Author's response

Referee #1

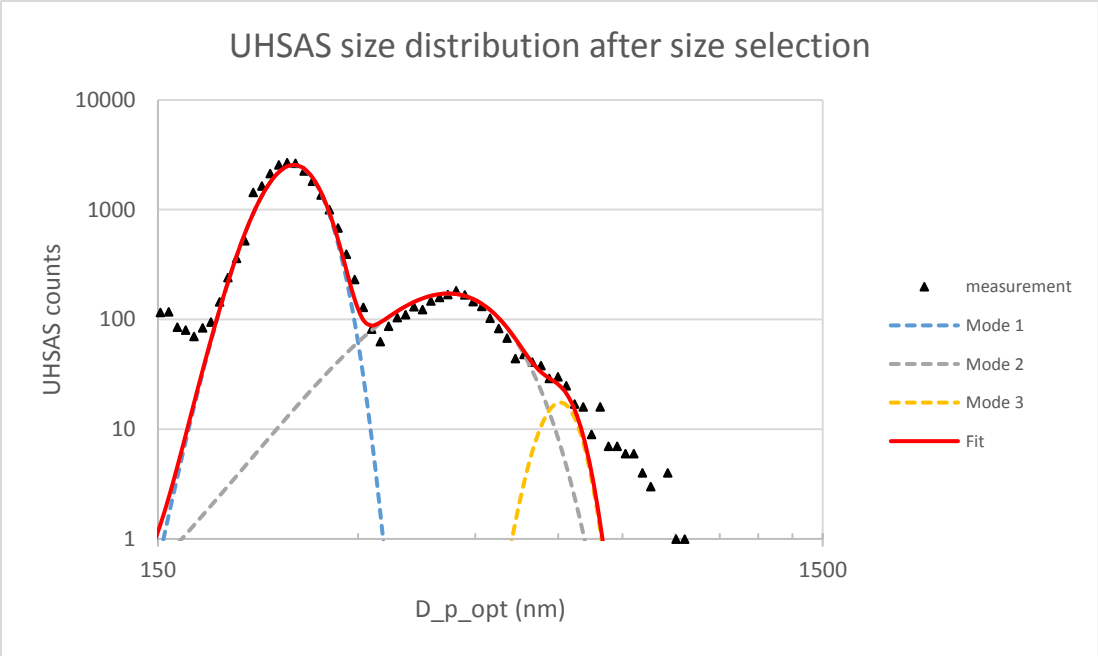
We would like to thank the referee for reviewing the manuscript once again and for pointing out still existing ambiguities. The referee comments are colored, our answers are given in black.

I would like to thank the authors for improving the quality of their manuscript and for clarifying many important points listed by all 4 reviewers. Although most on the points highlighted in my original review were addressed (mainly the specific comments), there are key points that need to be clarified before the manuscript can be accepted. The main points are listed below:

1. The addition of Table 1 with the fraction of doubly charged particles is very valuable. However, I am surprised there are not triply charged particles in the studied ash samples. Note that you provided the triply charged particle fraction in the answer to point #4 but they are not given in the Table 1. The authors did not provide the particle size distribution (PSD) of the 300 nm size selected particles as requested. I think this needs to be part of the main text. Note that the PSD should be in log scale to better identify the doubly and possibly triply charged particles.

We are not sure in what way the results of the UHSAS measurements could contribute to the overall comprehensibility of the manuscript. Such a graph would only contain information that has already been included in the form of Table 1 (note: Table 1 gives the double charge fractions of the dry generated particles, only!). In our answers to the referee comments of the first discussion round, we did include a graph showing the size distribution of dry fly ash particles from UHSAS measurements. Because the referee asked for it a second time, we included the same example, now in logarithmic scale and showing explicitly how we determined the multiple charge fractions (see the three modal fit in the figure below). From the analysis of this measurement, we found a single charge fraction of 80 %, a double charge fraction of 18.9 % and a triple charge fraction of 0.9 %, i.e., the number of triply charged particles was negligibly low. The results for the other dry generated samples are presented in Tab. 1. As stated in the manuscript, the triple charge fractions were determined to be smaller than 1% in all cases. As none of the remaining referees saw a need for including the UHSAS measurements in the manuscript, we would like to avoid adding another graph which is not substantial to the topic itself.

