

We thank the referee for the useful comments, all of which we considered carefully. In the following, we respond to them separately, where the original comments are colored, while the answers are given in black.

Review of “The immersion freezing behavior of ash particles from wood and brown coal burning” by Grawe et al.

This manuscript presents an interesting data set regarding the ice nucleating abilities of ash particles which are currently poorly understood. Given the lack of information on this topic, and the potential that ash particles may have to influence mixed-phase cloud formation, the present results are a valuable contribution to the ice nucleation community. Although the present manuscript possesses many similarities with the Umo et al. (2015) study, I still see a small level of novelty on it. I got attracted by the title of the paper which indicates that the ice nucleating abilities of wood and brown coal burning ash particles were studied, but I am disappointed that a clear explanation of why brown coal ash particles are better INP than the wood ash particles is not provided. Additionally, the conclusions are not clearly supported given the lack of some key experiments. Therefore, I think that this paper could be accepted in ACP only after the following points are clearly addressed. Note that this review was prepared without reading the comments given by referee #3; therefore, I apologize for any overlap between the two reviews.

Major comments:

1. Multiple charge correction was applied to the dry samples only. Which percentages of the particles were multiple charged? Based on what data was this correction conducted as the authors indicate that the UHSAS did not clearly detect the multiple charged particles? How good is the agreement between the SEM and the UHSAS at detecting multiple charged particles? I encourage the authors to report the size distribution for each sample and the resulted size distributions after size selection (300 nm).

The multiple charge correction was performed based on size distribution measurements with the UHSAS. New UHSAS and SEM measurements show that we saw a discrepancy between the two because the cyclone, which we used to minimize multiply charged particles, is usually filled after 30 min. Filter samples were taken for several hours, meaning that multiply charged particles accumulated as soon as the cyclone was filled and not immediately cleaned. The new measurements show a good agreement between UHSAS and SEM, as long as the cyclone is cleaned sufficiently often. As LACIS measurements typically last around 20 minutes only (due to wall glaciation effects), and the cyclone was cleaned after each LACIS measurement, we are certain that the UHSAS determined doubly charged fractions (which have been added to the manuscript in Tab. 1) correspond to the actual fractions in the flow tube.

We omitted Fig. 2b) from the original manuscript to avoid confusing the reader with the occurrence of large particles which are only present on these particular filters but not in the LACIS measurements. In light of the new observations, we changed the paragraph on P5 L19-30 of the original manuscript accordingly (P9 L14-24).

2. There is a poor consistency in the experiments conducted with the 5 ash samples as shown in the table below. I am wondering why there is too much data missing. This lack of information reduces the robustness of the drawn conclusions regarding the particle generation methods and the effect of treating the samples with ultrasound. I suggest conducting more experiments to fill out the table below.

	Material	Fly/Bottom	Dry Generation	Wet Generation	Ultrasound	Without ultrasound	Filtered	SEM	AA
Wood	Spruce	B	X	X	X				X
	Birch	B	X						X
	Beech	B	X						
Coal	Brown coal	B	X	X	X			X	X
	Brown coal	F	X	X	X	X	X	X	X

You are right in suggesting that further experiments would shed more light on some of the drawn conclusions. However, LACIS measurements are very time consuming so that we do not see a possibility to provide the missing data on a time scale of weeks.

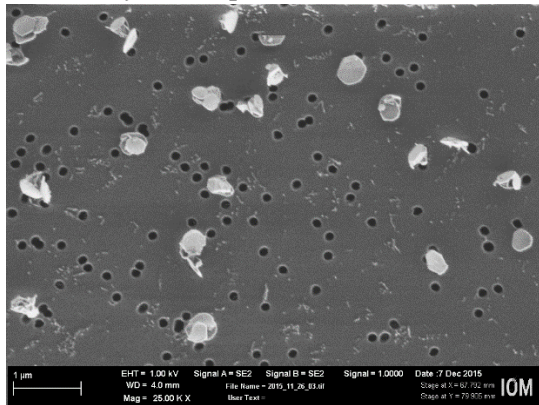
We investigated the most efficient of our samples (coal fly ash) most intensely, also including filtering of the suspension and suspensions without ultrasonic treatment as we expected the biggest difference for this sample. Measurements of the bottom ash suspensions without ultrasonic treatment would not be adding much, as they were already close to the detection limit with ultrasonic treatment.

