} are introduced into HINC at approximately room temperature conditions, however, F_{sheath} is introduced at the beginning of HINC (prior to F_{AP}) and thus will reach steady

state conditions of temperature and water vapor upon entering the chamber prior to joining the aerosol flow. F_{AP} (~1/10th of F_{OPC}) should equilibrate with the temperature and to the saturation conditions in HINC within 0.2 - 2 s, as described by Kanji and Abbatt (2009) and Lacher et al. (2017) depending on the temperature in HINC."

We also changed on p.8, I.2 (initial manuscript):

"For all experiments presented here a particle residence time of $\tau \approx 16$ s was chosen, allowing the nucleated ice crystals to grow to sizes of a couple of micrometers in diameter within the chamber."

To (page 8 line 22, revised manuscript)

"For all experiments presented here a particle residence time of $\tau \approx 16$ s was chosen. This is well above the maximum time needed for the airstream to reach steady state conditions within HINC (0.2 – 2 s) and allows the nucleated ice crystals to grow to sizes > 1 μ m (ice detection threshold size) in diameter within the chamber."

Also, on the opposite side, could settling of the particles to the lower plate be an issue?

Particle settling in HINC is a valid concern. This issue has been addressed in Kanji and Abbatt (2009) and Lacher et al. (2017). Owing to the different residence times used in this work than in the previously mentioned studies, we have added another section (D2) to the appendix of our manuscript, to discuss hydrometeor growth and settling.

(12) page 8, line 31: Certainly you mean for sizes from 1 μ m onwards, and not only in the 1 μ m channel? Correct this.

This is correct; the AF is defined as the ratio of all particles larger than 1 μ m to the total number of particles entering HINC. This is consistent with our statement on p.8 I.5 of the original manuscript:

"The OPC can count and size particles in the size range between 0.3 μ m and 10 μ m (optical diameter) and can be operated at six different, customizable size bins within this range. However, it does not have phase discrimination capability, as such discrimination between interstitial aerosol particles, cloud droplets and ice crystals is based purely on optical particle size. Here, we choose the 1 μ m size bin as the threshold to detect ice crystals in HINC, i.e. particles with optical diameters >1 μ m."

For clarification, we have added the following statement on page 8 line 28 of the revised manuscript:

"The OPC was operated in normal (cumulative) mode such that the number counts within each channel correspond to particles of that optical size and larger."

Besides we have changed our nomenclature from $n_{ice,CH1\mu m}$ to $n_{ice,CH>1\mu m}$ for clarification (page 9 line 17 in revised manuscript).

(13) Chapter 2.4: This chapter is an interesting and impressive addition to the ice nucleation measurements - but it would be good to know which of these measurements were performed on the bulk samples and which on the size segregated particles, and for the latter, if then the same set-up described above was used. Please add information on this to the text.

TEM and DMA-CPMA measurements were performed on size segregated particles. TGA, BET and DVS measurements were performed on bulk soot samples.

For clarification, we now added the following (page 10 line 6 of revised manuscript):

"Therefore, the TEM sampler and the CPMA were operated directly downstream of the flow splitter depicted in Fig. 1, i.e. on (mobility) size selected aerosol particles." For the case of the DMA-CPMA measurements this is already described in more detail on p.27 I.15-21 (initial manuscript, now at page 29, line 23):

"For this purpose, DMA-CPMA are coupled in series in such a way that aerosol particles are first sent into the DMA, classifying the particles by electrical mobility (selecting by drag:charge), resulting in a narrow size distribution. [...] The particles are subsequently passed through the CPMA, selecting monodisperse aerosol by mass to charge, and counted by a CPC (Model 3776, TSI Inc.) downstream of the CPMA, operated at a flow rate of 0.3 Lmin⁻¹, yielding the number concentration of size and mass selected aerosol."

In addition we changed p.9 I.16 (initial manuscript) from:

"In addition, all soot types were investigated by means of a thermogravimetric analyzer [...]"

To (page 10 line 7 in revised manuscript)

"In addition, bulk soot properties were investigated by means of a thermogravimetric analyzer [...]"

Further, we changed p.9 I.20 from:

"[...] water vapor sorption isotherms of the soot particles were measured by Dynamic Vapor Sorption (DVS, Model Advantage ET 1, Surface Measurement Systems Ltd., London, UK)."

To (page 10 line 11 in revised manuscript)

"[...] water vapor sorption isotherms of the bulk soot samples were measured by Dynamic Vapor Sorption (DVS, Model Advantage ET 1, Surface Measurement Systems Ltd., London, UK)."

Accordingly, we changed p.9., I. 21 from:

"Finally, the BET specific surface area of the samples was determined from additional N_2 adsorption measurements ($a_{BET,N2}$)."

To (page 10 line 12)

"Finally, the BET specific surface area of the bulk soot samples was determined from additional N_2 adsorption measurements ($a_{BET,N2}$)."

(14) page 9, line 13: Better replace "aid" by "contributed to".

Change made (page 10 line 2 in revised manuscript).

(15) Figure 2: The "blue dashed line" – is that the one that is almost at the RH_w = 1
 - line? This is almost impossible to see - use a different color, e.g., red, or small circles or something else.

We changed the color to red and slightly increased the line width for visibility. We changed relevant parts of the manuscript to refer to the red WDS line.

(16) page 11, line 11-13: Would this then not mean that every possible ice active material would be outcompeted by homogeneous freezing?

No, this would not be the case. It depends on how ice active the other types of INPs are that the reviewer refers to. For example, if a particle is only active as an INP at very low temperatures and high RH say close to the conditions of homogeneous freezing, then yes, homogenous freezing rates begin to get very high at such conditions and heterogeneous nucleation would not contribute to ice crystal formation in the atmosphere.

On the other hand if the ice active material was an INP at warmer temperatures like mineral dust e.g. for temperatures as warm as -20 °C, then of course homogeneous nucleation rates at these temperatures are negligible for volumes of droplets in the troposphere, as such heterogeneous freezing would outcompete homogeneous freezing.

Still, heterogeneous freezing is considered to play a role even for the cirrus cloud regime.

This is true, we agree with the reviewer, that heterogeneous freezing plays a role in cirrus clouds and is even believed to be the dominant freezing process (e.g. Cziczo et al., 2013) if dust aerosol and other species are present. However, this should be true only for cases where the heterogeneous freezing is observed to occur below the RH required for homogeneous freezing (see Kuebbeler et al., 2014). Again, if RHs as high as those required for homogeneous freezing are also required for heterogeneous freezing, then homogeneous freezing will outcompete heterogeneous freezing simply because there are orders of magnitude higher droplets in the atmosphere than INPs.

And if this (second) part of the sentence can be debated, I wonder if the first part (about 100 nm particles being not relevant) is not a trade of between the HINC detection limit and the abundance of these particles in the atmosphere?

We do not believe this statement has anything to do with the HINC detection limit. If a particle of a given aerosol type and size is only ice active at or above homogeneous freezing conditions, as our 100 nm soot particles tested here, then we can no longer state that freezing occurred heterogeneously, i.e. when water condensed on soot particles because of high excessive amounts of humidity like in a contrail. Since at these temperatures, ice germs can form within the bulk volume of water (i.e. an interface with the INP is not required, nor necessary to lower the energy barrier of nucleation of a new phase), the freezing is considered homogeneous, because the surface of the soot plays a role for water condensation, but is not necessary for the freezing process since this can occur in a bulk water droplet without any solid interface in it. In the atmosphere, if soot does not nucleate ice via deposition nucleation or water droplets will begin to freeze since their nucleation rates are would be significant at these conditions rendering any nucleation from soot particles negligible.

(17) page 11, line 25: Missing space between y and 2.

We added a space.

(18) page 11, line 32-33: Another reason could be that it takes up water better – could be worthwhile mentioning.

We agree with the reviewer that the lower ice nucleation onset of FW200 soot is caused by its enhanced ability to take up water (lower contact angle) compared to the other soots tested here. However, we see no need to discuss this at this point of the manuscript, as this is discussed in great detail in Section 3.5 and should ultimately become clear by the following statement on p.19, I.15 (initial manuscript, page 20 line 5 in revised manuscript):

"The high water affinity of FW200 revealed by the DVS measurements is consistent with the observed ice nucleation at relatively low ice supersaturations."

(19) page 12, line 4: A new sentence should start between "particles" and "they".

Change made (page 12, line 28 in revised manuscript).

(20) page 14, line 7: Add a "," between "increases" and "the" (it took me a while until I got the sentence).

Suggested change made (page 16, line 3 in revised manuscript).

(21) page 14, line 10: Tiny remark, but why "in prep.b" first (before "a")?

This reference is now updated to "submitted" and should resolve this issue (page 16, line 7 in revised manuscript).

(22) page 15, line 7: There is a space too much before the first letter.

We have amended that and indented the whole paragraph (added more space in front of "Highly"), in order to mark the change in paragraph (page 16 and line 21 in revised manuscript)

(23) Figure 6: One of the screens I used while working at this review did not show this graph well. The "yellow" color shading looked rather pinkish, and the shading of the two other panels was almost the same - maybe there is a better (or additional) way to refer to the panels? (Using a), b) and c) for example?)

We removed the shading and added arrows and labels (as suggested) for each temperature range to the figure.

For consistency, we also revised Fig. S13 and its caption accordingly.

(24) page 17, line 19-20: Are you really referring to S16 in the SI, here, so should this rather be S10? But in any case, I have difficulties following your argument – why does the lack of a change in the slope render this interpretation unlikely?

We are in fact referring to Fig. S16, as stated in the manuscript, however, we agree with the reviewer that the way it is written in the current version is confusing. We will adjust the manuscript to clarify our argument, which is as follows:

Fig. S16 shows an ice nucleation experiment using NH_4NO_3 , i.e. a salt aerosol, at 233 K which should freeze homogeneously at this temperature at RH conditions predicted by the Koop et al. (2000) parametrization (vertical black dashed line).

Our Fig. S16 shows how the injected (dry) salt aerosol particles deliquesce and grow by hygroscopic growth and ultimately form solution droplets between approximately 95% and 99% RH_w. This growth is associated with a moderate slope of the AF curves shown. Upon reaching the critical RH_w, homogeneous freezing of the solution droplets occurs (between 99% and 100% RH_w, i.e. within instrumental uncertainty), the slope of the AF curves becomes steeper ("step-like"), indicating the formation of ice crystals of nearly all solution droplets. This change in slope of the AF curves at homogeneous freezing conditions (within the uncertainty range given by the gray shaded region), indicates a change in mechanism occurring (i.e. the nucleation of ice crystals through homogeneous freezing). In other words, we expect this steepness in the slope of the AF curves, since we expect a large change in nucleation rate once homogeneous freezing conditions are reached.

Given that we do not observe any such change in the slope of the AF curves of our FS sample shown in Fig. S10, we believe that the FS samples do not form droplets that then freeze homogeneously in this case.

We now clarify this aspect in the manuscript on page 18 lines 13-16.

(25) page 17, line 33: Change "of" to "the"

Done! (page 18 line 29 in revised manuscript).

(26) Figure 7: If you used a log-scale for one of the two panels, it would be easier to see the hysteresis and the absolute values for the curves at the lower end. The way it is now, both panels look quite similar, anyway.

The pores relevant for an ice nucleation mechanism via PCF are mesopores (> 2 nm) start filling at approximately $RH_w > 60-70\%$, depending on the pore type (shape). Thus, our figure aims at showing the difference in water uptake of the soot types mainly at these high relative humidities, where also the resolution of our DVS scans is largest. Therfore we prefer the linear axes. However, we include the figure using log axis below for the reviewer's information. Mircoporosity on the contrary, which can be infered from the DVS scans at lower RH values, does not contribute to ice nucleation via PCF, as these pores are too small to accommodate an ice germ. They are, however, relevant for soot particle restructuring due to water uptake, which is not part of the current manuscript.



(27) page 19, line 21: Are citric acid and glutaric acid organics typical for the atmosphere? Any citation on that? Others might play a more important role (oxalic acid, formic acid, acetic acid, succinic acid, ...). But there must be a reason why you choose those. Explain that in a few words.

Glutaric acid is a common dicarboxylic acids in the atmosphere (Winterhalter et al., 2009, Kawamura and Ikushima, 1993) and its effects on soot have been studied in the past (Xue et al., 2009). Citric acid is less common but has also been identified in atmospheric aerosols (e.g. Kawamura and Yasui, 2005). Their hygroscopic growth is typical and a proxy for that of watersoluble organic aerosol fraction. Formic and acetic acid do not partition to the condensed phase in atmospheric aerosols while oxalic and succinic acid effloresce and deliquesce when RH is decreased and increased, respectively. Deliquescence/efflorescence is not expected for organic aerosols which are mixtures of many compounds (Marcolli et al., 2004) and therefore does not represent typical hygroscopic growth of atmospheric aerosols.

(28) page 20, line 18-21: The last few words "rather than the bulk aggregate size" puzzled me a bit. There is a difference in the freezing curves for FW200 particles of different sizes, and you say, quite correctly, that you observe 1% of particles ice active at similar RHs for a given particle size (BTW: exchange "aerosol size" with "particle size" here). But then why would you refer to "bulk aggregate size" in the end. Would anyone really assume that this plays role? I suggest to delete these few last words unless you feel they are needed.

The "bulk aggregate size" was meant in terms of an "overall" aggregate size. We agree that there is no need for this (repetition of sentence before) and changed the sentence accordingly to avoid confusion (page 21 line 18 in revised manuscript):

"The constant onset S_i indicates that the freezing is in fact determined by pore size and sootwater contact angle, which determine water filling of the pores and subsequent homogeneous freezing."

We also changed "aerosol size" to "particle size" (page 21 line 18 in revised manuscript)

(29) page 21, line 7: I suggest to tune down "confidently identify" a little.

We assume that the referee refers to p.22 I.7 instead. We changed it to (page 23 line 6 in revised manuscript) to:

"Combining our ice nucleation results with data obtained from TGA and DVS, we identify PCF as the dominant mechanism to cause the freezing of the tested soot particles."

(30) page 22, line 22: Concerning the use of the word "contact angle", I realize that you talk about the interaction between the soot surface and water vapor. But on the other hand, it has been shown for other materials that it never only is one contact angle describing the ice nucleation behavior of one substance, but a contact angle distribution instead. This might need to be mentioned.

The reviewer raises a good point here and we agree that it is more meaningful to think of a contact angle distribution, rather than one absolute value.

On p.13, I.4-10 we discuss the steepness of the AF curves of the FW200 sample ("step-like") and argue that none of the other soots reveal a similarly clear/steep AF curve. This is likely caused by the FW200 particles having the right properties (pore size and contact angle), but also more homogeneous physicochemical properties compared to the other soot types. We argue, for instance, that there is a freezing attributable to PCF for both lamp black samples in the cirrus regime (Fig. 3). One can think of the absence of any step-like activation for the lamp blacks to be caused by more heterogeneous particle properties, where not every soot aggregate has the "right match" of contact angle and pore size to fill and freeze within a narrow defined RH_w range, causing the AF curve to be less steep, i.e. activation over a broader range of RH conditions at a given temperature. In other words, the contact angle distribution and pore size distribution have a stronger interplay in case of the FW200 particles, compared to the

other soot types. We hint at this early in the manuscript and revisit it in a bit more detail later. We revised the manuscript as follows:

p.13, I.10: "[...] the observed difference must be related to the physical and chemical properties of the particles."

Is changed to (page 16 line 12 in revised manuscript):

"Thus, the observed difference must be related to other physical and chemical properties of the particles, in addition to the morphology, which might be more heterogeneous for the other soot types"

p.19, I.18: We added (page 20 line 14 in revised manuscript):

"The steep AF curves of FW200 compared to the other soots, as discussed in Sect. 3.2, can be thought of as an overlap of pore size distribution and associated contact angle distribution that favours condensing water in pores, resulting in particles with properties suitable to nucleate ice via PCF, whereas those soot types with less steep AF curves indicate a more heterogeneous distribution of particle properties (contact angles and pore sizes)."

Finally, we changed p.22, I.22 from:

"Specifically, our DVS results reveal that both pore structure and contact angle determine the ice nucleation ability of the soots studied."

To (page 23 line 21 in revised manuscript)

"Specifically, our DVS results reveal that both pore size distribution and contact angle distribution determine the ice nucleation ability of the soot particles studied."

(31) page 23, line 5: It should not be forgotten that solid fuels (from either biomass burning or wildfires) also produce ashes, so for observed atmospheric ice activities of respective particles, also these ashes could be responsible (Umo et al., 2015, Grawe et al., 2016).

Soot and ash particles differ in their chemical composition, as discussed for instance in Grawe et al. (2016). Nevertheless, we agree with the referee that such ash particles, which have been shown to be ice active, can be sourced from biomass burning and wildfires. We now add this on page 24 line 9 of the revised manuscript:

"At the same time such solid fuels can also produce ash particles, which can contribute to ice formation (Grawe et al., 2016, Grawe et al., 2018, Umo et al., 2015)."