With the triple charge fraction given in the answer to point 4 from the first discussion round, we were referring to an estimate for the suspensions (i.e., wet particle generation), which we calculated by weighing the bipolar charge distribution with the measured size distributions, i.e., this number is rather modeled than measured. The wet particle generation data was not corrected concerning these calculated values, because we produced particles from purely soluble material probably in all size ranges and cannot be sure how the size distributions look like for the particles from insoluble material only. This makes a correction impossible. This was discussed in our answers to point 4 in the last review, and parts of it were included in the manuscript (P15 L10-16).



2. It is really sad that the authors were not able to conduct the missing experiments. I think an effort in this direction could have been made by requesting an extension to submit the revised manuscript. "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." Although it is true that it is nice to show that the ice nucleating abilities of beech ash and the wood bottom ashes are comparable, the reviewer does not see the point to add this data if the reasons of why beech ash particles behave similarly to the wood bottom ashes are not provided. I mean, is this observation simply a coincidence, or is it because the chemical composition, soluble material, and/or particle's surface properties of both samples are really comparable?

We agree that additional LACIS measurements likely would have given some interesting insights. We would like to clarify that we usually obtain a few data points a day after hous of preparation and measurements, meaning that it would take us several months to conduct all the experiments that the referee proposed in the first discussion round. Furthermore, the instrument has been shut down for the last months because of construction work in our laboratory.

Admittedly, it is a bit unfortunate that we do not have the chemical composition analysis for the beech ash, because then we could have checked if its K content is similar to the one of spruce and birch. From our point of view, including the beech data is an interesting addition because its ice nucleation efficiency is so similar to the other wood ashes. We do not think that this is a coincidence but rather related to the amount of (in this case soluble) K. As this has been discussed in the manuscript already, nothing was changed.

3. The reviewer is not really satisfied with the answer given to this point: "Possibly, CaCO3 is the dominant phase of the water soluble fraction. During the combustion process, CaO is produced (present in the initial sample, see Fig. 1 and Table 3) which may react with H2O to form Ca(OH)2. CaCO3 may form from Ca(OH)2 upon reaction with CO2 from the air (Steenari et al., 1999). That we do not see any needles on the SEM image of spruce ash suspension particles (Fig. 2 (c)), even though this sample contains 11 % more CaO than the fly ash sample, is possibly due to the variety of different crystal shapes which CaCO3 is known to occur in and which include needles, hexagonal plates, and others (Kim et al., 2009). Particularly hexagonal plates might not be as easily

distinguishable from the insoluble particles as the prominent needles and might be seen, at least to some extent, in Fig. 2 (c), where the resolution of the pictures unfortunately does not allow a better analysis." The presence or absence of this large needle particles or small hexagonal plates after passing through the dryer needs to be better quantified given that they significantly change the size distribution of the particles entering the LACIS and hence the concentration and potentially the size of the cloud droplets. I think this points deserves a solid and clear explanation.

The fraction of solution particles should only depend on the concentration of ash in the suspension (which we kept constant throughout the experiments). As they are only a side effect of our particle generation, we focused on determining their abundance, which is important for the correction of the f_ice values. The size distribution of the droplets in LACIS is always comparably similar and independent of the shape of the aerosol we feed in, as high supersaturations (>10%) ensure that every single particle is activated to a droplet. Nothing was changed.