The beech ash was not investigated by means of atomic adsorption spectroscopy as it was provided later, after the other samples had already been analyzed in Sweden. We decided to include the data, even without the chemical analysis, because we wanted to show that beech ash is comparable to the other wood bottom ashes.

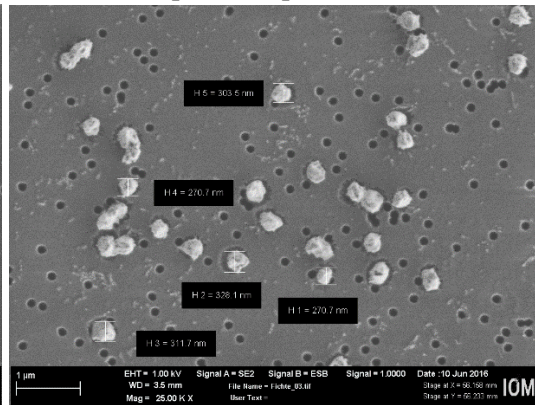
3. Is it the needle formation exclusive to fly-ash brown coal particles? Why SEM images of the bottom brown coal (suspension) are not presented? Why the SEM analysis was not applied to the wood ash samples? The authors indicate that the needle formation in the fly-ash brown coal particles may be caused by CaCO_3 which was formed by the presence of CaO detected by the atomic adsorption (AA) analysis. However, Figure 1 shows that the levels of CaO in the wood samples are much higher than in the brown coal samples. Therefore, it would be nice to see the SEM images of e.g. Spruce which has the highest concentration of CaO.

The only time when SEM images were needed for our evaluation was when we determined the fraction of fly ash particles vs. the fraction of solution particles for experiments with the fly ash suspension. Hence, with the selection of SEM images shown, we did not intend to give an overview for all samples. Now, we included an additional SEM picture of spruce ash particles from wet particle generation in the manuscript (Fig 2c) which does not show needle formation. However, we must mention that recent analyses of fly ash from wet generation did not show needle formation either. Here, we could observe crystals in the form of hexagonal plates (see below). Both needles as well as hexagons are among the shapes that can be formed by CaCO_3 (Kim et al., Journal of Materials Chemistry, 2009). We assume that the shape which the soluble components take upon drying, is influenced by slight changes in the relative humidity in our dryer unit. This might also be the case for spruce ash from wet generation. Potential hexagonal plates are difficult to distinguish from the irregularly shaped insoluble particles on the pictures because of the limited spatial resolution of the SEM (an example is shown below). Hence, we cannot rule out that CaO is responsible for the needle formation in case of the fly ash suspension just because we do not see any needles from the spruce suspension. This has been added to the manuscript (P11 L1-6).

Filtered fly ash suspension:



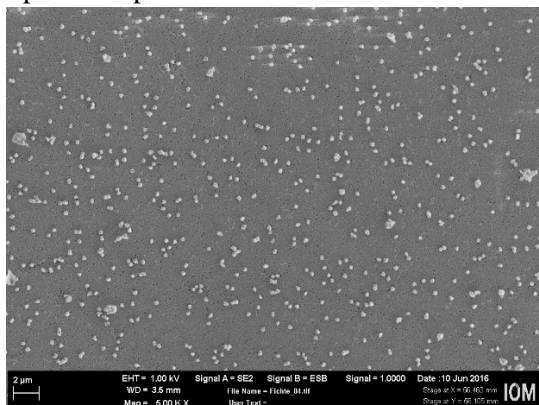
Unfiltered spruce suspension:



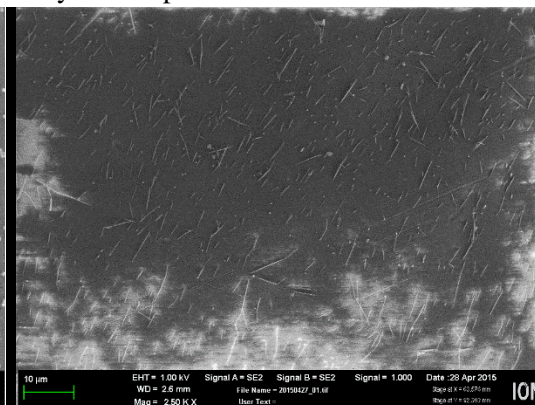
- I am not fully convinced that the particles produced through the wet system are less efficient. The authors conducted a direct comparison of the ice nucleating abilities of the wet and dry generated particles; however, it is necessary to demonstrated that the monodispersity of the 300 nm particles from both system is comparable.

