Reply to referee #1: 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 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, l.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 m^2g^{-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 l.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 l.10). We thus revised the sentence on p.7 l.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, l.2 (initial manuscript):

"For all experiments presented here a particle residence time of τ ≈ 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 τ ≈ 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 μm (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 μm onwards, and not only in the 1 μm channel? Correct this.

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

"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. Here, we choose the 1 μm size bin as the threshold to detect ice crystals in HINC, i.e. particles with optical diameters >1 μm."

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."

4

For the case of the DMA-CPMA measurements this is already described in more detail on p.27 l.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 l.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 l.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., l. 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 PCF, even up to RH required for homogeneous freezing ($T < \sim -36$ °C), then solution 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, l.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)

6

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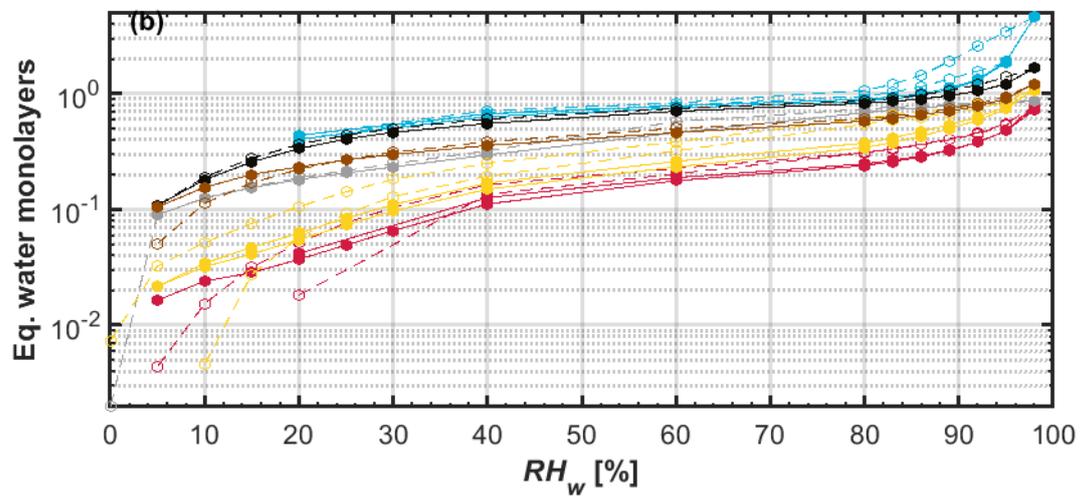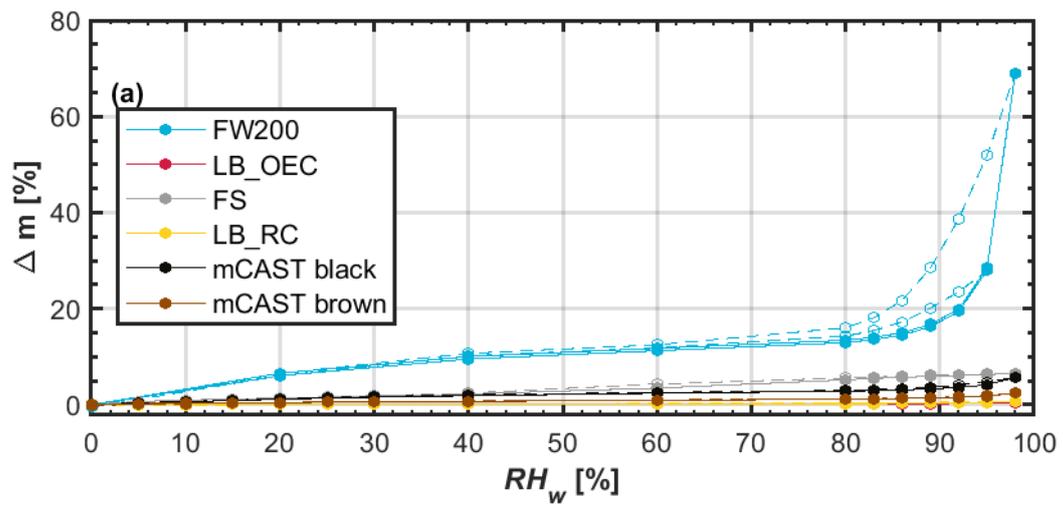
(27)   page 19, line 21: Are citric acid and glutaric acid organics typical for the atmosphere? Any citation on that? Others might play a more important role (oxalic acid, formic acid, acetic acid, succinic acid, ...). But there must be a reason why you choose those. Explain that in a few words.