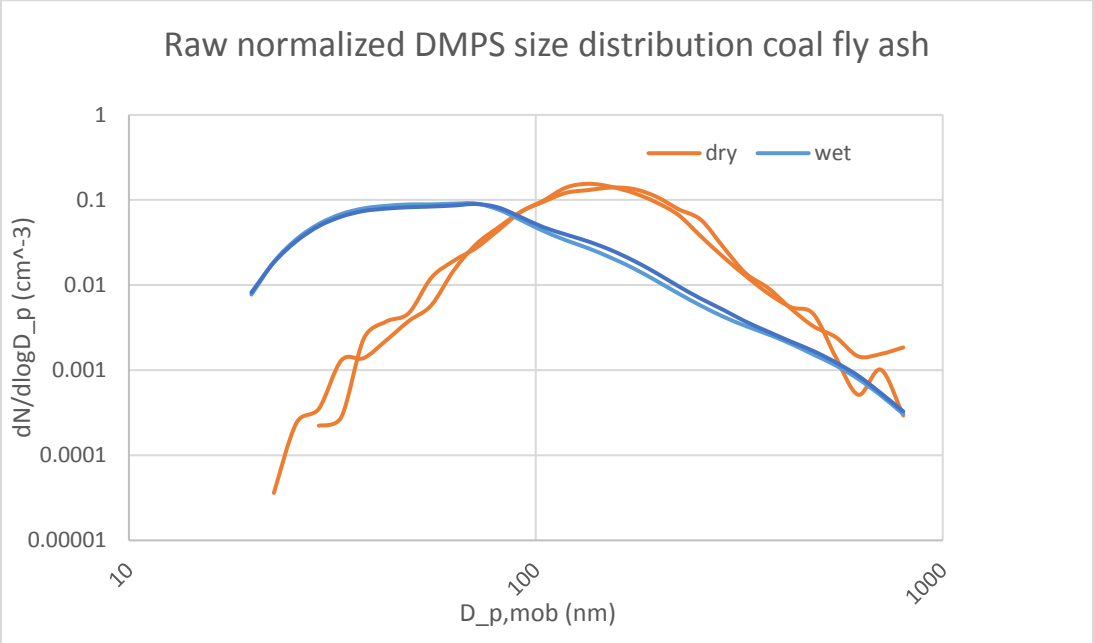
4. A good way to support the conclusion that the particles produced via the wet system are less efficient that those produced via the dry system will be adding the size distributions of the 300 nm (wet system) together with the size distribution of the dry system. In this figure readers will see how comparable the PSD are and what is the effect of multiple charges in the particles. The authors mentioned that the fraction of multiple charge particles is around 20% for the dry system and very low for the wet system. 20% is a large fraction and this can be the reason of why the dry particles showed a better ice nucleating efficiency. Is this 20% from the PSD obtained at the beginning of the experiment or at the end? The authors showed that the fraction of multiple charged particles increases with time.

As stated earlier, we likely produced a fraction of particles consisting of soluble material when we measured size distributions from atomizing the suspensions. Consequently, it would not make sense to directly compare the size distributions from wet and dry particle generation and expect to see a difference in the double charge fractions. We included this comparison here (see below) as it was requested by the referee, but we do not see any reason to include it in the manuscript. It might rather give the (wrong) impression that we know the size distribution of the insoluble particles generated from suspensions.

We indeed stated that the double charge fraction for particles from wet generation is possibly lower than what we determined for particles from dry generation, because we saw only few particles larger than 300 nm on the SEM images. However, this difference in the double charge fraction cannot be the reason for the higher ice nucleation efficiency of the particles from dry generation, because for the latter we performed a double charge correction. Basically, this means that we subtracted the ice fraction caused by the large doubly charged particles from our measured ice fractions (for details, see Hartmann et al., 2016, JAS). This correction was not done for the particles from wet generation, and the correction would rather decrease the f_ice values further. Regarding this, we said the following concerning the wet generated particles in the manuscript (P15 L11 ff): "We found that the highest amount of multiply charged particles was probably present in the experiments with the fly ash suspension with ultrasonic treatment (80.5 % singly, 16.8% doubly, and 2.7 % triply charged particles). Would we perform the multiple charge correction using these fractions, our measured data would be reduced by a maximum factor of 2 only." Therefore, an uncertainty related to the omitted multiple charge correction has been given in the text, which we feel is all that is needed.