(32) page 23, line 15: In your argument about the pore ice, it was not clear to me right away how it should have gotten there in the first place – after rereading the sentence I now assume that likely you imagine that ice nucleated in a previous cloud cycle, and in the following one, ice crystals can form now more readily? Maybe describe this more explicitly?

This is exactly what we mean. In order to clarify this we changed the sentence p.23 I.15 (original manuscript) from:

"In case of ice nucleation via a PCF mechanism, pore ice can remain trapped within the cavities between the cloud cycles, thus particles could grow into macroscopic ice crystals, as soon as the RH_i >100 %."

To (page 24 line 21, revised manuscript):

"In case of ice nucleation via a PCF mechanism, pore ice can remain trapped within the cavities (microscopic pore ice) between subsequent cloud cycles for certain conditions of T and RH, even though the macroscopic ice crystal is sublimated. For instance, an ice crystal formed on a soot particle leaving the cloud will experience an ice subsaturated environment and thus sublimate. However, given that RH conditions outside the cloud are high enough (at T < 273)

K), the ice within the pores can survive, due to the reduced saturation vapor pressure of ice within the cavity. This pore ice can then grow into macroscopic ice in subsequent cloud cycles when $RH_i = 100\%$ is exceeded."

(33) page 24, line 2-4: In the framework of "pore condensation and freezing", indeed liquid water is part of the concept. However, the fact that ice nucleation was observed below RH required for homogeneous freezing does not necessarily suggest that liquid water is required: Deposition ice nucleation could also happen! I agree with you that maybe pore freezing is the process rather at work here, but still, the reasoning between these two sentences is somewhat flawed. The observation described in the first sentence does not result in the conclusion you draw in the second sentence. Reformulate.

We agree with the reviewer and have reformulated the sentences to read (page 25 line 16 revised manuscript):

"In the MPC temperature regime no ice nucleation was observed below water saturation, while for some of the probed soot samples ice nucleation was observed below the RH required for homogeneous freezing of solution droplets in the cirrus regime. The absence of heterogeneous freezing in the MPC regime below water saturation suggests that deposition nucleation does not take place on the tested particles. While water can be taken up into the pores of the soot aggregates also at MPC conditions, the absence of any ice formation below water saturation indicates that there is a lack of active sites that could trigger heterogeneous ice nucleation at these temperatures. The observed ice nucleation in the cirrus regime could theoretically be caused through a (surface area dependent) deposition nucleation mechanism. However, the strong dependence of the ice nucleation efficiency on the HNT implies that it is the liquid water within the soot pores that freezes homogeneously, since particle properties considered relevant for deposition nucleation (if present) should be available for ice nucleation in both the cirrus and MPC regime. Such a dependence on the HNT relevant for liquid water freezing for ice nucleation onto soot particles investigated here is in-line with a PCF process and in contrast to classical deposition nucleation, where the liquid phase is absent. Overall, we conclude that the ice formation process on the soots is best described by a PCF mechanism and not deposition nucleation."

(34) page 25: Why does this start with Appendix B? What happened to A? (Probably an issue for typesetting, anyway.)

Thank you for spotting this. It is corrected now such that we start with Appendix A.

(35) Table B1: What do #1 and #2 stand for? And why does "C (#1)" occur twice?

#1 and #2 stand for two independent BET experiments performed on the bulk soot samples. The repeated occurrence of #1 is a typo, which we corrected within the table. We now clarify the two experiments within the table caption by adding:

"[...] We report the values of the C parameter used in Eq. B1 for the two independent experiments labeled #1 and #2, respectively."

(36) Figure E1: z-values do not fit to what is shown on y-axis - is this only a fraction of the profile that you show here? Please clarify.

This is correct, only a fraction of the vertical distance between the two plates is shown in Fig. E1. To avoid confusion we changed the first sentence of the figure caption to:

"Example of S_w for the mid-portion of the vertical distance between the cold (at z = 0 cm, bottom) and warm (at z = 2 cm, top) wall of HINC chamber [...]"

(37) Chapter B2: The here presented analysis, and others, were done for bulk samples, while ice nucleation was measured for size segregated particles – possible implications for this should be discussed somewhere (not here, but up in the main

text, where you draw conclusions about the connection between soot characteristics and their ice activity.

We agree with this limitation. The statement added on page 24 line 32 of the revised manuscript and posted in the reply to question (1) of reviewer #03 accounts for this.

(38) Table B4: Is there a reason why you give the factor C, but not (or not also) the effective density? The latter could be of interest for the readers.

The mass-mobility pre-factor, C, is derived from fitting a power-law of the form of Eq. B4 to all data points of a given soot type shown in Fig. 4, and is given for completeness and allows the calculation of any mass associated with a given mobility diameter for each soot type for the interested reader.

We have added a figure (Fig. S20) to the manuscript, which shows the effective densities corresponding to all our DMA-CPMA data. Effective density values for other soot diameters can be calculated using eq. B3.

(39) My only remark for the supplement: Fig. S18: Please mention in the caption, that the length of the bar in the picture is 800nm for all pictures in the left column and 200nm for all others - otherwise this needs blowing up quite a bit before these numbers can be seen, which is a bit annoying.

We added the following sentence at the end of the figure caption:

"The lengths of the scale bars correspond to 800 nm for the left column and to 200 nm for the middle and right columns."

***Additional changes by the authors:

Fig. 7: There was a "°C" vs. "K" error, so we changed from:

"[...] as measured by DVS at T = 298 °C. [...]"

To (page 19 in the revised manuscript)

"[...] as measured by DVS at T = 298 K. [...]"

The flow rate given for the miniCAST on p.7 I.8 should read 30 Lmin⁻¹, this value was corrected from:

"[...] in case of the FBG and 35 Lmin⁻¹ in case of the miniCAST."

To (page 7 line 21 in revised manuscript).

"[...] in case of the FBG and 30 Lmin⁻¹ in case of the miniCAST."

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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.

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 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:

$$d_{Aeq} = \sqrt{\frac{4Aa}{\pi}},$$

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 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 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 circus 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, I.32-p.13, I.7 (old manuscript).

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

p.12, I.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, I.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 200C 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, I.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, I.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, I.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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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.

(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, I.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, I.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 μ m 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, I.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 μ m OPC channel prior to ice formation. This is why we write on p. 9, I. 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 μ m, 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, I.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."

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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Ice nucleation abilities of soot particles determined with the Horizontal Ice Nucleation Chamber

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Abstract. Ice nucleation by different types of soot particles is systematically investigated over the temperature range from 218 to 253 K relevant for both mixed-phase (MPCs) and cirrus clouds. Soot types were selected to represent a range of physicochemical properties associated with combustion particles. Their ice nucleation ability was determined as a function of particle size using relative humidity (RH) scans in the Horizontal Ice Nucleation Chamber (HINC). We complement our ice

- 5 nucleation results by a suite of particle characterization measurements, including determination of particle surface area, fractal dimension, temperature dependent mass loss, water vapor sorption and inferred porosity measurements. Independent of particle size, all soot types reveal absence of ice nucleation below and at water saturation in the MPC regime (T > 235 K). In the cirrus regime ($T \le 235$ K), soot types show different freezing behaviour depending on particle size and soot type, but the freezing is closely linked to the soot particle properties. Specifically, our results suggest that if soot aggregates contain mesopores (pore
- 10 diameters of 2-50 nm) and have sufficiently low water-soot contact angles, they show ice nucleation activity and can contribute to ice formation in the cirrus regime at RH well below homogeneous freezing of solution droplets. We attribute the observed ice nucleation to a pore condensation and freezing (PCF) mechanism. Nevertheless, soot particles without cavities of the right size and/or too high contact angles nucleate ice only at or well above the RH required for homogeneous freezing conditions of solution droplets. Thus, our results imply that soot particles able to nucleate ice via PCF, could impact the microphysical
- 15 properties of ice clouds.

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1 Introduction

Soot, mainly composed of highly agglomerated carbon spherules, is a by-product of incomplete combustion of biomass and fossil fuels and represents a major anthropogenic pollutant. Globally, emissions of soot are estimated to reach 7500 Ggy^{-1}

(uncertainty range: $2000 - 29000 \text{ Ggy}^{-1}$, Bond et al., 2013), with a direct source in the upper troposphere from aviation emissions, and thus are of high relevance for climate (Ramanathan and Carmichael, 2008). Soot aerosols generally denote complex internal mixtures of black carbon (BC) and associated organic matter (OM, Petzold et al., 2013), and here we use the term *soot* to encompass internal mixtures of both. Soot aggregates usually have diameters on the nanoscale, ranging from

- 5 individual primary carbonaceous spherules to large, fractal-like aggregates (Adachi et al., 2007). The primary particle diameter itself can vary from around 10 nm to several hundred tens of nanometers, depending on the combustion source. The diverse physicochemical properties of soot aerosols make an analytical assessment of their environmental effects challenging. Soot particles can act as ice nucleating particles (INPs, Vali et al., 2015) (INPs) in cirrus clouds (DeMott, 1990; DeMott et al., 1999) and MPCs as well as in aircraft contrail formation (Seinfeld, 1998; Boucher, 1999; Popovicheva et al., 2004; Schumann,
- 10 2005; Kärcher et al., 2007; Heymsfield et al., 2010; Schumann and Heymsfield, 2017; Kärcher, 2018) and thus affect cloud properties such as emissivity, lifetime, albedo and cloud coverage. The pathways of ice formation have recently been reviewed by Vali et al. (2015) and Kanji et al. (2017). For instance, when acting as INPs in supercooled liquid and/or MPCs, aerosol particles can trigger glaciation of the clouds resulting in efficient precipitation formation causing a reduction in cloud lifetime (Lohmann, 2002). However, this so-called glaciation effect is rather uncertain due to unknowns in primary ice formation with
- 15 aerosol species such as soot (Lohmann, 2002). Additionally, particle properties such as coatings of BC with organic substances can reduce or inhibit their ice nucleation abilities (Hoose et al., 2008) thus adding further uncertainties to the contribution of soot to ice nucleation. Understanding the ice nucleation mechanism of soot aerosols is crucial in order to describe the fate of these particles in the atmosphere and resolve the uncertainties associated with aerosol-cloud interactions (Lohmann, 2015; Fan et al., 2016; Lohmann and Feichter, 2005). This will ultimately enhance our understanding of the anthropogenic influence on

20 clouds.

Numerous laboratory studies have investigated the ice nucleation ability of soot (e.g. DeMott, 1990; Diehl and Mitra, 1998; DeMott et al a review was recently provided by Ullrich et al. (2017). However, these studies have revealed a large variability in ice nucleation characteristics of soot particles, indicating that the ice formation ability of soot remains poorly understood. For instance,

- 25 DeMott et al. (1999) used commercially available lamp black soot (Degussa) to test the ice nucleation ability of soot in the cirrus regime ($T \le 235$ K), using a continuous flow diffusion chamber (CFDC). They found ice formation below water saturation for T < 231 K. However, since ice nucleation was observed very close to water saturation, whether the ice formation occurred through deposition nucleation or water sorption and subsequent freezing could not be determined. This finding is in direct contrast to Möhler et al. (2005a), who used soot produced by a graphite spark generator (GSG) and tested its ice nucleation
- 30 ability using the AIDA (Aerosol Interactions and Dynamics in the Atmosphere) chamber. They found bare (uncoated) GSG soot to nucleate ice in the deposition mode for T < 233 K, with ice formation onset observed well below homogeneous freezing conditions, even though their reported activated fractions made up only 0.3 % of the total aerosol population. Investigation of ice nucleation on propane fuel particles by Möhler et al. (2005b) revealed a dependence of the ice nucleation ability on the OM content of the soot particles. They showed that ice nucleation at 207 K on low OM soot (16 % by mass) was more efficient
- 35 compared to high OM content (40 % by mass) particles. While the ice nucleation onset for the low OM soot was similar to that

observed by Möhler et al. (2005a) for H_2SO_4 coated GSG soot, the high OM soot required homogeneous freezing conditions. The cause for this was interpreted as a suppression of deposition nucleation by the increased organic content covering the carbon spherules. A later study by Crawford et al. (2011) on the ice nucleation of propane soot particles came to the same conclusion by varying OM content. Specifically, they found that only the soot particles with the lowest OM content (5 % by

- 5 mass) were able to heterogeneously nucleate ice in the deposition mode (at T = 226 K), while higher OM content soot (30 % and 70 % by mass) required water supersaturation. Friedman et al. (2011) performed ice nucleation experiments on size selected soot particles produced by a propane burner at T = 233 K, 243 K and 253 K. They did not detect heterogeneous ice formation of bare soot particles before the formation of cloud droplets. At the same time they found that organic coatings resulted in an increased hydrophilicity, but not in a significant change in the ice nucleation ability of the particles. Koehler
- 10 et al. (2009) tested the ice nucleation ability of five different soot types with different physicochemical properties in the cirrus regime. They reported that the capacity of the soot particles to take up water strongly influenced their ice nucleation characteristics. Using the hydration property classification described in Popovicheva et al. (2008), they found hygroscopic soot, with water uptake caused by water-soluble material on the soot aggregates, to freeze only homogeneously, similar to any other hygroscopic particles. In contrast, hydrophobic and hydrophilic soots, associated with little or no water-soluble material both
- 15 froze heterogeneously. The authors therefore concluded that water affinity alone is insufficient to predict the ice nucleation ability of soot and that other particle characteristics such as porosity and surface polarity complicate predictions for the heterogeneous freezing of soot particles. A direct intercomparison of the ice nucleation results discussed above is challenging due to the complex characteristics of soot particles. Yet, the heterogeneity of the reported ice nucleation results arise partly from the irreproducibility associated with combustion particle properties (Popovicheva et al., 2008) and from the different techniques

20 used to probe ice nucleation.

In this study we systematically investigate the ice formation ability of six different soot samples. Testing the ice nucleation of soot particles with different physicochemical properties using the same experimental procedure, allows for a direct comparison and improves our understanding of the ice formation characteristics of soot aerosol. Ice nucleation was investigated in the MPC (T > 235 K) and cirrus cloud temperature regime, covering the range between 218 - 253 K, as a function of relative

- 25 humidity (*RH*) and aerosol size, using the Horizontal Ice Nucleation Chamber (HINC, Lacher et al., 2017), a continuous flow diffusion chamber. Our measurements extend the limited measurements of particle size dependent ice nucleation characteristics of soot aerosol, particularly in the cirrus regime. In addition, we characterize the particle properties and report measurements of morphological features, bulk heat sensitive fraction, hydrophilicity and porosity of the soot samples to interpret our INP measurements. By combining these auxillary measurements with our INP experiments, we draw fundamental conclusions on
- 30 the relationship between particle properties and the ice formation mechanisms of soot particles for atmospherically relevant conditions.

2 Experimental methods and materials

2.1 Soot samples

25

Soot samples were chosen to represent a wide range of combustion aerosol physicochemical properties as proxies of atmospheric soot and to allow for a direct comparison to previous studies which could still differ from those particles studied here. A summary of the characteristics of the soot samples used here is shown in Table 1. Below we briefly describe their properties and origin.

FW200: This commercially available carbon black (Orion Engineered Carbons GmbH, OEC, Frankfurt, Main, Germany) is produced in the gas black process, through the incomplete combustion of liquid hydrocarbons. A commercial carbon black was chosen to ensure reproducibility of the sample for future ice nucleation studies. The gas black method allows for production of particles with narrow primary particle size distributions with mean primary particle diameters of d
_{pp} = 22 nm, as found by transmission electron microscopy (TEM, see Table 1). The smaller the primary particle size the higher the surface area, a
_{BET} = 526 m²g⁻¹, determined by N₂ adsorption using the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938). Due to their slightly oxidized surface, gas blacks are acidic. Based on these characteristics, we choose FW200 soot with the goal to identify a potential laboratory surrogate for atmospherically aged soot.

LB_OEC: A lamp black carbon was obtained from OEC. Lamp black carbons generally have a broader primary particle size distribution and a lower specific surface area compared to gas black soots. In the case of LB_OEC, produced by the lamp

15 black process, the manufacturer specifies an average primary particle sizes of $\bar{d}_{pp} = 95$ nm, comparable to the $\bar{d}_{pp} = 119$ nm we derived by TEM (see Appendix C). Soot aerosols with a wide primary particle size distribution usually result in aggregates that span a relatively wide size range compared to soots with a narrow range of primary particle sizes. At the same time, the fraction of particles containing many primary particles should be limited when selecting a mobility diameter close to the reported \bar{d}_{pp} . Nitrogen BET surface area was measured to be 24 m²g⁻¹. Similar soot has been used for previous ice nucleation studies (DeMott et al., 1999), rendering a direct comparison of our results feasible.

