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.

Referee comments for manuscript acp-2016-208 by Grawe et al. "The immersion freezing behavior of ash particles from wood and brown coal burning"

Summary:

The manuscript presents results obtained at the Leipzig Aerosol Cloud Interaction Simulator, LACIS, on the ice nucleation behavior of ash particles from wood and coal combustion. The chemical composition of the different ash samples was obtained from atomic absorption methods. The main findings were that fly ash from coal burning was the most ice-active sample and was the sample with the highest fraction of SiO_2 . Furthermore, the effect of differences in the particle generation method (dry vs. wet, treating the sample in an ultrasonic bath vs. not using it) was investigated. It was found that wet generation reduces the ice nucleation ability of the ash particles compared to the dry generation method. Particles treated in an ultrasonic bath had a higher ice nucleation ability than non-treated wet generated particles.

Ice nucleation induced by ash particles has received only little attention by the scientific community. The presented measurements are therefore of interest to the readers of *Atmospheric Chemistry and Physics*. Also the investigation of the influence of the generation method on the results is interesting. However, the manuscript and particularly the discussion of the results is often written in a vague and imprecise way and hardly adds to our understanding of the underlying ice nucleation process. I thus only recommend publication after addressing the comments below.

I apologize for any overlap with the other reviewers' comments.

Major Comments:

Introduction:

- The literature summary on p.2 l.27ff lacks depth. Who measured what, at which conditions? What type of bottom ash did Murray et al. (2010a) investigate? Regarding the first lines of page 3 it is not clear to me which results were found by Umo et al. (2015) and which by Murray et al (2010a).

The cold stage used for the experiments by Umo et al. (2015) is described in Murray et al. (2010a), this is why the reference was added after "cold stage setup". We added Whale et al. (2015, AMT) where additional information concerning the setup is provided. The structure of the sentence was changed.

- Since the study is very similar to that by Umo et al. (2015), the earlier study should be described in more detail and the novelty of the present study should be described. What sizes did Umo et al. (2015) investigate? Which surface area? Already describe the freezing method here. And convince the reader why there is a need for your study.

We added that µL and nL droplets of 0.1 wt% ash in water were investigated by Umo et al. (2015), either by nebulizing droplets onto a glass slide or by pipetting (P3 L10-12). Total surface areas per droplet are not given explicitly in the Umo et al. (2015) paper which is why they are not mentioned here. We also added that there is a need for further investigations as there are only few measurements concerning the IN efficiency of ash particles which is why it is important to better understand the effect of sample origin and composition (P3 L20-21). Furthermore we were able to use different kinds of particle generation and sample preparation which has not been investigated by Umo et al. (2015).

- One could also add motivation from field observations of biomass burning, e.g.: Prenni et al. 2012, GRL; McCluskey et al. 2014, JGR

We added the suggested references on P2 L6, following the citation of Petters et al., JGR (2009).

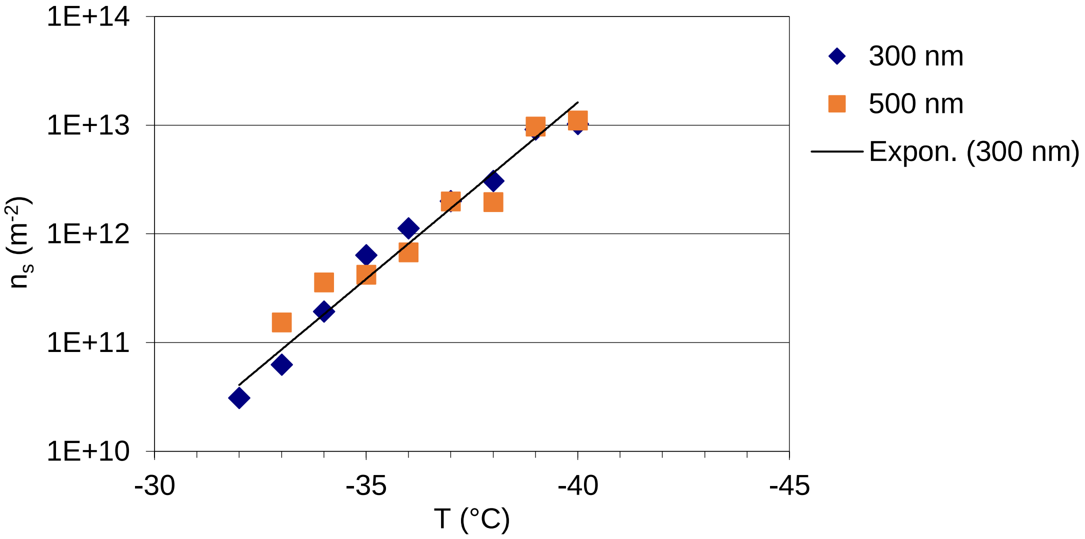
Methods:

- The representativeness of 300 nm particles is not shown or even mentioned. Why were particles of this size selected? How do the size distributions of the investigated ashes look like? Is 300 nm the mode diameter or at least close to it? Can it be assumed that larger/smaller particles have a similar composition and is the ice nucleation ability expressed as ice-active surface site density thus potentially scalable or are changes to be expected with size?

From size distribution measurements during coal combustion, we know that there is a bimodal distribution: one submicron peak below 0.1 µm and one broad supermicron peak in the range from 3 to 50 µm (Damle et al., 1981, Aerosol Science and Technology 1:1). As particle collection techniques are less efficient for submicron particles (Flagan and Seinfeld, 1988, Fundamentals of Air Pollution Engineering), these will be more abundant in the atmosphere, and we decided to select particles smaller than 1 µm. 300 nm particles were chosen because we could get sufficiently high and stable number concentrations from the variety of samples when selecting this size (the mode diameters vary from 130 to 200 nm for dry particle generation). While there are a lot of different particle types included in bulk fly ash (i.e., Ramsden and Shibaoka, 1982, Atmos. Environ. 16, 9), it has also been found from single particle analysis that the chemical composition of fly ash particles with aerodynamic diameters between 0.2 µm and 4.8 µm is remarkably consistent (Kaufherr and Lichtman, 1984, Envirn. Sci. Technol., 18). Hence, we would not assume to see a difference in n_s, would we select another particle size.

In case of bottom ash, exemplarily, measurements were performed with 500 nm brown coal bottom ash particles which showed no difference in n_s within the range of our measurement uncertainty compared to the measurements with 300 nm particles (see below, now also added in Fig. 4 as green triangles). As LACIS measurements are very time consuming and we do not expect to see a difference in n_s in the size range we are able to select, we would like to avoid performing further experiments with other particle sizes.

In the manuscript, a paragraph explaining why 300 nm were chosen was added on P4 L18-28.



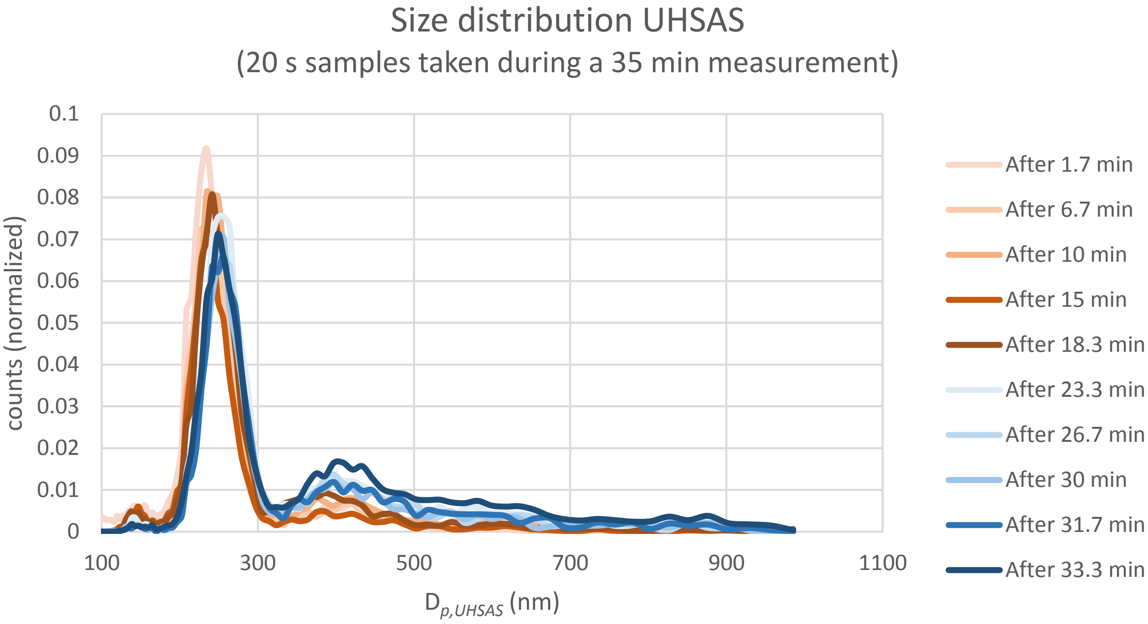
- The description of the wood samples is very vague. What was burned? Just the wood or in addition bark, leaves, needles, beechnuts…? Which part of the wood? How old was the wood (i.e. freshly cut, stored for a long term). What type of spruce, birch, and beech? Have the wood samples been treated in any way before burning? Are these commercially available fuels?