Even though we did not perform the multiple charge correction in the case of the suspension samples, our results show clearly that the ash particles from wet generation must be less IN efficient than the particles from dry generation. Accounting for multiply charged particles would only lead to a further decrease in f_{ice} and n_s , respectively (this has been stated in the original manuscript, P11L13-14). However, we understand your concerns and attempted to estimate the effect a large number of multiple charges could have on f_{ice} . By selecting 300 nm particles for the experiments, which is far to the right of the maximum of the size distribution, we already assured that a majority of multiply charged particles is not possible. To estimate the multiple charge fractions in the suspension measurements, we weighted the bipolar charge distribution (Wiedensohler, 1988, Journal of Aerosol Science), i.e., the probability of the particles to receive one, two or three negative charges in the neutralizer, with the measured size distributions of the ash-water suspensions. However, there is a caveat to this estimate, as crystals will probably have occurred in the size distribution measurements as well. It turned out, that the highest multiple charge fractions would probably occur for the fly ash suspension (+US), where we calculated 80.5 % singly, 16.8 % doubly, and 2.7 % triply charged particles. The multiple charge fractions were even lower for the other suspension samples. Would we perform the multiple charge correction using these fractions, our measured data would be reduced by a maximum factor of 2 only. A short version of this was added to the manuscript (P15 L10-16). Having a look at the SEM pictures of the suspension particles shows us, that we collected a rather monodisperse aerosol (apart from the needles in the case of fly ash). Large particles in the size range of doubly or triply charged particles are nearly absent (see figures below), telling us that the multiple charge fraction is likely even lower than the one from our example calculation.

Spruce suspension:



Fly ash suspension:



Specific comments:

- Page 1, line 20: The Hallett-Mossop (1974) study introduces one of the multiple secondary ice formation mechanisms only. I suggest using a better reference such as Heymsfield and Willis (2014): Heymsfield, A. J., and Willis, P. (2014), Cloud conditions favoring secondary ice particle production in tropical maritime convection. *J. Atmos. Sci.*, 71, 4500–4526, doi:10.1175/JAS-D-14-0093.1.

Done.

- Page 1, line 21: I suggest replacing this reference with a more appropriate one.

We now cited Rosenfeld and Woodley, *Nature* (2000), Koop et al., *Nature* (2000), Murray et al., *Phys. Chem. Chem. Phys.* (2010)

- Page 2, line 3: provide pages from P&K or the actual paper(s).

We now cited Szyrmer and Zawadzki, *BAMS* (1997)

- Page 2, line 5: Cite the studies here.

Done.

- Page 2, line 12: “coal ashes contribute a major proportion of anthropogenic aerosol emissions” please provide the reference and number (estimate).

Since we cannot provide an estimate, we now only state that ash is the primary coal combustion product and cite a report of the US Geological Survey (Kalyoncu and Olson, 2001).

- Page 2, line 15: “yields global annual emissions of 30 Mt” is this comparable to mineral dust? Please provide the mineral dust annual emissions.

We added that global annual dust emissions are estimated to vary between 700 and 3000 Mt/a. This is taken from Textor et al., *ACP* (2006).

- Page 2, line 17: delete “however”.

Done.

- Page 2, line 27: This needs to be better organized. The authors jump between old and recent studies back and forward.

We omitted the first reference to Umo et al., 2015. Now the studies are in chronological order.

- Page 2, line 32-34: “it could be shown that water soluble components were responsible for differences in the ice nucleation ability of fly ash samples from different power plants.” Provide reference here.

Done.

- Page 3, line 5: “Umo et al. (2015) assumed that the different” Did they assume or did they provide evidence of?

There is no evidence provided. We replaced “assume” with “suggest”, otherwise the sentence was not altered.