LB_RC: Another amorphous lamp black soot, lamp black Rublev Colours (RC), was purchased from Natural Pigments LLC, (Willits, California, USA). It is also produced by the lamp black process and we found an average primary particle size of $\bar{d}_{pp} = 152$ nm, by evaluating TEM images. Its specific surface area was measured to be 233–23 m²g⁻¹. This sample is directly comparable to the lamp black soot purchased from OEC, due to their very similar physical properties, thus, allowing for a direct comparison of the ice nucleation abilities of the same soot type stemming from different combustion sources.

miniCAST soot: Combustion aerosol was generated using a miniature combustion aerosol standard (miniCAST, Model: 4200, Jing Ltd., Zollikofen, Switzerland). The miniCAST produces soot aerosol in a co-flow diffusion flame, mixing two concentric, interleaved flows of propane (inner flow) and particle-free, VOC-filtered, synthetic oxidation air (outer flow). Changing the fuel-air ratio varies the properties of the resulting aerosols, such as mean aggregate size, morphology and OM content over

30 a wide range and in a reproducible fashion (Moore et al., 2014; Schnaiter et al., 2006; Mueller et al., 2015; Mamakos et al., 2013; Yon et al., 2015). It has been shown in the past that miniCAST soot can mimic the physicochemical properties of aircraft soot (Bescond et al., 2014). Here we test two soots that differ in OM content, namely a sample termed mCAST black produced

under fuel lean conditions, with a C:O ratio of 0.21 and $\bar{d}_{pp} = 31$ nm, as well as a more organic rich soot, termed **mCAST brown**, with a flow C:O ratio of 0.23 and $\bar{d}_{pp} = 21$ nm. Details about the miniCAST operation conditions used here are given in Appendix B. The specific surface area using N₂ absorption was measured at 120 m²g⁻¹ and 70 m²g⁻¹ for mCASTblack and mCASTbrown, respectively.

5

FS: Lastly, FS, a fullerene soot, was purchased from Sigma Aldrich, Darmstadt, Germany. Fullerenes are hollow molecules of carbon atoms, arranged in a highly symmetric manner (Krätschmer et al., 1990). This fullerene soot mainly consist of C_{60} molecules with a minor fraction of C_{70} (see Table 1). Fullerene-like soots are often used as surrogates for particles produced by emissions from diesel engines (Muller et al., 2005). The FS investigated here had a specific surface area of 265 m²g⁻¹ and the derived primary particle diameter was 41 nm.

Table 1. Particle characteristics of soot types investigated in this study, where \bar{d}_{pp} denotes the mean physical diameter of primary particles, as obtained from TEM evaluation of the number of primary particles indicated and $\sigma(d_{pp})$ the corresponding standard deviation; $a_{BET,N2}$ the BET specific surface area using N₂ adsorption at 77 K and ML₉₅₀ the mass loss at 950 °C measured by thermogravimetric analysis, as an upper limit of heat sensitive material associated with the soot. D_{fm} denotes the fractal dimension derived from power-law fits of the form of Eq. (A4) to mass-mobility data.

Type of soot	mCAST black	mCAST brown	FW200	LB_OEC	LB_RC	FS
Source	miniCAST ^a	miniCAST ^a	Orion Engineered Carbons Colour black FW200 powder Gas black process	Orion Engineered Carbons Flammruss FR101 powder Lamp black process	Natural Pigments LLC Lamp black process	Product no.: 572497, Lot no. MKBB8240V
Form/Dispersion method	combustion	combustion	Powder/FBG ^e	Powder/FBG ^e	Powder/FBG ^e	Powder/FBG ^e
General classification			amorphous CAS-no.: 1333-86-4	amorphous CAS-no.: 1333-86-4	amorphous CAS-no.: 1333-86-4	$\begin{array}{l} C_{60} \ (78.7 \ \%), \ C_{70} \ (18.8 \ \%), \\ \\ > C_{70} \ (1.6 \ \%), \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
\bar{d}_{pp} [nm]	31	21	22; 13 ^b	119; 95 ^b	152; 95 ^{<i>f</i>}	41
$\sigma(d_{pp})$ [nm]	5.9	4.9	3.9	43	55.7	12.9
Primary particles analyzed	122	129	166	141	137	142
ML ₉₅₀ °C [%]	15.62	18.58	31.43; 20 ^c	0.97	2.8	33.37
$a_{BET,N2} [\mathrm{m}^2 \mathrm{g}^{-1}]^d$	120	70	526	24	23 (20) ^f	265
D _{fm} [-]	1.86	2.31	2.35	2.64	2.83	2.5
Ice nucleation studies	Möhler et al. (2005b) Crawford et al. (2011) Friedman et al. (2011)			Dymarska et al. (2006) DeMott et al. (1999)	see LB_OEC	

 a Series 4200, see Table B1 for detailed flow settings

 $^{b} \bar{d}_{pp}$ specified by manufacturer based on ASTM (American Society for Testing and Materials) International standard D3849

 $^c~ML_{950}~^\circ\mathrm{C}$ specified by manufacturer based on DIN 53552

 d N_2 BET see Appendix A1

 e aerosolized using the Fluidized Bed Aerosol Generator, Model 3400A, TSI Inc.

f specified by manufacturer, technique/method not specified

2.2 Experimental setup

The experimental setup can be divided into three main sections as shown in Fig. 1, namely aerosol generation, aerosol selection and ice nucleation, which are briefly described below.

Aerosol generation: Soot aerosols were generated using different techniques, as specified in Table 1. Dry-dispersion was used for samples available in powder form through a Fluidized Bed Aerosol Generator (FBG, Model 3400A, TSI Inc.), operated

⁵ with a bed flow rate of 10 Lmin⁻¹, a chain purge flow rate of 2 Lmin⁻¹ along with a variable chain feed rate to achieve stable aerosol number concentrations. Particles from the FBG were subsequently passed to a 0.125 m³ stainless steel mixing volume, equipped with a fan to keep the particles suspended. Contrary, the miniCAST soot samples, were directly generated in the laboratory from the propane burner. Aerosol particles for ice nucleation experiments were sampled isokinetically from the miniCAST, using forward-pointing inlets centered at the outlet. The aerosol particles were then fed through a dilution system



Figure 1. Schematic of the experimental setup comprising three different stages: aerosol generation, aerosol size selection and ice nucleation measurements. Arrows indicate the direction of the aerosol flow. Aerosol particles were either produced by the miniCAST burner or generated from the FBG. See text for details of instrument details and abbreviations.

- 10 (Model VKL10, Palas) using particle-free, VOC-filtered air, prior to entering the mixing volume. Combustion particles for filter collection and mCAST samples collected for analysis were directly sampled from the miniCAST outlet, upstream of the VKL10, on 47 mm diameter quartz fiber filters (Tissuquartz Filters, Type 2500QAT-UP, Pall Inc.), using a 47 mm aluminum in-line filter holder. The filter holder was mounted at a distance of 10 cm downstream of the miniCAST exhaust pipe, using an air-cooled stainless-steel pipe and connected to a vacuum pump, operated at a constant flow rate of 20 Lmin⁻¹. Soot aerosols
- 15 were then carefully removed from the filters with a metal spatula for bulk particle analysis as specified in Sect. 2.4.
 Aerosol selection: From the mixing volume particles were size-selected size selected before being sampled into HINC for ice nucleation analysis (see Supplementary Information (SI) Sect. S6). Employment of a mixing volume enhances coagulation, increasing the size of the soot aggregates and buffers any fluctuations in particle generation allowing for a constant particle

number concentration during the ice nucleation experiments. From the mixing volume, particles were sent through a DMA (Differential Mobility Analyzer; Classifier 3080, with a 3081 column and a polonium radiation source, TSI Inc.), where they were size selected size-selected based on their dry electrical mobility diameter, d_m (see Supplementary Information (SI) SI Table S1 for flow settings). details of mobility sizes selected and associated flow settings within the DMA). The ice nucleation experiments presented below include multiple-charged particles, i.e. particles that are larger than the electrical mobility size

5 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). Downstream of the DMA, the flow was split using a four-way flow splitter (Model 3708, TSI Inc.) to the various instruments, as depicted in Fig. 1. Particle number concentration was monitored using a CPC (Model 3776, TSI Inc.), operated in the low flow mode (0.3 Lmin⁻¹).

Ice nucleation: Two similar HINC chambers were connected to the flow splitter, with the last port being used for exhaust

- 10 flow to avoid over-pressuring the setup. The two HINC chambers used encompass HINCST and HINCNE, where the suffix ST denotes standard and NE, non-evaporation operation conditions, respectively. An evaporation section at the end of HINCNE HINCNE can selectively be switched on or off and HINCNE HINCNE used here is identical to the chamber described in Lacher et al. (2017), i.e. not making use of the evaporation section and as such, identical to HINCSTHINCST. To ensure that results obtained from both chambers are comparable, the chambers were characterized prior to the soot experiments using aerosols
- 15 with thermodynamically well defined ice formation properties and good agreement was found within instrumental uncertainty (see SI Fig. S16). For this reason, we generally refer to both instruments as HINC in the following and combine their data for our analysis. To avoid external contamination from entering the setup, the system was run with an over-pressure from the aerosol generation source to the splitter. The over-pressure was regulated with a needle-valve controlled exhaust, mounted to the mixing volume, where the pressure was continuously monitored using a pressure sensor. This was possible as the total flow
- 20 from the aerosol generation was approximately 12 Lmin⁻¹ in case of the FBG and 35 Lmin⁻¹ in case of the miniCAST. In addition, a stable correct flow through the DMA was ensured by checking the flow between the DMA and the flow splitter over regular intervals of approximately 3 h.

2.3 Ice nucleation experiments and data processing

- 25 Ice nucleation experiments with HINC were conducted in deposition and/or condensation mode between 218 K and 253 K, in 5 K steps. HINC is a continuous flow diffusion chamber (Rogers, 1988; Rogers et al., 1998), based on the design of the UT-CFDC (University of Toronto Continuous Diffusion Chamber; Kanji and Abbatt, 2009) and is described in detail by Lacher et al. (2017). Briefly, two parallel, horizontally oriented copper plates separated by a 20 mm polyviniylidene fluoride (PVDF; Angst+Pfister AG, Zurich, Switzerland) spacer are lined with borosilicate glass fiber filter paper (Type A/C, Pall Corporation)
- 30 which is wetted prior to cooling. Upon cooling of the walls (copper plates) to subzero temperatures, a smooth ice layer is formed on the wetted filter paper. The wall temperatures are controlled by two thermostats (LAUDA ProLine RP890C) to keep temperature fluctuations around 0.1 K and are monitored through four equally spaced thermocouples along each wall. When held at different temperatures, a linear temperature gradient is established between the upper (relatively warmer) and lower

(relatively colder) wall, resulting in a parabolic water vapor supersaturation profile across the chamber, due to the nonlinear relationship between saturation vapor pressure and temperature (Clausius-Clapeyron equation). Cloud-Ice particles can be formed within the chamber by exposing the injected aerosol particles to RH conditions conditions of $RH_i > 100$ %, where the subscript *i* denotes evaluation with respect to ice, and cloud droplets can be formed for conditions $RH_w > 100$ %, where the subscript *w* denotes evaluation with respect to water. Freezing experiments with salt particles have been performed and

- 5 compared to theoretical predictions from the water activity based homogeneous freezing parametrization of solution droplets (Koop et al., 2000) to verify chamber performance (Lacher et al., 2017). The flow in HINC is maintained by two mass flow controllers (MFC, G-Series, MKS Instruments, Andover, USA), which control the sheath air and total flow. The sheath air flow (F_{sheath}) is made up of particle-free N₂ and confines sampled particles to a lamina at the center of the two walls, corresponding to a specific temperature and RH while preventing interaction of the particles with the walls. The total flow through HINC
- 10 (F_{OPC}) denotes the flow that is sampled by the optical particle counter at the chamber outlet. The aerosol containing sample flow (F_{AP}) , drawn into HINC, is given by the difference of F_{OPC} and F_{sheath} . The aerosol flow was chosen such that the ratio of F_{AP} to F_{sheath} was between 1:10-1:12, by adjusting F_{sheath} and keeping F_{OPC} fixed at 2.83 Lmin⁻¹. Both F_{AP} and F_{sheath} are introduced into HINC at approximately room temperature conditions, however, F_{sheath} is introduced at the beginning of HINC (prior to F_{AP}) and thus will reach steady state conditions of temperature and water vapor upon entering
- 15 the chamber prior to joining the aerosol flow. $F_{AP} (\approx 1/10^{th} \text{ of } F_{OPC})$ should equilibrate with the temperature and to the saturation conditions in HINC within 0.2 2 s, as described by Kanji and Abbatt (2009) and Lacher et al. (2017), depending on the temperature in HINC. The particle residence time within HINC is purely a function of the position of the movable injector as described by Lacher et al. (2017), for a constant total flow (F_{OPC}). Assuming a perfectly parabolic velocity profile across the chamber, the aerosol particles are assumed to travel at the maximal velocity at the centre-center of the profile,
- 20 which is used to derive the particle residence time in the chamber. i.e. the time it takes a particle to cross the chamber. The residence time is the sum of a nucleation and water dropletor ice crystal growth time in the can be divided into the time it takes to nucleate an ice crystal (or activate a water droplet) and the subsequent growth time of the particle within the chamber. For all experiments presented here a particle residence time of $\tau \approx 16$ s was chosen, allowing the. This is well above the maximum time needed for the airstream to reach steady state conditions within HINC (0.2 2 s) and allows the nucleated ice
- 25 crystals to grow to sizes of a couple of micrometers > 1 mum (ice detection threshold size) in diameter within the chamber. At the HINC outlet, an optical particle counter (OPC, Model GT-526S, MetOne) is used to detect particles. The OPC can count and size particles in the size range between 0.3 µm and 10 µm (optical diameter) and can be operated at six different, customizable size bins within this range. However, it does not have phase discrimination capability, as such discrimination between interstitial aerosol particles, cloud droplets and ice crystals is based purely on optical particle size. The OPC was
- 30 operated in *normal* (cumulative) mode such that the number counts within each channel correspond to particles of that optical size and larger. Here, we choose the 1 μ m size bin as the threshold to detect ice crystals in HINC, i.e. particles with optical diameters > 1 μ m. This threshold size was set above the size of aerosol particles entering HINC but small enough to capture the onset of ice formation. Conditions at which water droplets grow to sizes larger to the ice crystal threshold size is referred to as water droplet survival (WDS) relative humidity and is a function of *T*, initial aerosol size and residence time in the chamber.

- 35 Beyond that size (bin) ice crystals and cloud droplets cannot be distinguished any longer. Water droplet growth was calculated assuming pure diffusional growth based on Rogers and Yau (1989) for a given initial diameter corresponding to the size of the selected aerosol, and assuming the entire residence time within HINC is available for diffusional growth, i.e. neglecting any nucleation time. Therefore, the calculated values represent an upper limit of droplet growth and thus a lower limit of the WDS relative humidity reported. In our case the WDS line is only slightly above water saturation due to the 1 μm OPC
- 5 channel used to report ice nucleation (see Fig. 2). Data points occurring above the WDS line are not considered to represent heterogeneous ice nucleation. Nevertheless, we cannot exclude that heterogeneous ice formation takes place simultaneously with or after droplet formation. For all experiments the OPC was operated at a logging interval of 5 s, such that the detected counts within a given size channel yield the cumulative counts detected during this period. While most of the samples were probed using the six channel MetOne OPC, some experiments were performed using a four channel LightHouse OPC (Model
- 10 R3014) during instrument unavailability. However, the same settings and analyses were applied to ensure consistency in data treatment and comparable results. Ice nucleation abilities of the soot aerosol were probed by so-called RH ramps where the aerosol is exposed to increasing RH at fixed T. To achieve this, the desired lamina (center) temperature is set and then the RH is increased by cooling and warming the temperatures of the two walls at the same rates. Instrumental noise from HINC, including occasional frost particle detection, was determined with a particle-free flow in HINC at the beginning and the end of
- 15 each RH scan. The background counts, corresponding to a linear interpolation of the OPC counts detected during the particlefree periods, were subtracted from the data and all of our reported values are above this background level, as described in detail in Lacher et al. (2017).

The fraction of aerosol particles that nucleated ice is called the activated fraction (AF), defined as the ratio of the number concentration of ice particles detected by the OPC in the 1 μ m size channel, $n_{ice,CH1\mu m}$ $n_{ice,CH21\mu m}$, to the total number concentration of particles entering the chamber, n_{tot} , as determined by the CPC in parallel to HINC:

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$$AF = \frac{\frac{n_{ice,CH1\mu m}}{n_{tot}} \frac{n_{ice,CH>1\mu m}}{n_{tot}}}{\frac{n_{tot}}{n_{tot}}}.$$
(1)

The uncertainty range in AF is ± 14 %, resulting from a 10 % counting uncertainty in each of the OPC and CPC. The fractallike nature of soot aggregates causes the structure of monodisperse aerosols to vary on a particle to particle basis (Park et al., 2004), affecting aerosol properties such as shape and surface area thus adding to the complexity when size-selecting soot

- 25 aggregates. This resulted in larger aerosol particles (optical diameter > 1 μ m) being detected in the ice channel making it necessary to aerosol-correct some of the AF curves, when evaluating the 1 μ m OPC channel. 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. Finally, all ice nucleation results presented below correspond to mean AF values observed over a range of two to eight RH scans performed at a given
- 30 temperature. We constrained the ramp rate of our RH scans to below 3 %min⁻¹, evaluating RH with respect to water. The CFDC data was then linearly interpolated into bins of 0.25 % RH_w , where the subscript *w* denotes evaluation with respect to water. Thus, each reported curve represents the arithmetic mean of all binned and interpolated RH_w scans performed at a given temperature for a given soot sample.