Yes, the fraction of doubly charged particles increases with time. However, this increase is only small over the first 30 minutes of particle generation. As said in the manuscript, and our answers in the first discussion round, all LACIS measurements are done within these first 30 minutes. After thawing

and re-icing, our particle generation setup was prepared for a new experiment, which includes cleaning of the cyclone and checking of the flows. The double charge fractions presented in Table 1 correspond to the mean values of doubly charged particles in LACIS during these first 30 minutes of dry particle generation. Unfortunately, we could not check the multiple charge fractions continuously with the UHSAS over the entire measurement period, as the instrument was not available at all times. However, they were checked on several occasions.



5. Given that lack of data I think the following statement should be softened or the lack of data acknowledged: “There is a trend of beech bottom ash being the most effective”

We are only talking about a trend here, meaning that a tendency can be seen but there is no profound evidence. We are not sure how to soften this statement further, so nothing was changed.

6. “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”. The reviewer considers that there is no need to keep this in the manuscript. It does not add anything valuable to the paper and it will confuse readers which are not very familiar with this topic/calculation.

We are still of the opinion that Sec. 4 should remain in the manuscript because it puts our results into perspective. Furthermore, we have often been asked to include an estimate of the atmospheric relevance in other papers from our group in the past. As none of the remaining referees wants any more changes with respect to this section, we would not want to omit it.

Referee #2

We would like to thank the referee for reviewing the manuscript once again. The original comments are colored, our answers are given in black.

General comments:
I have two more comments regarding the BET calculations:
- First, the new left y-axis in Fig. 4 is dispensable from my point of view as it is the same as the right y-axis. The concern to compare the same metrics to each other is not addressed with this second y-axis. I agree that it might be too much to get the BET surface for your samples, however, since you did already an estimate of the conversion factor between your ns and the ns, BET provided by Umo et al. (2015), why don't you use it in the plot? You could provide an uncertainty area around the curve. This would be more valuable than duplicating the y-axis.

It was our intention to convey the difference between the two n_s metrics by adding the second axis label. Converting our data into BET based n_s values and using only one axis might make the wrong impression, i.e., that we know the specific surface area which we did not measure. In the text, we discuss the possible uncertainty that may arise from comparing geometric and BET based n_s values. As a result, we would prefer to leave Fig. 4 unchanged.

- Second, for the calculation on P17,L24 the volume of the particles needs to be calculated, therefore the volume equivalent diameter needs to be used instead of the mobility diameter (Kulkarni 2011). You assumed a spherical shape and a mobility diameter of 300nm for your particles. The validy of using the mobility diameter depends on the shape factor of the ash particles. This is not considered in the calculations. From your manuscript I understand that for fly ash particles the assumption of sphericity seems to be valid. However, the SEM images do not support this assumption for the bottom ash particles. Please re-consider your calculations. This should be included in an uncertainty band around the curve in Fig.4

You are of course right in saying that the volume equivalent diameter needs to be used for the calculation. However, when assuming spherical particles, volume equivalent and mobility diameters are identical. The assumption of spherical particles has been made because we cannot give a profound estimate of the shape factor without analyzing a statistically relevant amount of particles on SEM images with higher resolution than the ones currently available. Furthermore, we do not expect the deviation from the spherical shape to cause a difference of 3 orders of magnitude in n_s, i.e., a significant improvement in the agreement between our data and those from Umo et al. (2015) is not expected. Hence, we would like to avoid the time consuming derivation of the volume-equivalent diameter of the non-spherical ash particles.

Technical comments:
- Delete "(a)" on p.13, first line of Figure 3 caption. The full circles are shown in all other subplots as well, not only in (a).

Done.

Referee #3

Referee #3 agreed with the current version of the manuscript and supported publication.

Marked differences

Nothing was changed in the manuscript except the deletion of (a) on the first line of the caption of Fig. 3.