All wood ashes were burned in private fireplaces, and the detailed information you ask for is mostly not available. As the conditions were different, it is astounding that the wood ashes are all very similar in terms of their IN ability. This supports that wood bottom ash in general might be similar in its IN activity, and we do not see a reason to go that far into detail. In the manuscript, we added that no leaves or small branches were included and that the wood was stored for drying prior to the combustion process (P6 L6-8).

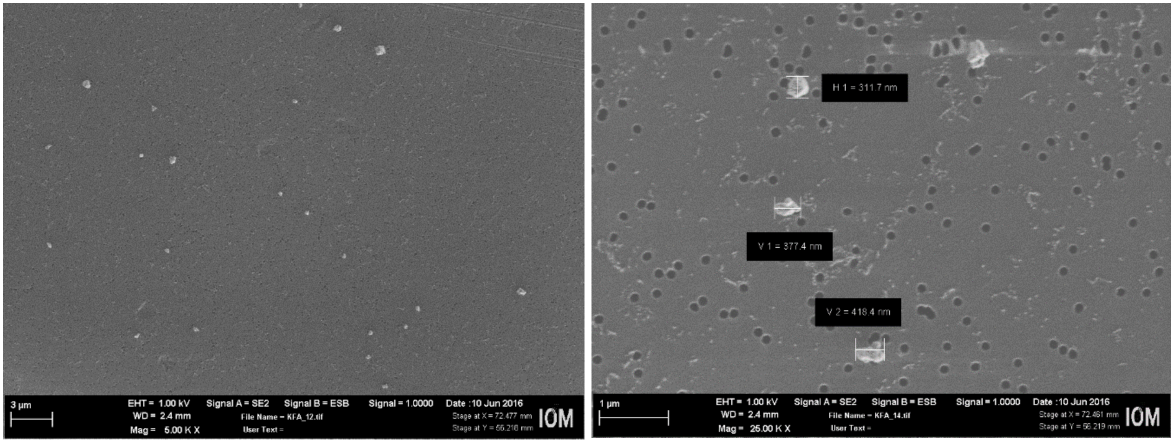
- The disagreement between the measurements with the UHSAS and the observations of multiple charged particles on the SEM filters is disturbing. I am glad this is discussed in the manuscript but I encourage the authors to put more effort in finding the reasons for this discrepancy. That the filter analysis is not representative appears as an oversimplified argument. If this is the case then the analysis should be done in a way that it is representative, e.g. analyze a larger area of the filter. How representative are other conclusions drawn from the filters?

The multiple charge correction was performed based on size distribution measurements with the UHSAS (optical diameter). For this, 300 nm particles were generated in the same way as for LACIS measurements and sampled for several minutes. The filter samples, however, were collected over several hours to assure a sufficiently high concentration on the filter surface. New UHSAS measurements (see below) show that the cyclone, which we used to minimize multiply charged particles, is filled after around 30 minutes, so that more larger particles are detected than in the beginning of the UHSAS measurement. 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 multiple charge fractions (now in the manuscript as Tab. 1) correspond to the actual fractions in the flow tube. The large particles which could be seen in the original manuscript as Fig. 2 a) and b) have accumulated during the long collection time for the filter, during which the cyclone was not cleaned often enough. Following your suggestion, we did additional tests, where we added an optical particle measurement for the detection of super-micron particles (APS, aerodynamic particle sizer, TSI), and indeed saw that while there were no super-micron particles visible during the beginning of the particle generation (~30 min), these particles became more and more abundant afterwards. Based on that, we decided to collect fly ash particles from dry generation on filters once again, now cleaning the cyclone every 30 minutes. The new SEM pictures (see examples below, another one was added to the manuscript as Fig 2 b) show a majority of particles in the size range of 300 nm. 68 of 84 counted particles were in the size range of around 300 nm, while 16 particles classified as particles larger than 500 nm. This might not be significant from a statistical point of view, but it is similar to the findings of the UHSAS measurements, where on average 19 % of all particles were identified as doubly charged. This was derived from measurements as shown in the figure below for ~30 min of sampling, during which already some increase in doubly charged particles can be seen.