2.4 Auxillary measurement for sample characterization

A suite of auxiliary measurements were conducted to characterize the physicochemical properties of the tested soots, which ultimately aid in determining contribute to their ice nucleation behavior. Details of the measurements can be found in Appendix A and are briefly described in the following. The fractal extent of the soot aggregates was determined through TEM and coupled

- 5 DMA-CPMA (Centrifugal Particle Mass Analyzer, Cambustion Ltd., Cambridge, UK) measurements to assess the fractal nature of the soots. Therefore, the TEM sampler and the CPMA were operated directly downstream of the flow splitter depicted in Fig. 1, i.e. on (mobility) size selected aerosol particles. In addition, all soot types bulk soot properties were investigated by means of a thermogravimetric analyzer (TGA; Model Pyris 1 TGA, PerkinElmer) to determine the particle fraction that can be volatilized as a function of temperature, referred to hereafter as the mass loss at a given temperature. This was done to
- 10 determine the presence of any secondary material coating the carbon spherules of the soot aggregates. In order to determine the hydrophilicity and infer the porosity of the samples, gravimetric water vapor sorption isotherms of the soot particles bulk soot samples were measured by Dynamic Vapor Sorption (DVS, Model Advantage ET 1, Surface Measurement Systems Ltd., London, UK). Finally, the BET specific surface area of the bulk soot samples was determined from additional N₂ adsorption measurements ($a_{BET,N2}$). The $a_{BET,N2}$ values were used in combination with the water sorption measurements to derive
- 15 equivalent water monolayer coverage.

3 Results and discussion

3.1 Overview of ice nucleation measurements

- An overview of the ice nucleation experiments is given in Fig. 2. From this overview a few key features are inferred concerning the ice nucleation ability of the tested soot particles. A clear dependence of ice nucleation of soot on the temperature regime
 can be identified. For T > 235 K all soot types require water saturation for activation into ice crystals and/or cloud droplets. The fact that the activation onset conditions for all soot types (independent of particle size) lie at RH_w ≥ WDS (dashed blue red line in Fig. 2), indicates an absence of heterogeneous freezing for RH_w < WDS. However, we re-iterate that we cannot unambiguously distinguish between cloud droplets and ice crystals at RH_w ≥ WDS, given that cloud droplets can grow to 1 µm by water vapor diffusion and be detected as ice crystals. Furthermore, evaluating the ice nucleation data for the 5 µm
 OPC channel, where WDS is well above water saturation for the residence time of τ ≈ 16 s, reveals that activation onset only takes place for RH_w ≥ WDS (see SI Sect. S3). Thus, we can conclude that no condensation/immersion freezing of soot takes place in the region 100 % < RH_w < WDS for the MPC temperature regime. This interpretation is consistent with Koehler et al. (2009), who did not find ice nucleation at temperatures above 233 K. Conversely, in the cirrus temperature regime some soot particles nucleate ice below homogeneous freezing conditions. From this, we conclude that the unprocessed soot types
- 30 investigated here can significantly contribute to ice nucleation only in the cirrus regime.

A strong increase in the freezing ability below the homogeneous nucleation temperature (HNT, 235 K) has been observed before for kaolinite (Welti et al., 2014) and suggests the involvement of a liquid water phase in the ice formation process,


Figure 2. Onset saturation ratio with respect to ice (S_i) of freezing where 1 % of the aerosol particles are activated as a function of temperature for <u>size-selected particles with mobility diameter of</u> (a) 100, (b) 200 (c) 300 and (d) 400 nm <u>size-selected particles (see SI Sect. S6)</u>. The black, solid lines denote water saturation using the water saturation pressure parameterization given by Murphy and Koop (2005); gray, dashed lines indicate offsets from this line in steps of 0.1 to guide the eye. The black, dashed lines mark the homogeneous freezing threshold for supercooled solution droplets according to Koop et al. (2000). The <u>blue red</u> dashed line indicates WDS conditions. WDS appears close to water saturation for the 1 µm OPC channel used. Each dot represents the mean of a minimum of two *RH*-scans performed with HINC. Temperature uncertainty is 0.1 K and S_i uncertainties, outlined in Appendix D1, are indicated as vertical bars. We note that mCAST black and brown do not activate to 1 % and are thus not plotted for some conditions (see SI Sect. S2 for complete *AF* curves).

similar to the soot particles tested here.

Moreover, a clear size dependence is observed, with larger soot aggregates showing activation at lower RH at a given temperature. A size dependence is consistent with the INP requirements reported in Pruppacher and Klett (1997) proposing that INP typically have (physical) diameters $\geq 200 \text{ nm}$. While these findings are confirmed by more recent studies for mineral dust (e.g. Archuleta et al., 2005; Welti et al., 2009), ice nucleation measurements of size selected (e.g. Friedman et al., 2011; Kulkarni

- 5 et al., 2016) or nearly monodisperse soot particles (DeMott, 1990) are limited, especially in the cirrus regime. The observation that the 100 nm soot particles only induced ice formation above homogeneous freezing conditions, suggests that particles of this size are not relevant for forming ice crystals at T < 233 K, irrespective of morphology and composition since homogeneous freezing of droplets will out-compete any heterogeneous nucleation by soot particles in the cirrus temperature regime. Besides a dependence on the minimum aerosol size, ice nucleation has been suggested to depend on the chemical composition
- ⁵ of the INP (Pruppacher and Klett, 1997). This is consistent with our results, which only show differing ice nucleation abilities among the soot types for particles with sizes of 200 nm or larger tested here. Nevertheless, the absence of freezing of our 100 nm soot particles, at conditions below homogeneous freezing of solution droplets reveals that both particle size and chemical properties determine the ice nucleation ability of the investigated soots. To further elucidate which properties provide soots with ice nucleation activity, we focus here on the ice nucleation results of the most active 400 nm particles in the cirrus regime. We show the complete activation curves in Fig. 3, in order to discuss differences in the ice nucleation mechanisms associated

5 with the soot types with information gained from the auxiliary measurements performed on the soot samples.

3.2 Ice nucleation dependency on soot type

Figure 3 shows the AF as a function of RH_w for all investigated 400 nm soot samples, covering the temperature range 218 – 233 K. Given that the RH_w range between homogeneous freezing condition and water saturation at T = 233 K spans only approximately 2 % RH_w , which is within our instrumental uncertainty, we cannot exclude that water saturation conditions

- 10 were reached for the observed freezing at 233 K. Overall, soot particles require high ice supersaturations to nucleate ice, rendering them unlikely to contribute to heterogeneous freezing at T = 233 K within the residence time of HINC. An exception is FW200, which shows activation well below homogeneous freezing conditions for all temperatures shown in Fig. 3. This becomes more apparent at lower temperatures. At T = 218 K FW200 shows significant freezing at RH as low as $RH_w = 70$ %. This heterogeneous freezing ability of FW200 is even more pronounced than that found by Koehler et al. (2009), who
- 15 reported AF of roughly 1 % below homogeneous freezing conditions, when testing thermal oxidized soot, i.e. soot processed in a mixture of nitric and sulfuric acid, at T = 233 K. The lower ice nucleation onset of FW200 soot can be interpreted as a more active deposition nucleation process due to the larger surface area of the FW200 compared to the other soots (see Tables 1 and A1). However, the absence of ice nucleation below water saturation for T > 233 K is incompatible with a classical deposition nucleation (Welti et al., 2014). As mentioned above, the dependence on the HNT supports the interpretation that
- 20 liquid water is involved in the freezing mechanism prior to reaching water saturation. This suggests a homogeneous freezing mechanism for the FW200 particles below water saturation, most likely not directly related to the particle surface area. Soot aerosols typically consist of agglomerated chains of spherical particlesthey. They are prone to form cavities and/or pore-like features between the primary spherules and the individual chains, in which water can condense at water subsaturated conditions (inverse Kelvin effect, Marcolli, 2014), and can subsequently freeze homogeneously through a so-called pore condensation
- and freezing mechanism (Higuchi and Fukuta, 1966; Fukuta, 1966; Christenson, 2013; Marcolli, 2014). During PCF, water that is taken up in capillaries well below water saturation, can freeze homogeneously if the temperature is below the HNT and if the pore diameter is large enough to accommodate the critical ice germ. Freezing of pore water can subsequently trigger



Figure 3. Mean RH scans of 400 nm mobility diameter soot particles, showing AF as a function of RH_w for different temperatures in the cirrus regime. Red dashed lines represent expected homogeneous freezing conditions according to Koop et al. (2000), and the gray shaded regions indicates the calculated RH_w variation across the aerosol lamina in HINC. Uncertainties, given for every 5th data point, are as in Fig. 2.

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macroscopic ice growth, resulting in ice crystal formation. The steepness of the activation curves for FW200 shown in Fig. 3 resemble a step-like activation when reaching a critical RH, consistent with a PCF type mechanism which requires the pores on the soot aggregate to fill and subsequently freeze homogeneously. In fact, the large specific surface area of FW200 itself (see Table 1 and A1), must be caused by concave and convex surfaces formed from the sintered primary particles and potentially indicates the presence of cavities. Additionally, aggregate porosity in the form of voids formed between sintered primary particles is supported by our TEM analysis (see Sect. 3.3). Yet, we note that none of the other soots tested shows a



Figure 4. DMA-CPMA data for the different soot types: Electrical mobility diameter (d_m) vs. median particle mass (m_p) derived from fitting the resulting mass distribution with a log normal distribution. 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.

similarly clear ice nucleation behavior attributable to PCF, which should be more heterogeneous for the other soot types. Thus, the observed difference must be related to the physical and chemical properties of the particles. We discuss these in the context of possible different freezing mechanisms between the soots in the following.

3.3 Soot particle fractal structure

- 5 Soot morphology was derived from DMA-CPMA measurements (see Appendix A4), and qualitatively from analysis of TEM images (see Appendix C). The fractal dimensions, $D_{\rm fm}$, of the different soot types are reported in Table 1 and the corresponding DMA-CPMA data is shown in Fig. 4. A $D_{\rm fm}$ value of 1 corresponds to a straight chain-like structure, whereas $D_{\rm fm} = 3$ indicates a compact sphere like structure. In general the values of the fractal dimensions lie within those observed in previous studies, such as the values reported for Diesel soot by Olfert et al. (2007), ranging from 2.2 to 2.9, or Abegglen et al. (2015), who
- 10 observed values from 1.86 to 2.88 for particulate matter from aircraft turbine exhaust. Our DMA-CPMA measurements reveal a similar mean fractal structure of the different soot types. However, we cannot identify a direct relationship of the fractal dimension to the ice nucleation efficiency of the soot types reported in Fig. 3 above.

Interestingly, the two lamp black soots (LB_OEC and LB_RC) show significantly higher masses for a given mobility diameter compared to the other soots. The higher mass for a selected size of the lamp black soots translates into larger effective

15 densities for these soots, given as median particle mass divided by the equivalent volume of a sphere with this mobility di-

ameter. From our TGA mesurements we can exclude the contribution of secondary material to cause the higher masses of the lamp black soots (see Sect. 3.4). The higher masses for the lamp black soots are more likely caused by larger primary particles making up these aggregates resulting from the wider size distribution of the primary particles. As noted above, the lamp black soots have a rather wide primary particle size distribution, causing the resulting soot aggregates to be composed of primary particles with different masses. This is also reflected in the relatively larger error bars of the lamp black soots in Fig. 4 and further supported by our TEM analysis.

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Figure 5. Exemplary TEM images of representative soot aggregates of the different soot types when selecting 400 nm mobility diameter particles with the DMA.

In general our TEM results reveal large, fractal like aggregates composed of primary particles that form a variety of different micro structures. In Fig. 5 we show exemplary TEM images of the different soot types for 400 nm size selected aggregates (see also SI Fig. S18). Images of both the LB_RC and LB_OEC reveal a range of differently sized primary particles making up the aggregates. This is further supported by the size distribution of primary particles shown in SI Fig. S17, for which a larger number of aggregates and primary particles has been evaluated between 10 to 50 aggregates and a minimum of 122

primary particles have been evaluated for each soot type. From the TEM images depicted in Fig. 5 we further note that the most ice active FW200 soot shows particularly densely clustered aggregates, whereas the other soots exhibit more branched, chain-like aggregates. It should be noted that these TEM images constitute only a 2D projection of the soot aggregates and

can thus not be directly compared with the 3D fractal dimension derived from our CPMA-DMA measurements. We conclude from our TEM analysis that all soot types demonstrate aggregate structures that encompass cavities and pores, which could enable a PCF freezing mechanism. 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

- 5 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. Indeed, a recent study by David et al. (submitted) showed that macroscopic ice can only grow out of cylindrical pores if they are closely spaced. Therefore, it is possible that the enhanced ice nucleation capabilities of FW200 are caused
- 10 by its small spherule size and the associated increased propensity for pores. However, it is important to note that the mCAST brown soot shows a similar spherule size distribution to the FW200 soot, but also a significantly more branched 2D projection of the aggregate and exhibits significantly lower ice nucleation ability compared to FW200 soot. Thus, the observed difference must be related to other physical and chemical properties of the particles, in addition to the morphology, which might be more heterogeneous for the other soot types. Next we discuss the presence of volatile material on the soot particles.

3.4 Temperature dependent mass loss

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Besides carbon, soots usually contain OM which can include compounds with hydrophilic functional groups such as hydroxyls, carbonyls or carboxyls. Heating the soot samples leads to the loss of this OM, depending on the heat resistance of the compounds. A loss in mass encompasses the volatilization of associated OM and/or the thermal decomposition of OM at higher temperatures. The mass loss of the soots as a function of T, measured by TGA, is shown in Fig. 6. Here we focus on the mass decrease within three different temperature regimes (color shading ranges labelled A, B, and C, respectively, in Fig. 6).

Highly volatile compounds, classified as volatile at temperatures below 200 °C, evaporate under inert gas flow (yellow shading region A in Fig. 6). In the range below 100 °C FW200 shows the strongest reduction of mass of approximately 7 %

- 10 (7.5 % and 6.5 % for samples with solid and dashed lines, respectively). We interpret the strong decrease in mass of FW200 to be caused by the loss of adsorbed/condensed water and/or low molecular weight organic substances. The observed mass decrease of approximately 9 %, when drying the FW200 sample for 1000 min at 25 °C by continuous N₂ flushing prior to the DVS measurement, supports the interpretation that the mass loss is due to evaporation of water (see SI Fig. S14). Besides, the mass loss rate is highest below 100 °C, likely due to evaporation of adsorbed water vapor and stays approximately constant
- 15 between 100 °C and 400 °C (see SI Fig. S13). Overall, the strong mass decrease of FW200 below 200 °C may reflect the presence of strongly hydrophilic sites on this sample, where moisture can adsorb. The high affinity of FW200 to adsorb water is further reflected by the DVS experiments (see Sect. 3.5). In contrast, the equivalent mass loss for the mCAST black and the lamp black soots is significantly lower, measured as less than 1 % up to temperatures of 100 °C. A water content of at most 1 % indicates only a limited number of hydrophilic active sites or pores where water can be adsorbed. While most soot
- 20 types show strong mass loss below T = 100 °C the mass of mCAST brown is relatively constant within this temperature



Figure 6. Results of the TGA analysis of the investigated soot types in a nitrogen atmosphere, showing the relative sample mass as a function of sample temperature. Solid and dashed lines indicate the results of two individual TGA runs. Shadings-Indicated regions correspond to different ranges of volatilization, namely adsorbed water and highly heat sensitive material (yellowA), medium heat sensitive material (grayB) and low heat sensitive material (blueC). Pyrolysis is expected to contribute to mass loss at temperatures above the vertical red dashed line.

range but then decreases for temperatures between approximately 140 °C and 200 °C. Up to T = 200 °C the mass loss of the mCAST brown soot is likely associated with highly volatile, low molecular mass polyaromatic hydrocarbons (PAH), that have previously been associated with brown carbon from the miniCAST burner (Mueller et al., 2015) and which have been reported to volatilize between approximately 100 °C and 200 °C (Portet-Koltalo and Machour, 2013). Conversely, the mCAST black samples show a smaller mass reduction, indicating a lower proportion of volatile OM, illustrating the chemical difference to the mCAST brown sample. The increased OM content on brown carbon results from a reduced combustion temperature and a less complete combustion compared to mCAST black as a consequence of an increased amount of N₂ premixed to the fuel for this test point (see Appendix B). This supports the interpretation from above that the mass loss observed for mCAST brown is mainly due to OM and not due to sorbed water vapor, which above T = 100 °C should have already been desorbed. The lack

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30 of sorbed water also suggests that the OM is likely hydrophobic in nature. Considering our ice nucleation results reported in Fig. 3, the shift of the onset of mCAST brown to higher supersaturation compared to the mCAST black (and the other soots) suggests that these hydrophobic hydrocarbons suppress the freezing abilities of the soot. This interpretation is in agreement with the results from Crawford et al. (2011) and Möhler et al. (2005b) who find freezing for propane soots with higher organic carbon content required higher supersaturation for ice nucleation.