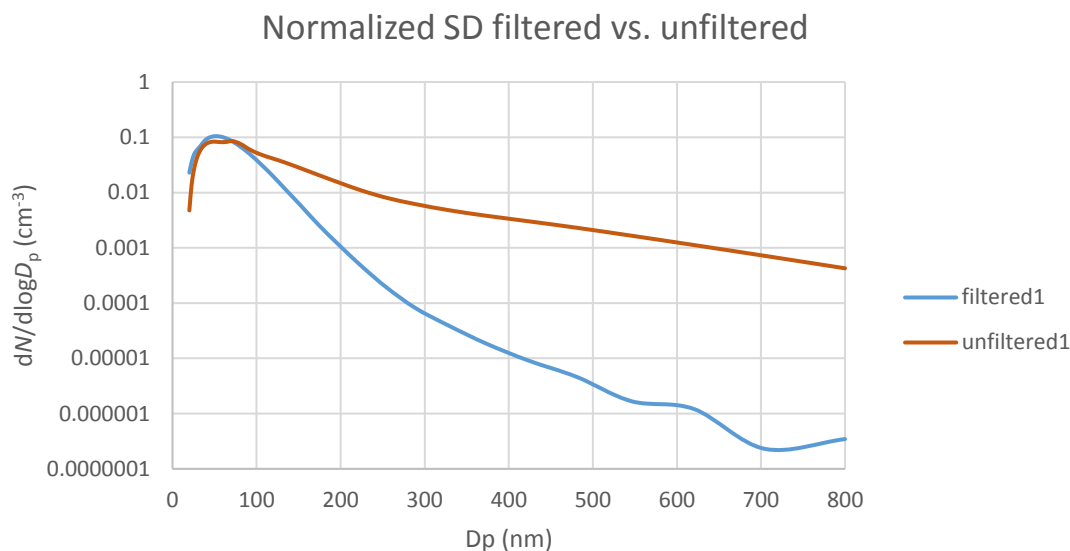
- Pages 3-4, lines 32-1: “the number of particles with three or more negative charges was negligible”. Please report the fractions or percentages of the multiple charged particles.

A table with the doubly charged fractions was added in the manuscript (Tab. 1). We replaced “negligible” with “smaller than 1 %” to be more precise.

- Page 5, line 7: why 200 nm? What did not the authors try a smaller size to ensure that insoluble particles are not present? Please provide the resulting size distributions of the atomized filtered solution.

Filtering down to sizes as small as 100 nm would be possible but would require more effort. We cannot rule out that insoluble particles smaller than 200 nm passed through in the process of filtering. The SEM images of the filtered ash suspension indicate that the fraction of insoluble particles is low. Below, we added a comparison of the size distributions of the filtered and not filtered fly ash suspensions. It can be seen that a significant fraction of particles larger than 200 nm has been removed. Those that are still there are formed from dissolved material.

Also, LACIS measurements of the filtered fly ash suspension yielded f_{ice} values close to what was found for ammonium sulfate particles. This shows us that the particles from the filtered suspension only have very little, if any, IN activity, and this is the point we wanted to make. The LACIS measurements of the filtered fly ash suspension, as well as the ammonium sulfate measurements, have been added in the manuscript (Fig. 3d).



- Page 5, line 9: Why was not beech bottom ash particles analyzed by AA?

The beech ash sample was provided late in the course of our experiments. At this point, the other samples had already been analyzed in Sweden. However, we did not want to omit the quite interesting data. We added an explanation in the manuscript (P6 L24-P7L1).

- Page 5: What are the uncertainties associated with the data presented in Figure 1?