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 water-soluble 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 soot-water 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 l.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, l.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, l.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, l.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, l.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 l.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 l.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."

CZICZO, D. J., FROYD, K. D., HOOSE, C., JENSEN, E. J., DIAO, M., ZONDLO, M. A., SMITH, J. B., TWOHY, C. H. & MURPHY, D. M. 2013. Clarifying the Dominant Sources and Mechanisms of Cirrus Cloud Formation. *Science,* 340**,** 1320-1324.

GRAWE, S., AUGUSTIN-BAUDITZ, S., CLEMEN, H. C., EBERT, M., ERIKSEN HAMMER, S., LUBITZ, J., REICHER, N., RUDICH, Y., SCHNEIDER, J., STAACKE, R., STRATMANN, F., WELTI, A. & WEX, H. 2018. Coal fly ash: Linking immersion freezing behavior and physico-chemical particle properties. *Atmos. Chem. Phys. Discuss.,* 2018**,** 1-32.

GRAWE, S., AUGUSTIN-BAUDITZ, S., HARTMANN, S., HELLNER, L., PETTERSSON, J. B. C., PRAGER, A., STRATMANN, F. & WEX, H. 2016. The immersion freezing behavior of ash particles from wood and brown coal burning. *Atmos. Chem. Phys.,* 16**,** 13911-13928.

KANJI, Z. A. & ABBATT, J. P. D. 2009. The University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC): A Simple Design for Ice Nucleation Studies. *Aerosol Science and Technology,* 43**,** 730-738.

KAWAMURA, K. & IKUSHIMA, K. 1993. SEASONAL-CHANGES IN THE DISTRIBUTION OF DICARBOXYLIC-ACIDS IN THE URBAN ATMOSPHERE. *Environmental Science & Technology,* 27**,** 2227-2235.

KAWAMURA, K. & YASUI, O. 2005. Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere. *Atmospheric Environment,* 39**,** 1945-1960.

KOOP, T., LUO, B. P., TSIAS, A. & PETER, T. 2000. Water activity as the determinant for homogeneous ice nucleation in aqueous solutions. *Nature,* 406**,** 611-614.

KUEBBELER, M., LOHMANN, U., HENDRICKS, J. & KÄRCHER, B. 2014. Dust ice nuclei effects on cirrus clouds. *Atmos. Chem. Phys.,* 14**,** 3027-3046.

LACHER, L., LOHMANN, U., BOOSE, Y., ZIPORI, A., HERRMANN, E., BUKOWIECKI, N., STEINBACHER, M. & KANJI, Z. A. 2017. The Horizontal Ice Nucleation Chamber (HINC): INP measurements at conditions relevant for mixed-phase clouds at the High Altitude Research Station Jungfraujoch. *Atmospheric Chemistry and Physics,* 17**,** 15199-15224.

MARCOLLI, C., LUO, B. P. & PETER, T. 2004. Mixing of the organic aerosol fractions: Liquids as the thermodynamically stable phases. *Journal of Physical Chemistry A,* 108**,** 2216-2224.

UMO, N. S., MURRAY, B. J., BAEZA-ROMERO, M. T., JONES, J. M., LEA-LANGTON, A. R., MALKIN, T. L., O'SULLIVAN, D., NEVE, L., PLANE, J. M. C. & WILLIAMS, A. 2015. Ice nucleation by combustion ash particles at conditions relevant to mixed-phase clouds. *Atmos. Chem. Phys.,* 15**,** 5195-5210.

WINTERHALTER, R., KIPPENBERGER, M., WILLIAMS, J., FRIES, E., SIEG, K. & MOORTGAT, G. K. 2009. Concentrations of higher dicarboxylic acids C-5-C-13 in fresh snow samples collected at the High Alpine Research Station Jungfraujoch during CLACE 5 and 6. *Atmospheric Chemistry and Physics,* 9**,** 2097-2112.

XUE, H. X., KHALIZOV, A. F., WANG, L., ZHENG, J. & ZHANG, R. Y. 2009. Effects of dicarboxylic acid coating on the optical properties of soot. *Physical Chemistry Chemical Physics,* 11**,** 7869-7875.