- The FS sample demonstrates a strong mass loss above $350 \,^{\circ}$ C, indicating a relatively large abundance of material with medium volatility compared to the other soots. While some portion of this mass loss is attributable to OM with medium volatility (see Fig. 5), it is likely that thermal decomposition in the form of pyrolysis also contributes to mass loss (Bredin et al., 2011; Song and Peng, 2010). Besides, we cannot exclude combustion of carbon in the presence of trace amounts of oxygen (trapped within the sample, instrument parts or from gas impurities), which has been shown to contribute to mass loss between 430 650
- ⁵ °C, even for N_2 prepurged samples. Bredin et al. (2011) found combustion (in the presence of oxygen) contributing to a mass change of a Printex U soot (gas black) in TGA measurements performed in a N_2 atmosphere. They reported combustion starting around 400 °C and reaching a maximum rate around approximately 500 °C, similar to the behavior of our FS soot. In conclusion, both pyrolysis and combustion can occur in this temperature range, depending on the presence of O_2 in the reaction chamber. The consistent mass loss in this temperature range for both independent TGA runs with FS (solid and dashed line),
- 10 combined with the negligible mass loss of the lamp blacks and the mCAST black in this temperature range, suggests that most of the mass loss is caused by the evaporation of low-medium volatility OM. For mCAST brown, this likely includes larger, higher molecular weight PAHs which have been reported to volatilize between approximately 125 °C and 670 °C (Wang et al., 2012). If the observed mass loss of the FS aggregates was due to water-soluble material, this material could take up water and lead to the formation of aqueous solution droplets which subsequently freeze homogeneously. This process could
- 15 account for the freezing reported in Fig. 2, however the lack of any change in the slope in the AF curves of FS at homogeneous freezing conditions (see SI Fig. S16) S10) similar to the change in slope of the AF curves observed for homogeneous freezing of ammonium nitrate (see SI Fig. S16), render this interpretation unlikely.

Around 400 °C the organic fraction should be completely vaporized and desorbed (Stratakis and Stamatelos, 2003). Thus soot samples which exhibit a strong mass loss beyond this temperature, namely FS, FW200, mCAST brown and to some extent also mCAST black, undergo continuous pyrolysis or contain inorganic heat sensitive material.

Altogether, TGA analysis confirms that mCAST black and the lamp blacks can be considered as pure carbons, with minimal impurities in the form of OM, while it illustrates the presence of organic material on the mCAST brown and on the FS. Overall the only sample that shows a significant mass loss for T < 100 °C (likely adsorbed or condensed water) is FW200, which corroborates its high ice nucleation ability compared to all the soot samples investigated.

25 3.5 The role of soot-water vapor interaction

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An important parameter for the ice nucleation ability of the different soot types is their potential to take up water (Dubinin, 1980). The water uptake capacity is controlled by both the soot morphology (surface area and microstructure, Dubinin and Stoeckli, 1980) and the chemical composition, i.e. the availability of soluble material on the soot surface and/or the presence of hydrophilic functional groups, such as carboxyl, carbonyl and hydroxyl groups (Ferry et al., 2002). We used DVS to measure

30 the water vapor sorption and desorption isotherms of the soots, allowing to infer of the particle porosity and hydrophilicity at the same time. Figure 7 shows an overview of the water uptake of the different soots, measured by DVS at T = 298 K and covering the range of 0-98 % RH_w . The water uptake is calculated from gravimetric data, expressed in percent as relative mass change difference between the initial dry mass and the quasi-equilibrated, moist sample mass at the probed RH (Fig. 7a), and



Figure 7. Water uptake (solid lines, filled symbols) and loss (dashed lines, open symbols) isotherms, given as (a) relative sample mass change and (b) equivalent water monolayers, as a function of RH_w , as measured by DVS at T = 298 K. Each set of curves corresponds to an individual, independent soot sample. The data points represent water uptake/loss at quasi-equilibrated RH_w conditions. Each soot type was probed for two independent experiments in the DVS and the curves of the two independent runs lie on top of each other. Exceptions are the mCAST samples, which were only probed once in the DVS. Curves are linear interpolations between quasi-equilibrated sample points to guide the eye. The curves of the LB_OEC and LB_RC samples lie on top of each other in panel (a). All experiments were performed to a maximum RH_w of 98 %, with the exception of one FW200 sample showing a maximum relative mass change of approximately 30 %, which was only probed up to $RH_w = 95$ %.

expressed in terms of equivalent adsorbed water monolayers (Fig. 7b). We use the term *water uptake* to encompass both effects of adsorption and absorption. Adsorption describes the enrichment of water molecules on the solid soot surface through binding of water molecules to hydrophilic sites and the formation of water molecule clusters or equivalent monolayers. Absorption, on the other hand, refers to water molecules dissolving into soluble material associated with the particles (Popovicheva et al., 2008; Thommes et al., 2015). In Fig. 7, water uptake curves are shown by solid lines along with filled symbols, whereas

5 water loss curves are shown by dashed lines and open symbols. Each set of (uptake/loss) curves corresponds to an individual,

independent experiment, using a fresh sample of the corresponding soot type.

The uptake curves of FW200 soot rise strongly at low RH ($RH_w \le 20$ %), exhibiting a convex shape, followed by a a slow rise at intermediate RH ($20 \% \le RH_w \le 80 \%$), and a sharp increase in water mass taken up at high RH ($\ge 80 \%$), typical for a type IV(a) isotherm (following classification recommendations according to IUPAC, see Sing et al., 1985; Thommes et al., 2015). In the FW200 aggregates water is initially taken up by *equivalent* monolayer adsorption on the soot surface (see Fig.

- 5 7b). The increase in mass at higher *RH* marks the transition to multilayer adsorption followed by the transition to capillary (pore) condensation at *RH*_w ≥ 89 %, signified by the sudden rise in mass. This is particularly clear from the FW200 sample probed until a maximum value of *RH*_w = 98 % (water uptake curve with maximum mass change Δm_{max} ≈ 70 % in Fig. 7a). Due to the strong mass increase of the FW200 soot when probed until *RH*_w = 98 % and the long time scales required to equilibrate the sample at these high *RH* (around 800 min) we restricted further measurements of FW200 to *RH*_w = 95
- 10 %. However, all other soots were tested up to $RH_w = 98$ %. We attribute this strong water uptake at high RH_w to mesopores (2-50 nm, IUPAC, Thommes et al., 2015) formed by inter-particle cavities of the soot aggregates which create the porous structure of soot already discussed above (see Sect. 3.3). The high water affinity of FW200 revealed by the DVS measurements is consistent with the observed ice nucleation at relatively low ice supersaturations. We interpret this as a low soot-water contact angle for this sample. Besides, the availability of mesopores inferred from DVS supports our hypothesis that the mechanism
- 15 of ice formation on the FW200 soot is indeed PCF. The steep AF curves of FW200 compared to the other soots, as discussed in Sect. 3.2, this can be thought of as an overlap of pore size distribution and associated contact angle distribution that favours condensing water in pores, resulting in particles with properties suitable to nucleate ice via PCF, whereas those soot types with less steep AF curves indicate a more heterogeneous distribution of particle properties (contact angles and pore sizes).
- This further corroborates our discussion above that the mass loss of FW200 observed in the TGA at temperatures $T \le 100$ °C is associated with desorbing water. Water uptake by OM could also contribute to the mass increase observed in our DVS experiments. Taking citric acid (CA) and glutaric acid (GA) as surrogates for typical atmospheric organics and using the mass growth factors reported in Zardini et al. (2008), we find a mass fraction of 13.6 % (CA) and 20 % (GA), respectively, to be required to explain the observed mass change of almost 30 % at $RH_w = 95$ %. However, our TGA results only indicate a mass change of approximately 8 % and 10 % at the boiling points of CA (310 °C) and GA (200 °C, see Fig. 6). Thus, we
- 25 confidently 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. The water uptake on FW200 is associated with a hysteresis as the water uptake and loss curves do not overlap over the complete *RH* range. The presence of a hysteresis loop further indicates that the mechanism of water uptake cannot be attributed to absorption by hygroscopic OM, but is indeed caused by the availability of pores and capillary condensation. The form of the
- 30 hysteresis loop can be used to infer information on the pore structure. For the FW200 sample probed until a maximum RH of $RH_w = 98$ % the hysteresis looks like a H3-type hysteresis loop that is relatively narrow, where adsorption and desorption curves are almost parallel (Thommes et al., 2015), but associated with a very steep desorption branch. In contrast, the FW200 sample probed until $RH_w = 95$ % ($\Delta m_{max} \approx 30$ % in Fig. 7a) resembles an H4-type hysteresis with a shallow hysteresis loop, observed for aggregated, non-rigid particles such as mesoporous soots (Thommes et al., 2015). Contrary to typical H3

- or H4-type hysteresis loops, the FW200 soot shows hysteresis down to very low RH_w , reflecting that either micropores are developed or present to some extent on FW200 or that some water vapor is taken up through chemisorption on active sites of the OM. While most of the hysteresis values of the FW200 soot lie within the DVS uncertainty of approximately $\Delta m = 0.75$ %, micropore filling is supported by the values of the *C* constant in the classical BET equation, describing the adsorbate-adsorbent interaction strength. The *C*-value of FW200 was found to be > 650 (see Table A1), indicating filling of narrow micropores
- 5 (Thommes et al., 2015). The shape of the hysteresis loop indicates involvement of mainly conical and slit-like pores as the majority of the water is lost already at high RH_w . Pores with narrow necks, so-called ink-bottle shaped pores, which remain filled during desorption until low RH (Kittaka et al., 2011), would cause a much stronger hysteresis at lower RH_w and are thus likely absent. This is consistent with the different hysteresis types, namely H3 and H4, associated with the FW200 probed up to different maximal RH_w . The H3 hysteresis loop indicates *narrow* slit-like pores formed through sintering of carbon spherules.
- 10 The H4 hysteresis includes also (normal) slit like pores formed in between spherules that are not adjacent (but positioned along different branches of the soot aggregate, see Fig. 5). From these observations we conclude that particle morphology and contact angle determine the water uptake by soot particles, confirming a PCF mechanism for the observed ice nucleation on FW200. This interpretation is also consistent with the observed ice nucleation onsets reported in Fig. 2. Therefore, our interpretation that the mass loss of FW200 during the TGA analysis is consistent with the evaporation of adsorbed water vapor and that
- 15 the ice nucleation proceeds via a PCF mechanism can further explain the difference in freezing behavior between FW200 and the *hygroscopic* soot tested by Koehler et al. (2009). Their Aircraft Engine Combustor soot showed freezing only close to homogeneous freezing conditions for T = 233 K and 221.5 K, both for testing $d_m = 250$ nm and polydisperse aerosol. Our ice nucleation results for FW200 reveal that the conditions for 1 % of the particles being activated in the cirrus regime are met at roughly the same *RH* across all temperatures, for a given aerosol particle size. The constant onset S_i indicates that the freezing
- is in fact determined by pore size and soot-water contact angle, which determine water filling of the pores and subsequent homogeneous freezing, rather than the bulk aggregate size. The different onsets reported for the different particle sizes (see SI Fig. S1) suggest that the pore size distribution is a function of the overall soot aggregate size and the associated number density of spherules, forming these cavities (see Fig. 5). An exception are the results of at T = 233 K, where the nucleation rate is likely possibly too small for the volume of the pore water to freeze within the 16 s residence time of the particles in HINC
- 25 (David et al., submitted). This causes the significant increase in S_i required for ice to to nucleate via homogeneous freezing of bulk solution droplets, as can most clearly be seen for both 300 nm and 400 nm particles of the FW200 soot, depicted in Fig. 2c and d, respectively.

The isotherms of both lamp black soots, LB_OEC and LB_RC, resemble a type-III isotherm. Taking the (specific N_2) surface area into account, the isotherms are characterized by a small amount of sorbed water vapor at (nearly) saturated conditions of

30 approximately an equivalent monolayer coverage (see Fig. 7b). Such a weak interaction of the water molecules with the soot is also reflected in our ice nucleation results, where we only observe a modest freezing ability on these soots, below S_i conditions of homogeneous freezing of solution droplets. This suggest a more hydrophobic character, i.e. a high soot-water contact angle, and/or limited availability of pores of the correct size, which would inhibit pore-filling well below water saturation conditions (David et al., in prep.). The lower affinity to water as compared to FW200 indicates a higher soot-water contact angle and is

- 35 further supported by the relatively lower values of the C parameter (see Table A1). Furthermore, our TGA experiments indicate that these samples are mainly composed of pure carbon, so we can exclude absorption of water by OM for these soots. This is further supported by the absence of a steep increase in AF at the homogeneous freezing line, indicating a lack in the formation of solution droplets, which has been observed (e.g. by Koehler et al., 2009). However, care must be taken when comparing equivalent monolayer coverages, as they neglect the effect of water being taken up in patches into the porous structure of
- 5 the soot aggregates. Our DVS runs reveal a slight hysteresis of the lamp black soots (see Fig. 7b) suggesting the presence of some mesopores, but again lie within the uncertainty of approximately $\Delta m = 0.75$ %. The availability of some slit-like pores was also inferred from TEM images (SI Fig. S18). At the same time our TEM images reveal that both lamp black soots have significantly broader primary particle size distributions with overall larger mean spherules compared to e.g. FW200 as discussed above (see Sect. 3.3). Thus, for a given mobility diameter selected in the DMA, lamp black aggregates are composed
- 10 of fewer spherules and thus likely contain less cavities formed by sintered spherules compared to soots with smaller spherules, lowering the probability that a sufficient number of pores of the right size (and contact angle) are present (David et al., in prep.). The presence of some mesopores is further supported by the shape of the water uptake curves of LB_OEC and LB_RC, which both show a non-linear increase for $RH_w \ge 90$ %, related to capillary condensation. Thus, we believe that the ice formation associated with LB_OEC and LB_RC is indeed caused by a PCF mechanism, but that the more hydrophobic character of these
- 15 soots (higher water-soot contact angles) decreases the efficiency of this process compared with the more hydrophilic FW200. This interpretation is consistent with the slightly larger water uptake of the LB_RC compared to the LB_OEC (see Fig. 7b), resulting in a slightly better ice nucleation ability of the LB_RC compared to the LB_OEC (see Fig. 3). The water uptake of the FS sample is roughly six times larger than that of the lamp black samples at the highest *RH*, but

does not show a strong increase at RH > 80 %(see Fig. 7a). We believe that this reduced water uptake of the FS is caused by a lack of mesopores and a prevalence of narrow micropores, which take up water as observed by the mass increase at relatively low RH_w . Micropore water uptake has been reported for fullerenes (Hantal et al., 2010) and is further supported by the absence of any hysteresis of the desorption isotherm. Additionally, the presence of micropores on the FS is also supported by the rather large surface area compared to the lamp blacks (see Table A1) and is consistent with Ferry et al. (2002), who

found liquid water to exist in micropores of soot particles produced by a kerosene burner down to temperatures of T = 200

- 25 K. Also the value of the C constant in the classical BET equation, describing the adsorbate-adsorbent interaction strength, was found to be C = 478 (see Table A1). Such a high value of C is usually associated with narrow micropores (Thommes et al., 2015). Nonetheless, water within micropores is not able to nucleate ice via the PCF mechanism, as these pores are too small to allow formation of a critical ice embryo (e.g. Marcolli, 2014). The absence of any sharp increase along the water uptake isotherm of FS at high RH_w further suggests that the mass loss during TGA cannot be associated with hygroscopic
- 30 material responsible for water sorption, as a similar (non linear) increase in water mass would be expected for OM (e.g. Zardini et al., 2008). Altogether, the ice nucleation mechanism of FS remains inconclusive and requires further studies since the results from TGA and DVS do not give a consistent picture favoring either PCF or homogeneous freezing of solution droplets as the prevailing mechanism for the observed ice nucleation activity of this soot in the cirrus regime. Finally, the water sorption isotherms for the miniCAST samples reveal their general hydrophobic character, consistent with our ice nucleation

results. In particular, it is worthwhile to note that the mCAST brown shows a reduced water uptake capacity compared to the mCAST black. This supports our hypothesis from above, that the OM associated with mCAST brown is water-insoluble,

- 5 suppressing the ice nucleation activity possibly by filling the mesopores thus blocking water uptake in them. The larger water uptake of the mCAST black compared to the lamp blacks could result from a larger number of mesopores on the mCAST black aggregates, which are generally composed of more and smaller primary particles compared to the lamp blacks. This is consistent with the slightly larger hysteresis observed for the mCAST black sample compared to the lamp blacks. Mesopores are indeed present on most tested samples (with the exception of FS), as can be inferred from the DVS experiments and are
- 10 consistent with ice nucleation below homogeneous freezing conditions of solution droplets for large enough soot aggregates (see Fig. 3). Combining our ice nucleation results with data obtained from TGA and DVS, we confidently identify PCF as the dominant mechanism to cause the freezing of the tested sootssoot particles. Nevertheless, FW200 is the only sample out of the six probed soots that shows significant ice nucleation well below conditions for homogeneous freezing of solutions. Thus, the presence of pores (mechanical active sites) is insufficient for PCF, but the sites need to have a hydrophilic character in the
- 15 form of hydrophilic surface functional groups to initiate interaction of the soot surface with water vapor within a pore, i.e. a sufficiently low contact angle (David et al., in prep.).