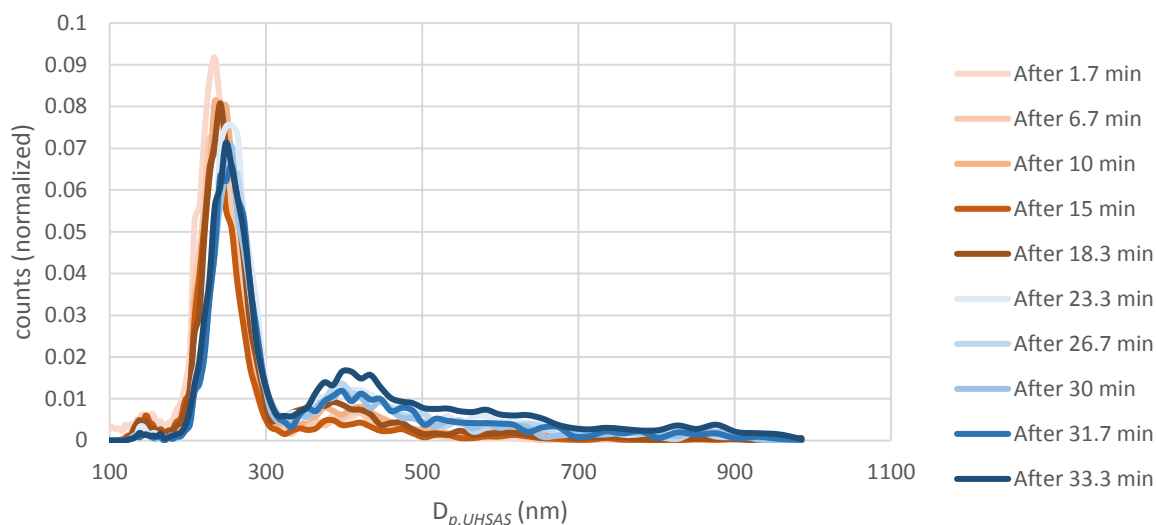
We decided to show the results of the atomic adsorption spectroscopy measurements, which are presented in Fig. 1, in the form of a table as well (Tab. 3). Here, the uncertainties are reported for each sample and each investigated compound.

- Page 5, lines 24-30: I am wondering how consistent and how reproducible is the data obtained from the dry generation system. Can the authors provide the size distributions obtained with the dry system separated by 15 or 30 minutes? Was it the multiple charged particles checked continuously with the UHSAS?

UHSAS measurements were not performed continuously during the course of the experiments as the instrument was not available over the entire period. However, the multiple charge fractions were checked on several occasions for each of the five samples. Therefore, particles were generated in the same way as for LACIS measurements and sampled for several minutes. We included a time series of a 35 min UHSAS measurement below. During this time, the fraction of multiply charged particles does indeed increase. As our measurement time with LACIS is in the range of 20 minutes, we are certain that a comparable amount of multiply charged particles was led into the flow tube as was determined in the UHSAS measurements.

We do not see a need to include this graph in the manuscript as it does not contribute to a better understanding of the presented results.

Size distribution UHSAS
(20 s samples taken during a 35 min measurement)



- Page 5, lines 33-34: Can the authors provide an activation scan with the filtered solution to confirm this?

CCNc measurements with the filtered fly ash sample have been performed. We added the following to the manuscript (P11 L17-21): “CCNc measurements with particles from the filtered fly ash suspension indicated a rather low hygroscopicity ($\kappa = 0.06 \pm 0.01$). However, this does not necessarily mean that the components in the generated particles are not soluble. Sullivan et al. (2009) give a value of $\kappa = 0.011$ for CaCO_3 , which is weakly soluble (Plummer and Busenberg, 1982). The generated particles could hence be composed of a mixture of CaCO_3 together with other compounds.”. We also added a sentence concerning the CCNc in the methodology section (P5 L3-4).

- Page 8, lines 8-10: Which fraction of particles passed through? Was this confirmed with the size distributions from the UHSAS?

From the UHSAS measurements of the filtered fly ash suspension we cannot derive the fraction of insoluble particles left after filtering. This is due to the overlapping signal of the two particle populations. On the SEM images of the filtered suspension, however, we do not see any other particles than the crystals. We could detect an ice fraction of 25 % at -35°C for the unfiltered ash suspension (this is the value we obtained when accounting for the occurrence of the crystals, i.e., only for the non-crystalline particles). For the filtered suspension, we only detected 1.3 % ice fraction which is close to our detection limit. This tells us a) that there cannot be a lot of the insoluble particles in the filtered suspension (because these were found to be IN active), and b) that the crystals are not very good INPs.

- Page 8, lines 15-16: Why the data from the water soluble material remaining in the filtered ash-water suspension is not shown?

We changed Fig. 4 from the original manuscript in so far as that it is a multiple panel figure now (Fig. 3). This gives us the opportunity to show the requested data, as well as the ammonium sulfate data points (Fig. 3d) without overcrowding the plot.