4 Atmospheric implications

Our results are direct evidence that bare, large hydrophilic soot aggregates can nucleate ice via PCF. To what extent our results are transferable to atmospheric soot is discussed here. The absence of freezing below water saturation for T > 233 K suggests

20 that the impact of soot on ice nucleation in MPCs is negligible, at least for unprocessed soot particles. For temperatures above 233 K our results show activation only above water saturation, indicating droplet formation for all of the soot types and sizes tested, confirming the results of Friedman et al. (2011), who found no heterogeneous ice formation at water subsaturated conditions at 233 K.

Our ice nucleation measurements of 400 nm size selected particles demonstrate that soot particles can nucleate ice in the cirrus

- regime, below RH for the homogeneous freezing of solution droplets, if the particles have the required physicochemical properties. Specifically, our DVS results reveal that both pore structure size distribution and contact angle distribution determine the ice nucleation ability of the soots soot particles studied. In the case of extremely hydrophobic soot (very high soot-water contact angles), such as mCAST brown, the lack of ice nucleation below homogeneous freezing conditions of solution droplets, even for the largest particle sizes tested here, suggests that such soot does not play a role in atmospheric ice nucleation, at least for
- 30 the cirrus temperatures covered by our experiments. However, slightly less hydrophobic soot (lamp blacks), still characterized by high soot-water contact angles, can promote ice nucleation heterogeneouosly for $d_m \ge 200$ nm. This limits the relevance of the majority of freshly emitted soots for atmospheric ice nucleation at cirrus conditions, which are generally believed to be hydrophobic. In contrast, hydrophilic soot (FW200) has the capability to act as effective INP ($AF > 10^{-3}$ for $RH_w \approx 80$ %, see SI Fig. S1h) even at sizes $d_m > 100$ nm, making it potentially important for the anthropogenic forcing on global climate. Nevertheless, most of the combustion aerosols emitted into the atmosphere have significantly smaller diameters usually

below 100 nm (e.g. Rose et al., 2006; Kim et al., 2001; Moore et al., 2017) and can represent more complex internal mixtures. 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

- 5 they are mixed with soluble material. internally mixed with other ice active material. Thus, the role of bare small soot particles would be limited to a condensation sink for semivolatile water-soluble species. This finding is important for instance for the fate of soot particles associated with aviation emissions in the atmosphere (Kärcher, 2018) from aviation emissions, which are generally found to be even smaller than 100 nm in diameter (Moore et al., 2017; Yu et al., 2017). Thus, the role of bare small soot particles would be limited to a condensation sink for semivolatile water-soluble species. However, Such particles are
- 10 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 for larger soot aggregates up to 1 µm in diameter in the atmosphere (Posfai et al., 2003; Chakrabarty et al., 2014), mainly sourced from biomass burning
- 15 and wildfires. At the same time such solid fuels can also produce ash particles, which can also contribute to ice formation (Umo et al., 2015; Grawe et al., 2016, 2018). In addition, atmospheric aerosol particles have been reported to contain large black carbon inclusions (up to 1 μm in diameter, Moffet et al., 2016). In regions of the atmosphere where these large soot particles are found, with the required physicochemical properties, these soot particles will be able to nucleate ice similar to the 400 nm particles discussed here. Finally, the results reported here only encompass soot particles that activate within the residence
- 20 time of HINC ($\tau \approx 16$ s) and within a single cloud cycle. 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. At the same time, the atmospheric life time of soot is around 5 - 7 days (Jiao et al., 2014; Reddy and Boucher, 2007). During this time the
- 25 soot aggregates undergo atmospheric processing, for instance in the form of multiple cloud formation cyclesencompassing 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, e.g. Wei et al., 2017). Of particular interest here is the cloud processing of soot particles, i.e. the change in
- 30 physicochemical properties as the particles are involved in cloud microphysical processes such as cloud droplet or ice crystal formation. In case of ice nucleation via a PCF mechanism, pore ice can remain trapped within the cavities between the cloud cycles, thus particles could (microscopic pore ice) between subsequent cloud cycles for certain conditions of *T* and *RH*, even though the macroscopic ice crystal is sublimated. For instance, an ice crystal formed on a soot particle leaving the cloud will experience an ice subsaturated environment and thus sublimate. However, given that *RH* conditions outside the cloud are high enough (at *T* < 273 K), the ice within the pores can survive, due to the reduced saturation vapor pressure of ice within the cavity. This pore ice can then grow into macroscopic ice erystals, as soon as the *RH*₁ > 100 in subsequent cloud cycles when

 $RH_{i} = 100$ % is exceeded. Such a pre-activation effect has been discussed before (D' Albe, 1949; Fukuta, 1966; Mossop,

- 5 1956; Marcolli, 2016) and should be addressed in future work, as this may have implications for the enhanced freezing ability of soots in both the cirrus and MPC temperature regime. Moreover, the wettability (contact angle) of soot particles can increase (decrease), as these particles undergo atmospheric processing. Even though the more hydrophobic soots tested here reveal only a weak ability to nucleate ice via PCF below homogeneous freezing conditions, this likely changes during atmospheric processing and subsequent cloud cycles, with significant implications for the role of soot in atmospheric ice nucleation. It is
- 10 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
- 15 abilities. Certainly, atmospheric soot particles can be more complex than the particle types investigated here. At the same time laboratory studies are needed to provide a more fundamental understanding of the properties relevant for ice nucleation.

5 Conclusions

The ice nucleation ability of a variety of soot types has been systematically evaluated in controlled laboratory measurements. The soot types investigated cover a wide range of physicochemical properties as proxies of atmospheric soot particles, including

- 20 different commercially available black carbons such as gas blacks (FW200), lamp blacks (LB_RC and LB_OEC) and fullerene soots (FS), as well as propane flame soot with different OM content derived from a miniCAST burner (mCAST black and mCAST brown). Ice nucleation was probed on dry, size selected aerosol particles, for four different sizes of 100, 200, 300 and 400 nm (mobility diameter), covering a temperature range between 253 and 218 K, using HINC. Ice nucleation activity was investigated in relation to particle morphology deduced from TEM and coupled DMA-CPMA measurements, temperature
- 25 dependent mass loss obtained from TGA analysis, as well as water vapor uptake capacity derived from DVS experiments. The results discussed in this paper show that soot particles can contribute to ice formation below homogeneous freezing conditions of solution droplets only if particle diameters exceed $d_m > 100$ nm. One distinct finding of our work is that there is a marked dependence on the HNT for all of the investigated soot types. In the MPC temperature regime no ice nucleation was observed below water saturation, while for some of the probed soots soot samples ice nucleation was observed below
- 30 *RH* the RH required for homogeneous freezing of solution droplets in the cirrus regime. This strongly suggests a dependence on liquid water for ice nucleation. The absence of heterogeneous freezing in the MPC regime below water saturation suggests that deposition nucleation does not take place on the tested particles. While water can be taken up into the pores of the soot aggregates also at MPC conditions, the absence of any ice formation below water saturation indicates that there is a lack of active sites that could trigger heterogeneous ice nucleation at these temperatures. The observed ice nucleation in the cirrus regime could theoretically be caused through a (surface area dependent) deposition nucleation mechanism. However, the strong dependence of the ice nucleation efficiency on the HNT implies that it is the liquid water within the soot pores that

freezes homogeneously, since particle properties considered relevant for deposition nucleation (if present) should be available

- 5 for ice nucleation in both the cirrus and MPC regime. Such a dependence on the HNT relevant for liquid water freezing for ice nucleation onto soot particles investigated here . We is in-line with a PCF process and in contrast to classical deposition nucleation, where the liquid water phase is absent. Overall, we conclude that the ice formation process on the soots is best described by a PCF mechanism and an absence of not deposition nucleation. Auxiliary measurements performed along with our ice nucleation experiments indicate that physical and chemical properties of combustion aerosol varied markedly and
- 10 influenced the ice nucleation ability of the particles. The TEM results revealed the presence of cavities and pores on all soot types investigated. Nevertheless, the pore number density likely depends on primary soot spherule size. More importantly, the potential of pores to take up water through capillary condensation strongly depends on their size and the soot-water contact angle, i.e. the hydrophilicity of the soot, as revealed by our TGA and DVS measurements. The presence of hydrophobic matter on the soot aggregates impedes ice nucleation probably due to blocking of pores. Our TGA, however, is limited to an overall
- 15 assessment of the presence of heat sensitive matter and conclusions about the chemical nature of this material is not possible and should be investigated in future studies. In addition, the water affinity obtained from the DVS measurements alone cannot be used to draw direct conclusions about the ice nucleation efficiency and/or freezing mechanism, but has to be related to surface area and spherule size. Our TEM evaluation indicates that spherule size influences the availability of pores. Future studies should focus on how atmospheric processes change the hydrophilicity (contact angle) of a given aggregate and spherule size in order to further our understanding of the interplay between pore size and number density and contact angle.

A1 BET surface area

Particle surface area was determined with the Autosorb-1MP surface area analyzer (Quantachrome, Odelzhausen, Germany)

5 by N₂ adsorption using the BET method. Specific surface area values were determined from the linear BET plot of the N₂ isotherm up to $p/p^{\circ} \approx 0.28$, where p is the equilirbium pressure and p° denotes the saturation vapor pressure, assuming a N₂ molecular cross sectional area of $\sigma_{N2} = 16.2$ Å², and a minimum of three adsorption points, using the linear form of the BET equation (Thommes et al., 2015):

$$\frac{p/p^{\circ}}{n(1-p/p^{\circ})} = \frac{C-1}{n_m C} (p/p^{\circ}) + \frac{1}{n_m C},$$
(A1)

- 10 where *n* is the total amount of nitrogen adsorbed on the particle system and n_m is the specific monolayer capacity. The constant *C*, reported in Table A1 for the investigated soots, gives information about the shape of the isotherm (Gregg and Sing, 1982; Thommes et al., 2015). N₂ adsorption was conducted at the temperature of liquid N₂ (\approx 77 K). The primary factor determining the specific surface area is the primary particle size, with smaller primary particle sizes resulting in higher specific surface areas. Prior to determination of specific surface areas, soot samples were outgassed and dried in a desiccator. First, soot samples where
- 15 outgassed at 323 K until pressure dropped below 300 mbar. Temperature was subsequently increased step-wise to 353 K and the samples were dried for a period of 15 h at this temperature, under nearly vacuum conditions, before the surface area was determined.

Table A1. Detailed results of the specific surface area measurements for the soot samples as determined by N₂ adsorption following the BET-method. All specific surface area values, $a_{BET,N2}$, are given in units of $[m^2/g]$. The mean values are reported in Table 1. Besides, we report the values of the *C* parameter used in Eq. A1 for the two independent experiments labeled #1 and #2, respectively.

	$a_{BET,N2}$ (#1)	C (#1)	$a_{BET,N2}$ (#2)	C (# <mark>1</mark> 2)
FW200	524.3	896.3	528.2	650.9
LB_OEC	24.8	132.8	22.5	218.5
FS	271.6	455.8	258.3	500.0
LB_RC	23.2	135.3	22.8	181.4
mCAST black	121.0	118.3	118.8	115.1
mCAST brown	127.6	59.9	122.9	50.4

A2 Temperature dependent mass loss: Thermogravimetric analysis

The temperature dependent mass loss of the soot samples was determined using a thermogravimetric analysis. Soot powder was deposited into a platinum crucible and subsequently exposed to three different temperature stages in a Thermogravimetric Analyzer. For the miniCAST samples, not available in powder form, soot was collected on 47 diameter quartz fiber filters (Tissuquartz Filters, Type 2500QAT-UP, Pall Inc.), using a 47 aluminum in-line filter holder. The filter holder was mounted at a distance of 10 downstream of the miniCAST exhaust pipe, using an air-cooled stainless-steel pipe. Soot aerosols were then carefully removed from the filter with a metal spatula prior to TGA analysis. During thermogravimetric analysis, mass changes are continuously monitored while the heating program reported in Table A2 was applied to all samples. Time, sample

- 5 weight, temperature and gas flows are continuously recorded during the heating program. For TGA analysis performed within this work, a sample purge flow of 30 mLmin⁻¹ and a balance purge flow of 40 mLmin⁻¹ was used. N₂ was used for both flows so that the sample only reacts to temperature due to thermal decomposition. For every experiment an equilibration time of approximately 1-2 min was used before starting the TGA program. This is done in order to allow the (sample-) pan to come to complete rest, as any swing movement of the pan can cause inaccurate mass measurements (Lapuerta et al., 2007).
- 10 Lapuerta et al. (2007) reported a non-linear increase in loss of material with increasing heating rates, but found the difference to be below 10 % when heating rates were constrained to a maximum of 20 °Cmin⁻¹. Hence, our samples should not be affected, by using the maximum heating rate of 20 °Cmin⁻¹ (see Table A2).

Table A2. Heating program used for thermogravimetric analysis of soots in a pure N_2 atmosphere.

Step	Specification
1	Isothermal at $T = 30$ °Cmin ⁻¹ for 5 min
2	Ramp 15 °Cmin ⁻¹ to $T = 350$ °C
3	Isothermal at $T = 350 \ ^{\circ}\text{C}$ for 30 min
4	Ramp 15 °Cmin ⁻¹ to $T = 650$ °C
5	Isothermal at $T = 650$ °C for 15 min
6	Ramp 20 $^{\circ}$ Cmin ⁻¹ to $T = 1000 ~^{\circ}$ C
7	Isothermal at $T = 1000$ °C for 10 min
8	Ramp 30 $^{\circ}$ Cmin ⁻¹ to $T = 30 ~^{\circ}$ C

A3 Water uptake and loss: Dynamic Vapor Sorption

During DVS experiments, the sample is constantly weighed (against a reference) as the sample is exposed to changing *RH*15 in so-called *RH*_w-scans. Samples in powder form are placed in a metal pan to prevent static electrical loading and the total gas flow (H₂O and N₂) was held at a constant flow rate of 200 smLmin⁻¹ throughout the experiment. *RH*_w is automatically scanned in predefined steps and the sample mass at quasi-equilibrium conditions is measured whenever the temporal change in sample weight falls below a defined threshold. Since a *constant* mass is not reached during DVS, we refer to these conditions as *quasi*-equilibrium. The time needed to reach quasi-equilibrium conditions is dependent on the slow water adsorption kinetics

20 (Popovitcheva et al., 2000) and is proportional to the surface area available for uptake. Here we considered a mass change rate

 ML_{100} °C ML_{150} °C ML_{200} °C ML_{250} °C ML_{300} °C ML_{350} °C ML_{650} °C ML_{950} °C LB OEC 0.10 0.16 0.25 0.36 0.44 0.53 0.68 0.97 3.97 FS 2.27 2.60 2.92 3.24 22.95 33.37 1.85 FW200 8.04 6.88 7.64 8.52 9.35 10.67 22.66 31.43 LB_RC 0.090 0.16 0.24 0.41 0.57 0.75 0.93 2.80 0.94 1.34 mCAST black 1.18 1.44 1.48 1.48 5.27 15.62 mCAST brown 0.55 1.61 3.39 5.71 7.52 10.25 15.68 18.58

Table A3. Relative mass loss as determined by TGA analysis in a pure N_2 atmosphere. Mass loss (ML) for soot samples is expressed as cumulative, relative weight loss at a given reference temperature, and are given as percentage mass loss from initial weight. Reported values indicate mean values of two TGA experiments performed for a given soot type.

at/or below 0.0005 %min⁻¹ to correspond to quasi-equilibrium conditions, for an approximate sample weight of 10 mg. Each soot sample was dried at 298 K for a period of 1000 min prior to the measurement of a sorption isotherm, in order to remove any sorbed water vapor, by flushing the soot samples with only N₂ at atmospheric pressure. DVS runs were performed at T = 298 K. Mass change was monitored in intervals of 5 % for 0 % $< RH_w < 30$ %, at 40 %, 60 % and 80 % in the medium RH_w range and in steps of 3 % between 80 % and 98 % to investigate the presence of mesopores. Note that the FW200 was only probed in intervals of 20 % below $RH_w = 80$ %. Each soot type was probed for two independent experiments in the DVS and good agreement was found. Exceptions are the mCAST samples, which were only probed once in the DVS. The desorption was probed at the same RH_w values so that a hysteresis could be derived. Similar to the TGA, no out gassing at

A4 Soot aggregate morphology and effective density: DMA-CPMA measurements

elevated temperature or high vacuum was performed, in order to preserve the original surface properties.