- Page 10, lines 3-4: “There is a trend of beech bottom ash being the most effective”. I am wondering why out of the three wood samples beech was the least studied (although it was the most effective at nucleating ice)?

See our answers above (P2 and P5 of this document).

- Page 10, lines 15-18: “The fact that the wood ashes contain significantly more K than the brown coal ashes, which in this case is soluble, is a possible reason for the lower ice activity in comparison to the brown coal ashes. According to this, insoluble K could be the decisive element determining the freezing behavior of the brown coal ashes” What about CaO ?

According to our hypothesis, the CaO in both wood and coal ashes would react with water to form Ca(OH)₂. This would happen both in the suspension and as well as for dry particle generation (after activation to cloud droplets in the flow tube). However, if the larger CaO content in the wood ashes really is the reason for them being less IN efficient, then why would the coal fly ash be more efficient than the bottom ash, even though it contains more CaO? This is not logical from our point of view and hence we did not mention CaO as a possible factor in the original manuscript.

- Page 10, lines 20-22: “the brown coal ash particles might be more efficient at nucleating ice because of surface defects such as lattice dislocations caused by impurities or crystallographic dislocations.” This is not clearly supported by the presented data. I am wondering why the authors did not provide SEM images for the bottom wood ashes to compared the surface defects with those of the bottom coal ash particles.

An SEM image of spruce particles from wet generation was included (Fig. 2c). Unfortunately, we cannot make clear statements about the surface defects because of the limited spatial resolution. This is why we formulated our hypothesis in the form of a speculation. We do not know if this really is the case, but we wanted to share our thoughts with the reader.

- Page 11, Lines 1-3: “It has been shown that certain types of amorphous particles are able to nucleate ice (Murray et al., 2010b; Wilson et al., 2012), but it remains to be examined whether the amorphous components in fly ash are ice active as well”. This only happens at very low temperatures relevant to cirrus clouds.

Amorphous fly ash particles are likely composed of aluminosilicate glass (Ramsden and Shibaoka, Atmospheric Environment, 1984; Querol et al., Atmospheric Environment, 1996). This has been added to the manuscript (P14 L17-19). Unlike the glassy SOA particles which were investigated in the references you cited, glass is stable at temperatures higher than -38 °C (even at temperatures higher than 0 °C). Hence, in case the amorphous particles in the fly ash cause IN, we assume that this would happen at temperatures higher than the homogeneous freezing limit.

- Page 11, lines 4-6: “Tab. 1 and Fig. 4 additionally show the 5 parameters and fit curves to measurements with K-feldspar and mineral dust particles (K-feldspar, Arizona Test Dust, NXillite, Fluka kaolinite) coated with sulphuric acid (clay mineral baseline, Augustin-Bauditz et al., 2014). I may have missed but I could not find the Arizona Test Dust, NXillite, and fluka kaolinite data.

For the data presented in Augustin-Bauditz et al. (2014), K-feldspar, ATD, illite and kaolinite particles were coated with sulfuric acid. Their immersion freezing behavior was then investigated with LACIS. It turned out that all coated particles featured the same freezing behavior, even though they differed from another before coating. Because the data was on the same line, and because weathering feldspars turn into clay minerals, it was proposed to call this line the “clay mineral base line”. This was added to the manuscript (P14 L30-P15 L1). Only this line is shown in Fig. 3, not the results of the individual dusts. We hope that this brings more clarity.

- Page 11, lines 26-30: “By counting ~ 900 particles on SEM images, it was determined that ~ 78 % of all particles are crystals. This value may be smaller in the flow tube as the fragile crystals could break upon impact on the filter leading to a multiplication. As only 22 % of the droplets contained a spherical fly ash particle during the experiments with the suspension sample (+US), the original data was corrected by a factor of $1/0.22 = 4.54$ which is also shown in Fig. 4 for a direct comparability to the ice nucleation ability of dry particles from the same sample.” How confident are the authors about this calculation? What is the uncertainty associate to it? $900 \pm ??$, $78\% \pm ??$, $22\% \pm ??$, $4.54 \pm ??$

These numbers were determined by counting the number of crystals and spherical particles on an SEM image. In doing so, particles that have been counted were marked so that there is no possibility for double counts. In case you are alluding to the statistical significance of this estimate, we now included the confidence interval for the 95 % confidence level, which is +/- 3% of the given values. This means that the actual fraction of needle shaped crystals is between 75% and 81% with a probability of 95%. This is now included in the manuscript (P15 L27-28).

- Page 11, lines 32-35: “which is a clear lowering of the ice nucleation activity by a factor of 4 compared to dry particle generation, i.e., suspending the particles in water reduced their ice activity in the temperature range below -31 °C.” I am not sure how valid is to directly compared the ice nucleating abilities of the ash particles generated from the wet and dry systems given that those obtained from the wet generation are not corrected for multiple charged particles.

Here we would like to refer to the estimate given above (P3 of this document). Accounting for the multiple charges in the experiments with wet particle generation would only lead to a further lowering of f_{ice} and n_s . After the cited sentence we added “Note that this lowering might be larger depending on the multiple charge fractions in case of wet particle generation.” (P16 L4).

- Page 12, lines 4-13: This is an interesting observation. I am wondering why the authors did not further expand this with other samples (e.g., bottom ash brown coal).

In case of the other ash suspensions (brown coal bottom ash and spruce bottom ash), the result are already close to the LACIS detection limit. As omitting the ultrasonic treatment only makes the samples less IN efficient, we would not expect to see a significant difference for these samples. Also, this behavior has been observed for soil dust suspension particles (cited in the original manuscript P12L10).

- Page 12, lines 4-5: “the f_{ice} values of the fly ash suspension which was not put in the ultrasonic bath are clearly lower than those of the fly ash suspension with ultrasonic treatment.” Here and along the results section, how many scans were conducted for each sample for each specific set of conditions? How reproducible are they?

As stated in the caption of Fig. 4 on P9 of the original manuscript, at least three measurement were performed in case there is an error bar on the data point. In case there is no error bar shown, we performed one or two measurements (added on P11 L30-32). For each measurement at least 2000 particles were detected by our optics. LACIS measurements are very reproducible due to this large number of counted particles and the small temperature uncertainty (added on P5 L21-22). But they are also very time consuming which is why we need to consider costs and benefits of repeating measurements.

- Page 14, lines 1-14: This part is too speculative with many unsupported assumptions. This should be deleted.

We revised this section in terms of citing more field observations of fly ash particles and calculating the in-stack concentration especially for the power-plant Lippendorf. Even though the section contains a lot of speculation, we would like to keep it in the manuscript. Firstly, we clearly state when we make a certain assumption and secondly we think that this estimate supports the relevance of the topic.

Figures:

- Be consistent with the labels (a and b, or 1 and 2)

Done.

- Figure 1. I am not sure how useful is panel 2.

We would like to include the second part of the analysis, as this actually shows measured fractions of the investigated elements, whereas the first part was estimated by recalculating the measured concentrations of major ions into their most common oxide forms. The second part hence provides valuable information on top of the calculated composition.

- Figure 3: It would be nice to have a similar image of the wet generation system of a bottom ash sample. Additionally, Fig. 1 indicates that Wood ashes contain much more CaO than the coal ashes. Therefore, the needle crystals should be more pronounced in the wood ashes if the reasoning presented here is correct.

An SEM image of spruce ash suspension particles has been added to the manuscript (Fig. 2c). As stated earlier the non-existence of needles on this image does not necessarily disprove our hypothesis. At one occasion, we also observed hexagonal plates on the SEM images of fly ash particles from wet generation. This could also be the case here and we cannot distinguish the plates from the insoluble spruce ash particles due to the limited spatial resolution of the SEM.

References cited in our answers:

- Augustin-Bauditz et al., GRL (2014)
Kalyoncu and Olson, US Geological Survey (2001)
Kim et al., Journal of Materials Chemistry (2009)
Koop et al., Nature (2000)
Murray et al., Phys. Chem. Chem. Phys. (2010)
Plummer and Busenberg, Geochimica Et Cosmochimica Acta (1982)
Querol et al., Atmospheric Environment (1996)
Ramsden and Shibaoka, Atmospheric Environment (1984)
Rosenfeld and Woodley, Nature (2000)
Sullivan et al., ACP (2009)
Szyrmer and Zawadzki, BAMS (1997)
Textor et al., ACP (2006).
Umo et al., ACP (2015)
Wiedensohler, Journal of Aerosol Science (1988)