5

- 10 The Centrifugal Particle Mass Analyser uses two nested, rotating, charged metal cylinders between which injected particles can be selected based on mass. The two opposing electric and centrifugal forces, arising from the potential difference and the rotation, respectively, are used to classify particles by mass to electrical charge ratio (m/q). Details on its operation may be found in Olfert and Collings (2005). In conjunction with a DMA, density and mass mobility exponent $(D_{\rm fm})$ of aerosol particles can be determined. For this purpose, DMA-CPMA are coupled in series in such a way that aerosol particles are first sent into
- 15 the DMA, classifying the particles by electrical mobility (selecting by drag:charge), resulting in a narrow size distribution. It should be noted that this distribution contains predominantly singly charged particles of the mobility diameter chosen, but is not perfectly monodisperse, with some fraction of larger, multiply charged particles also being present (see SI Fig. S15). The particles are subsequently passed through the CPMA, selecting monodisperse aerosol by mass to charge, and counted by a CPC (Model 3776, TSI Inc.) downstream of the CPMA, operated at a flow rate of 0.3 Lmin⁻¹, yielding the number concentration of size and mass selected aerosol. For a given mobility size, the CPMA is operated in scanning mode, measuring the number

Table A4. Mass-mobility pre-factor, C, and fractal dimension, D_{fm} , derived from power-law fits of the form of Eq. (A4) to mass-mobility data shown in Fig. 4a. A D_{fm} value of 1 corresponds to a straight chain-like structure, whereas $D_{fm} = 3$ indicates a compact sphere like structure. The value in brackets indicates the standard error.

$C [\mathrm{kgm}^{-\mathrm{D}_{\mathrm{fm}}}]$	$D_{\rm fm}$ [-]
0.02 (0.2)	2.35 (0.07)
0.17 (0.19)	2.50 (0.07)
3.65 (4.6)	2.64 (0.09)
0.07 (0.12)	2.38 (0.13)
$0.01 (3.8e^{-6})$	1.86 (0.05)
0.01 (0.01)	2.31 (0.07)
	$C [kgm^{-D_{fm}}]$ 0.02 (0.2) 0.17 (0.19) 3.65 (4.6) 0.07 (0.12) 0.01 (3.8e^{-6}) 0.01 (0.01)

concentration of particles at discrete mass set points. Due to the fractal like morphology of soot aggregates a range of different masses can correspond with a selected mobility diameter, such that soot particles with a more uniform morphology would have a narrower mass distribution (Dickau et al., 2016). The DMA-CPMA output function can be used to derive aerosol properties,

5 such as the fractal dimension and the effective density. The effective density (ρ_{eff} , e.g. Dickau et al., 2016; Olfert et al., 2017; Abegglen et al., 2015) is defined as the density particles would have if they were spherical, i.e. by the ratio of particle mass to particle spherical equivalent volume based on the selected mobility diameter in the DMA, $d_{\rm m}$, given by (McMurry et al., 2002):

$$\rho_{eff} = \frac{6}{\pi} \frac{m_p}{d_{\rm m}^3}.\tag{A2}$$

10 Here, m_p denotes the median mass obtained by fitting the mean mass spectral number density distribution from the CPMA scan of the DMA-classified particles with a log normal distribution. Typically ρ_{eff} is expressed as a power law fit of the form:

$$\rho_{eff} = C d_{\rm m}^{(D_{\rm fm}-3)},\tag{A3}$$

where $D_{\rm fm}$ is the mass-mobility exponent and C is a constant pre-factor with units of kgm^{-D_{fm}}. The fractal dimension $D_{\rm fm}$ is a useful quantity to describe aerosol properties. $D_{\rm fm}$ can be inferred from the power-law relationships relating particle mobility 15 and mass (Schmidt-Ott, 1988; Schmidt-Ott et al., 1990):

$$m_p = C d_{\rm m}^{D_{\rm im}},\tag{A4}$$

where C is a constant called the mass-mobility pre-factor. Here, the fractal dimension of the soot particles was obtained by performing a least-square fit, using a power-law relationship of the form of Eq. (A4) applied to the mass-mobility data, where the median mass was used.

20 Appendix B: miniCAST

Within the miniCAST, the combustion process is interrupted by quenching the flame with N_2 . While the quenching of the flame within the burner takes place at a fixed height, the flame size can be varied by changing the absolute flow of fuel gas and oxidation air, holding the C:O ratio, i.e. the flame chemistry constant. At the same time, changing the ratio of the fuel gas and the oxidation air, or premixing the fuel gas with N_2 allows for a controlled adjustment of the C:O ratio. For a high absolute

flow of fuel and oxidation air, the flame is large and thus is quenched relatively low within the flame. On the other hand, a small absolute flow of fuel and oxidation air causes the quenching to take place close to the flame tip. We aimed at comparing the ice nucleation abilities of combustion generated soot by varying organic carbon mass. We therefore altered both, the position of flame quenching and the ratio of fuel to oxidation air. The miniCAST was operated at two different test points (TP). We use the fuel-air flame equivalence ratio, Φ , its inverse, the air-fuel ratio, λ , and the atomic carbon-to-oxygen ratio, C:O, to characterize the flame chemistry at the two TP.

The flame C:O ratio can be calculated based on the fuel and air densities at normal temperature and pressure (NTP) according to:

5
$$C: O = \frac{Q_f 10^{-3}}{Q_{ox} 10^{-3}} \cdot \frac{\rho_{f,NTP} F_{Cinfuel}}{\rho_{ox,NTP} F_{O2inair}},$$
 (B1)

where Q_f and Q_{ox} denote the fuel and oxidation air flow rates, respectively (see Table B1), $F_{Cinfuel}$ denotes the C-fraction in C₃H₈ (0.818), $F_{O2inair}$ the fraction of O₂ in air (0.232) and $\rho_{f,NTP}$ and $\rho_{ox,NTP}$ denote the mass densities of C₃H₈ (1.882 kgmol⁻¹) and air (1.205 kgmol⁻¹).

Assuming the combustion reaction to be:

10
$$C_3H_8 + 5O_2 \to 3CO_2 + 4H_2O$$
, (BR1)

we calculate Φ , as fuel-air mass ratio divided by the stoichiometric fuel-air ratio, given by:

$$\Phi = \frac{(m_f/m_{ox})}{(m_f/m_{ox})_{st}} = \frac{1}{\lambda}.$$
(B2)

Here m_f denotes the mass flow of C₃H₈, m_{ox} the mass flow of oxidation air and the subscript *st*, denotes the stoichiometric fuel-air ratio. Using reaction BR1 and a mass percentage of O₂ of 23.2 % the stoichiometric fuel-air ratio is given by:

15
$$(m_f/m_{ox})_{st} = \frac{44.096 \,\mathrm{gmol}^{-1}}{5 \cdot 31.998 \,\mathrm{gmol}^{-1}} \cdot \frac{23.2}{100} = 0.0639.$$
 (B3)

Thus the combustion process is *fuel rich* for $\Phi > 1$ and $\lambda < 1$ and *fuel lean* combustion occurs for $\Phi < 1$ and $\lambda > 1$, where *lean* refers to conditions where fuel is the limiting reactant.

It should be noted that the parameters described above characterizing the flame chemistry, allow only for limited comparison with other studies, since they do not include additional factors such as the N₂ quench gas flow rate, Q_{N2} , the N₂ flow rate premixed to the fuel, $Q_{N2,mix}$, the dilution air flow Q_{dil} or any differences in burner geometries (Durdina et al., 2016), which influence the soot characteristics. We use these parameters to characterize our miniCAST soot samples termed mCAST black and mCAST brown, as shown in Table B1.

Table B1. Summary of the settings for miniCAST Series 4200, used to produce mCAST black and mCAST brown presented in this study. Q_f denotes the volumetric C₃H₈ (fuel) flow^c, Q_{ox} the oxidation air^a flow, $Q_{N2,mix}$ the N₂^b flow premixed with the fuel, Q_{N2} the quench N₂^b and Q_{dil} the dilution air^a flow, respectively. All flows are given in units of standard [Lmin⁻¹]. λ , Φ and C:O indicate the air-fuel equivalence ratio, the fuel-air ratio and the atomic carbon:oxygen ratio, respectively, as described in the text.

Soot type	Q_f	Q_{ox}	$Q_{N2,mix}$	Q_{N2}	Q_{dil}	λ	Φ	C:O
mCAST black	0.06	1.55	0.0	7.5	20.0	1.0576	0.9455	0.2132
mCAST brown	0.06	1.42	0.25	7.5	20.0	0.9689	1.0321	0.2327

^a VOC filtered (wall) synthetic air, ^b Carbagas 5.0 grade, ^c Carbagas quality 25

Appendix C: TEM sample preparation and evaluation

- 5 We used TEM to visualize the dimensions and morphology of the soot particles. Size selected soot particles were collected on standard Cu-TEM grids having 400 mesh with a single coated continuous carbon film (Quantifoil Micro Tools GmbH, Großlöbichau, Germany), using the Zurich Electron Microscope Impactor (ZEMI). ZEMI is a semi-automated, custom built rotating drum impactor, holding a total of 24 TEM grids. The aerosol containing air stream is directed onto the TEM grid. Soot particles with inertia are impacted onto the TEM grid, while the surrounding gas molecules are laterally sucked away. A
- step motor (R208 Microstepping Driver, RMS Technologies, Carson City, USA), controlled over a LabView program allows to adjust the time period that each grid is exposed to the aerosol flow and the to control the sampling flow rate using a MFC (G-Series, MKS Instruments, Andover, USA). The distance between the exit of the nozzle and the impaction plate (TEM grid) can mechanically be adjusted. Here, we used a constant flow rate of 1 $Lmin^{-1}$ and varied the sampling time between 100 – 600 s, depending on the number concentration of the size selected aerosol, in order to ensure a high enough loading of the TEM grid.
- 15 Images of the aggregates were obtained from a JEOL TEM-1400+ (JEOL Ltd., Tokyo, Japan) with a LaB6 filament, operating at 120 kV. Finally, particle morphology and primary particle size were obtained upon image analysis using the MATLAB (R2017b, MathWorks Inc., Natick, USA) image analysis tool box. Therefore, a custom developed program in MATLAB was used which reads in the intensity images obtained from TEM. The program then allows to select regions of interest (ROIs), where individual primary spherules were sized using MATLAB's *imellipse* function, using the average of the minor and major
- 20 axis describing the ellipse. For each aggregate a minimum of 3 different ROIs were selected to ensure that more weight was not given to certain regions of the soot aggregates under investigation. A minimum of around 100 primary particles were sized for each soot type.

Appendix D: Horizontal Ice Nucleation Chamber

10

D1 Uncertainty in temperature and relative humidity

The main uncertainty of the ice nucleation measurements results from uncertainties in temperature control and flow changes that alter the ratio of aerosol to sheath flow ratio, resulting in variations of the humidity profile across the aerosol lamina (located at the chamber center). We report uncertainties in S_w/S_i arising from the variability of humidities across the aerosol lamina and temperature uncertainty, thus capturing the possible range of humidity conditions experienced by any aerosol particles that are confined within the lamina. We first calculate the aerosol lamina coordinates and in a second step the supersaturation at these coordinates. Due to the horizontal orientation of the chamber walls and the absence of any internal buoyancy (convection), the velocity profile is simply given by (Rogers, 1988):

$$v(z) = \frac{3}{2}\bar{v}\left[1 - \frac{z^2}{(d/2)^2}\right],\tag{D1}$$

where z denotes the vertical height coordinate, d/2 = 1 cm the half width between the cold and warm walls and \bar{v} the mean

- 5 flow velocity given by the ratio of the total volumetric flow rate, $Q_{tot} = \int_{z=0}^{z=d} v(z) dz$, and the cross-sectional area of the chamber. Assuming that 50 % of the volumetric aerosol flow is on either side of the chamber center line (position of aerosol injector), the coordinates of the lamina limits, *a* and *b*, are found by integrating the flow profile symmetrically around the center line until the integrated flow matches the given aerosol flow. Hence, *a* and *b* depend on the *ratio* of aerosol to sheath flow (F_{AP}/F_{sheath}).
- 10 The temperature at any location z within the chamber can be calculated from the linear temperature profile Rogers (1988):

$$T(z,\Delta T) = T_{\rm c} + \frac{\Delta T}{D}z,\tag{D2}$$

where T_c and T_w denote the temperature of the cold and warm plates, respectively, and $\Delta T = \frac{T_w - T_c}{d}$. Similarly, the linear profile of vapor pressure with respect to ice, e_i is given by:

$$e_{i}(z) = e_{s,i}(T_{c}) + \frac{e_{s,i}(T_{w}) - e_{s,i}(T_{c})}{d}z,$$
(D3)

where $e_{s,i}$ denotes the saturation vapor pressure with respect to ice after Murphy and Koop (2005).

Overall, the range of saturation ratio experienced by particles in the aerosol lamina is a function of the ratio of aerosol to 5 sheath flow, F_{AP}/F_{sheath} , center temperature, T_{center} , and temperature difference between the two walls, ΔT , i.e.:

$$\Delta S_{\text{x,lam}} = \Delta S_{\text{x,lam}} (F_{AP} / F_{sheath}, T_{center}, \Delta T), \tag{D4}$$

where the subscript x denotes evaluation with respect to water (S_w) or with respect to ice (S_i) . For a given F_{AP}/F_{sheath} and T_{center} , activation mostly took place for high RH_w , i.e. large ΔT values. Large values of ΔT (i.e. large values of RH) also result in larger uncertainties in RH, thus for a variety of F_{AP}/F_{sheath} and T_{center} , we report the calculated uncertainty and variation in $S_{x,lam}$ for a S_w ,center value of 1.05 as an upper limit of RH uncertainty.



Figure D1. Example of S_w profile for the mid-portion of the vertical distance between the cold (at z = 0 cm, bottom) and warm (at z = 2 cm, top) wall of the HINC chamber, illustrating the variations in S_w across the aerosol lamina (black solid line) for exemplary conditions of $T_{center} = 218$ K, $S_{w,center} = 1.05$ and different F_{AP}/F_{sheath} flow ratios (red and blue shading). The S_w profiles given by the dashed and dash-dotted lines take into into account uncertainty in temperature control arising from the thermocouples. The red dashed line indicates the position where particles are injected into HINC.

The temperatures can ultimately only be controlled within the uncertainty range of the thermocouples used for temperature control and monitoring, having an uncertainty of ± 0.1 K. Hence, for given conditions of F_{AP}/F_{sheath} , T_{center} and $S_{w,center}$, $\Delta S_{x,lam}(F_{AP}/F_{sheath}, T_{center}, \Delta T)$ was calculated for three different cases, covering the possible range of thermocouple uncertainties, but all leading to the same center conditions (T_{center} , $S_{w,center}$), namely:

15



- Case 2: $T_w = T_{w,set} + 0.1$, $T_c = T_{c,set} 0.1$
- Case 3: $T_w = T_{w,set} 0.1$, $T_c = T_{c,set} + 0.1$

The variation and uncertainty of the saturation profile across the aerosol lamina for these three cases is shown exemplarily in Fig. D1 for $T_{center} = 218$ K, $S_{w,center} = 1.05$ and different ratios of F_{AP}/F_{sheath} . In this study we use a flow ratio $F_{AP}/F_{sheath} = 1:10$ to calculate our aerosol lamina boundaries and uncertainties associated with our ice nucleation results.

5 Figure D2 finally illustrates the effect of flow ratio, i.e. aerosol lamina coordinates, on the overall uncertainty in *RH* across the aerosol lamina.



Figure D2. Relative humidity variation and uncertainty across the aerosol lamina, $\Delta S_{w,lam}$ as a function of T_{center} for different *ratios* of F_{AP}/F_{sheath} within HINC. Each reported value denotes the maximum spread in S_w across the aerosol lamina considering all three cases of TC-temperature uncertainty (see text) and a center S_w value of 1.05. The work presented here used flow ratios between 1:10 and 1:12.

D2 Hydrometeor growth and settling

Growth of ice crystals and cloud droplets is a function of the T and RH conditions within the chamber as well as the residence time of the particles within HINC. The final size the hydrometeors grow to, can be estimated using theoretical diffusional

- 10 growth equations. In Figs. D3 and D4 we show examples of expected diffusional hydrometeor growth (orange lines) and the corresponding distance from gravitational settling (blue lines) for ice crystals (solid lines) and cloud droplets (dashed lines) within HINC for cirrus and MPC temperatures, respectively. The examples shown assume an initial hydrometeor diameter of 200 nm and the complete residence time to be available for diffusional growth, i.e. neglecting any time dependence on ice nucleation, thus likely overestimating hydrometeor growth. Diffusional growth was calculated according to Rogers and Yau (1989).
- 15 The temperature dependency of the water vapor diffusion coefficient in air was taken from Hall and Pruppacher (1976) and that of the thermal conductivity coefficient from Beard and Pruppacher (1971). Finally, the temperature dependencies of the latent heat of condensation and sublimation were parametrized according to Murphy and Koop (2005). For simplicity we assumed spherical ice crystals, where the capacitance is equal to the ice crystal radius, and calculated growth for a mass accommodation coefficient, α , of 0.1 (Skrotzki et al., 2013; Magee et al., 2006). Diffusional growth was calculated in accordance to the vertical profiles of *T* and *RH* between the chamber walls. Therefore the (vertical) hydrometeor position was calculated at time
- 5 steps of 0.01 s, again assuming particle sphericity, and the T and RH conditions at this (vertical) position were used to calculate the diffusional growth. All hydrometeors were assumed to start growing and falling from the center line of HINC

(z = 1 cm), i.e. neglecting an aerosol layer thickness, and the vertical distance covered per time step was calculated using a sedimentation velocity derived from a balance of gravitational and drag force (Lohmann et al., 2016), where the factor $C_{\rm D}Re/24$ was approximated as 1 justified for particles $r < 30 \ \mu m$ (Rogers and Yau, 1989). For growth and settling we used the

- 10
 - temperature dependent density of supercooled liquid water given in Marcolli (2016) and of ice given in Pruppacher and Klett (1997). The vertical settling distance experienced due to gravity by the ice crystals and cloud droplets (blue lines), indicate potential loss of the hydrometeors. Particle impaction on the bottom wall is indicated by the blue lines (vertical hydrometeor position) reaching a value of 1 cm, as indicated by the horizontal, gray solid line. Calculation of growth and gravitational settling are aborted if a cloud particle has settled 1 cm. From the theoretical growth curves in Figs. D3 and D4 it becomes evident that cloud particles are not lost due to gravitational settling during the residence time used herein ($\tau = 16$ s), even for high humidities of $RH_{\rm w} = 101$ %, with the exception of the 253 K case, when assuming a mass accommodation coefficient of $\alpha = 0.1$ (magenta lines).

While ice crystal impaction onto the bottom plate of HINC could explain an AF < 1 as observed for most of our experiments

- 5 (see SI S2) we would expect a peak in the AF curves, followed by a gradual decrease in AF due to gravitation loss of the particles, as the RH is increased within the experiment. From the absence of any such signal in our soot AF curves we conclude that our calculations represent an upper limit of settling and diffusional growth values. This can be explained by a potential high time dependency of the soot aerosols to nucleate ice crystals or due to an underestimation of the time needed for the aerosols to equilibrate to the chamber conditions, with both processes reducing the diffusional growth time available for
- 10 particles within HINC.



Figure D3. Expected diffusional growth of spherical ice crystals, having an initial *diameter* of 200 nm, within HINC for different cirrus regime temperatures, T_{center} , (rows) and RH_w along the centerline of HINC (columns), as a function of residence time. Orange lines indicate the ice crystal radius (right hand ordinate). Blue lines indicate the vertical distance covered by the ice crystal (left hand ordinate). Calculations are aborted, once a particle has traveled the half-distance of the two copper plates (1 cm), i.e. has hit the bottom plate of HINC, indicated by the horizontal, gray line (left hand ordinate), i.e. wherever any blue line crosses the horizontal gray line.



Figure D4. Expected diffusional growth and gravitational settling of spherical ice crystals (solid) and cloud droplets (dashed) for MPC temperatures, having an initial *diameter* of 200 nm. Symbols and reference lines as in Fig. D3.

Author contributions. FM prepared the manuscript with contributions from ZAK, CM, ROD, UL, EBM and PG. FM and ZAK designed the experiment. FM conducted and analyzed HINC measurements and prepared all figures of the manuscript. PG ran DVS experiments and interpreted data. EBM took TEM images and helped with interpretation. FM, CM, ROD, UL and ZAK interpreted ice nucleation data. ZAK conceived the idea and supervised the overall project.

15 Competing interests. The authors declare that they have no conflict of interest.

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Acknowledgements. F. Mahrt was funded by and Z. A. Kanji acknowledge funding from ETH Grant ETH-25-15-1 that supported this work. The authors gratefully acknowledge the great technical support of H. Wydler from the Institute for Atmosphere and Climate Science in overseeing the maintenance of HINC, improving both the CFDC and associated software as well as with help in developing ZEMI. We also thank M. Vecellio and P. Isler from the Institute for Atmosphere and Climate Science for machining parts of our set up. The authors would like to thank J.C.H. Wong from the Laboratory of Composite Materials and Adaptive Structures for her training and help with the TGA and A. Röthlisberger, M. Rothaupt and M. Plötze from the Institute for Geotechnical Engineering for help with BET. The authors are grateful to I. Burgert from the Institute of Structural Engineering for providing access to the DVS facility. We also thank U. Krieger and S. Brunamonti from the Institute for Atmosphere and Climate Science for providing some of the soot samples and L. Lacher (KIT) and J. Atkinson for many helpful discussions on HINC and associated ice nucleation experiments. We thank J. Aerni for help with preparation of the TEM samples.

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S1 Introduction

This supporting information provides additional text and figures to support the main manuscript.

S2 AF curves for all soot samples and sizes 1 µm OPC chanel

- This section contains the complete activation curves for the different soot types. Data shown corresponds to the 1 μ m channel of the OPC, i.e. detecting particles that are equal/larger to the (optical) size selected for the OPC channel. Size selection was achieved using a DMA with aerosol to sheath flow ratios of 1:10 for 100 – 300 nm soot particles and 1:7 for 400 nm particles, respectively, as noted in SI Table S1 (F_{DMA}). We observe no ice nucleation in the MPC regime, but cannot completely exclude the possibility of ice crystals forming in parallel to cloud droplets at/above WDS evaluating the ice nucleation experiments at this OPC channel. However, some soot types show ice formation ability in the cirrus cloud regime as discussed in the main text
- 10 Sect. 3.2.



Figure S1. Relative humidity scans at constant temperature of FW200 soot particles, showing AF as a function of RH_w for different temperatures in the MPC regime (top row) and cirrus cloud regime (bottom row) for electrical mobility diameters of 100 nm (red circles), 200 nm (green squares), 300 nm (blue triangles) and 400 nm (black diamonds). Symbol types match those used in the main text. In each subpanel the red dashed line indicates homogeneous freezing conditions according to Koop et al. (2000) for a water-activity criterion of $\Delta a_w = 0.305$. Similarly, vertical, blue dashed lines indicate WDS conditions for an initial droplet diameter of 100 nm, a residence time within HINC of $\tau \approx 16$ s and assuming pure diffusional growth based on Rogers and Yau (1989). Uncertainties in RH_w are given as the mean spread in humidity across the aerosol lamina as detailed in Appendix D1. Error in AF is ± 14 %. All curves represent mean values over all humidity scans performed at a given temperature and for a given size. For clarity error bars are only given for each 5th data point.



Figure S2. Relative humidity scans at constant temperature of LB_OEC soot particles. Symbols and reference lines as in Fig. S1.



Figure S3. Relative humidity scans at constant temperature of LB_RC soot particles. Symbols and reference lines as in Fig. S1.



Figure S4. Relative humidity scans at constant temperature of FS soot particles. Symbols and reference lines as in Fig. S1.



Figure S5. Relative humidity scans at constant temperature of mCAST black soot particles. Symbols and reference lines as in Fig. S1.



Figure S6. Relative humidity scans at constant temperature of mCAST brown soot particles. Symbols and reference lines as in Fig. S1.

S3 AF curves for all soot samples and sizes 5 µm OPC chanel

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This section contains the complete activation curves for the different soot types. Data shown corresponds to the 5 μ m channel of the OPC, i.e. detecting particles that are equal/larger to the (optical) size selected for the OPC channel. Size selection was achieved using a DMA with aerosol to sheath flow ratios of 1:10 for 100 – 300 nm soot particles and 1:7 for 400 nm particles, respectively, as noted in SI Table S1 (F_{DMA}). We observe no ice nucleation in the MPC regime. However, some soot types show ice formation ability in the cirrus cloud regime as discussed in the main text Sect. 3.2.



Figure S7. Relative humidity scans at constant temperature of FW200 soot particles, showing AF as a function of RH_w for different temperatures in the MPC regime (top row) and cirrus cloud regime (bottom row) for electrical mobility diameters of 100 nm (red circles), 200 nm (green squares), 300 nm (blue triangles) and 400 nm (black diamonds). Symbol types match those used in the main text. In each subpanel the red dashed line indicates homogeneous freezing conditions according to Koop et al. (2000) for a water-activity criterion of $\Delta a_w = 0.305$. Similarly, vertical, blue dashed lines indicate WDS conditions for an initial droplet diameter of 100 nm, a residence time within HINC of $\tau \approx 16$ s and assuming pure diffusional growth based on Rogers and Yau (1989). Uncertainties in RH_w are given as the mean spread in humidity across the aerosol lamina as detailed in Appendix D1. Error in AF is ± 14 %. All curves represent mean values over all humidity scans performed at a given temperature and for a given size. For clarity error bars are only given for each 5th data point.



Figure S8. Relative humidity scans at constant temperature of LB_OEC soot particles. Symbols and reference lines as in Fig. S7.



Figure S9. Relative humidity scans at constant temperature of LB_RC soot particles. Symbols and reference lines as in Fig. S7.



Figure S10. Relative humidity scans at constant temperature of FS soot particles. Symbols and reference lines as in Fig. S7.



Figure S11. Relative humidity scans at constant temperature of mCAST black soot particles. Symbols and reference lines as in Fig. S7.



Figure S12. Relative humidity scans at constant temperature of mCAST brown soot particles. Symbols and reference lines as in Fig. S7.

S4 TGA results

Figure S13 shows the mass loss rates, corresponding to our TGA experiments to support the interpretation of the mass loss reported in Sect. 3.4 of the main text.



Figure S13. Mass change rate $(\% w/w/^{\circ}C)$ as a function of sample temperature. Curves are shown with an offset to allow for better comparison. Solid and dashed lines indicate individual TGA runs. Shading-Indicated regions corresponds to different ranges of heat sensitivity, namely adsorbed water and highly heat sensitive material (yellowA), medium heat sensitive material/OM (grayB) and low heat sensitive material (blueC). Pyrolysis is expected to contribute to mass loss at temperatures above those indicated by the vertical red dashed line.

S5 DVS results

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Figure S14 exemplarily shows the relative mass change (blue line) and the logarithm of the mass change rate (orange line) for a drying cycle of the FW200 soot, performed prior to DVS measurements. Drying was achieved through continuous flushing with N₂ at atmospheric pressure and a constant temperature of T = 298 K, at a relative water vapor pressure (p/p_0) of zero. From Figure S14 it becomes clear that the strongest mass loss occurs within the first few minutes (blue line), but that more than hundred minutes are required to completely dry the sample, as indicated by the noisy part of the orange line starting at times around t = 200 min, where the sample mass change rate approaches the detection limit of the instrument.



Figure S14. Relative mass loss (blue line, left hand ordinate) and logarithm of the mass loss rate (orange line, right hand ordinate) as a function of time, for an exemplary drying cycle of FW200 prior to DVS measurements.

S6 Quality of soot particle size selection

DMAs select particles based on electrical mobility size, which is identical to the physical diameter only for perfectly spherical particles, a poor assumption for soot particles (DeCarlo et al., 2004). We tested the size selection of the soot aerosols, by measuring the number size distribution of the size selected soot aerosol with an SMPS. Therefore we first size selected the soot aerosol in a DMA (Model: classifier 3080, column 3081, TSI Inc.), as was done for all our ice nucleation measurements, and subsequently measured the size distribution using another SMPS (Model: classifier 3082, column 3081, CPC 3772, TSI Inc.) downstream of the DMA. The aerosol to sheath flows used in the respective instruments are reported in Table S1. Exemplary

15 size distributions are shown in Fig. S15 for FS and FW200 soot, where the number size distribution is given in terms of number percentage corresponding to a given mobility size for ease of comparison. The sharpness of the size selection by the DMA depends on the transfer function, causing the resulting particles to spread in size around the selected midpoint diameter. The transfer function is preliminarily determined by the aerosol to sheath flow ratios within the DMA and SMPS reported in Table S1. Some heterogeneity in particle size results from different orientations of the fractal soot aggregates within the (electric field of the) DMA, as well as the presence of larger, multiply-charged particles. Finally, reliable size distribution measurements of fractal soot aggregates have been shown to be dependent on the primary particle size (Lall and Friedlander, 2006; Dastanpour

5 et al., 2016). Here, we note in general a better size selection for smaller particles, consistent with Park et al. (2004), who reported smaller diesel soot particles to be more compact, likely resulting in a better size selection for smaller aggregates.

Table S1. Electrical mobility diameter, d_m , used for size selection within DMA along with aerosol to sheath flow ratio in DMA (F_{DMA}) and SMPS (F_{SMPS}) used for size selection and size distribution measurements, respectively. Flows are given in volumetric liters per minute. DMA used for size selection: classifier 3080, column 3081 (polonium neutralizer). SMPS used for size distribution measurement: classifier 3082, column 3081 (X-ray neutralizer), CPC 3772.

d_m [nm]	$ F_{DMA}$	$ F_{SMPS}$
100	1/10	1/6
200	1/10	1/6
300	1/10	1/4
400	1/7	1/4



Figure S15. Number size distribution in terms of particle percentage corresponding to a given electrical mobility diameter, d_m , for size selected aerosols of (a) FS soot and (b) FW200, using the settings given in Table S1.

S7 Chamber validation

Chamber performance has been tested and documented in Lacher et al. (2017). Figure S16 exemplarily shows AF curves for 200 nm NH₄NO₃ obtained from our two CFDCs HINCST and HINCNE run in parallel, to verify chamber performance and intercomparability of the two ice chambers within instrumental uncertainty.



Figure S16. Exemplary RH_w scans of HINCST HINCST and HINCNE HINCNE at T = 233 K using 200 nm NH₄NO₃ and a residence time of $\tau \approx 10.4$ s. The vertical black dashed line represents expected homogeneous freezing conditions according to Koop et al. (2000) and the gray shading indicates variation in relative humidity across the aerosol lamina. Data corresponds to the 1 µm OPC channel.

S8 TEM analysis

We have used TEM to qualitatively determine primary particle diameters and overall aggregate morphology. In Fig. S17 we show the primary particle size distribution for the different soot types, as derived from analysis of TEM images having a minimum magnification of x20k. We note that the FW200, mCAST brown and black show a narrow primary particle size distribution, whereas the lamp blacks and the FS have a broader size distribution, consistent with our TEM images discussed in the main text and shown below. In order to support the exemplary TEM images shown in the main text, Fig. S18 shows an extended selection of TEM images of the different soot types. From the images taken at the lowest magnification (left column) it becomes clear, that the size-selected soot aggregates still show a considerable heterogeneity in terms of overall aggregate size and structure, supporting our size selection reported in Fig. S15. However, quantification of these effects are beyond the

10 scope of the present study. Finally, the presented images give examples of the studied aerosol types, but do not necessarily represent particles that were tested for ice nucleation, as the particles could undergo changes when impacting on the TEM grid. This becomes clear from Fig. S18a1, where the smaller particles are believed to result from splattering of the larger aggregate when impacting on the TEM grid.

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

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$$d_{\text{Aeq}} = \sqrt{\frac{4A_a}{\pi}},$$
 (1)

where A_{e} 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 ($d_{Aeq} < 200 \text{ nm}$) 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 relatively to the other soots types, which could account for its enhanced ice nucleation ability.

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Figure S17. Distribution of primary particle sizes for the different soot types, derived from evaluation of TEM images. The number in bracktes brackets indicates the number of primary particles sized for the corresponding soot type.



Figure S18. Exemplary TEM images of typical 400 nm mobility diameter selected soot aggregates of (a) FW200, (b) FS, (c) LB_OEC, (d) LB_RC, (e) mCAST black and (f) mCAST brown. Images of the different coloumns were taken at different magnification, but with the same microscope. The lengths of the scale bars correspond to 800 nm for the left column and to 200 nm for the middle and right columns.

S9 CPMA results



Figure S19. 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.

Next to a fractal dimension the DMA-CPMA data can be used to calculate an effective density of the tested soot particles. In Fig. S20 we show the effective densities of the different soot types, as calculated using eq. A2.



Figure S20. DMA-CPMA data for the different soot types: Electrical mobility diameter (d_m) vs. effective densities (ρ_{eff}) , corresponding to the data shown in Fig. 4 calculated using eq.A2.

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