We omitted Fig. 2 b 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. Fig. 2 a was left in the manuscript, as we did not manage to collect sample the coal bottom ash again in the limited time. In light of the new observations, we changed the paragraph on P5L19-30 of the original manuscript accordingly (P9 L14-24).



SEM images of fly ash particles from dry generation:



Results and Discussion:

- p.13 l.5 ff: It is not clear to me why you state that “the shape of the nucleation spectrum of fly ash suspension particles from our measurements correspond well to the findings by Umo et al. (2015),…”. The fly ash data points in Figure 5 to me look either mostly linear (open purple circles), consist only of 2 data points (open purple circles with cross) or have a plateau which starts at a temperature 8 K lower than the fit from Umo et al. (2015) (full purple circles). Keeping in mind that for a given particle size and concentration, n_s can only vary in a restricted range of 3-4 orders of magnitude in this case, the observed three orders of magnitude differences are massive.

We agree that 3 orders of magnitude in n_s are a massive difference. What we wanted to say with this sentence is that we observe a plateau in the temperature range between -24 °C and -32 °C which can also be seen in the measurements by Umo et al., 2015. We reformulated the sentence to avoid any misunderstanding (P17 L18-20).

- The correction factor 4.54 = 1/0.22 = 1/(1-0.78) is derived from the SEM images of the filters. It is already stated on p.11 l.27 that this value might be smaller in the flow tube due to less

> fractioning of the crystals. However, in the discussion of the results it is not considered as an upper limit but rather as a realistic estimate. Especially for the comparison of n_s to Umo et al. (2015) it would be helpful to be aware that this value might be considerably smaller.

As you suggested, we now mention that the number is an upper estimate more prominently in the manuscript. Would the number of crystals be lower than in our estimate, f_ice would be lower as well. The extreme case would be no crystals at all, meaning that our measurements would not need correcting. Then the gray circles in Fig 3 d) would correspond to f_ice of the fly ash suspension particles. Translated to n_s, this would correspond to a reduction of less than an order of magnitude, i.e. still two orders of magnitude above the n_s values reported by Umo et al. (2015). A short version of this was added on P15 L32-33 and P17 L20-22.

Atmospheric Implications:

I would recommend deleting this section completely as the calculation is not convincing nor adds value to the manuscript. To my understanding the dilution factor of 1000 over a distance of 80 km derived from Parungo et al. (1978a) only applies to very particulate atmospheric conditions and does not seem representative for general atmospheric situations. It seems to me that the background aerosol concentration has not been considered in the derivation of the dilution factor. Furthermore, are the emissions of coal-fired power plants today the same as in the 70's? Without having discussed how representative 300 nm particles are for ash particles in general and how likely the composition and morphology and thus n s of 300 nm and 1000 nm particles are similar the given estimate is not convincing. A short comment on the atmospheric implication could be included in the summary part. However, I would suggest referring here to direct field observations of ash particles as ice nucleating particle or ice crystal residual.

This section was partly rewritten and now includes more references to field observations of fly ash particles. In the new version, we estimated the in-stack particle concentration especially for the power-plant Lippendorf instead of relying on measurements at other sites. We now consider the background aerosol concentration and clearly state that the dilution factor is valid for this specific set of meteorological conditions. As we selected 300 nm particles in our measurements, we now use the same size for our estimate.
Even though the section includes speculation, we would like to keep it in the manuscript. In our opinion, it contains valuable insights into the potential effect of fly ash emission on immersion freezing in clouds close to the source or in the power-plant plume itself.

Language:

It seems to me that there is an overuse of "could". It you are talking about your findings then the use of phrases like "was shown" or "was confirmed" instead of "it could be shown", "could be confirmed",… is more appropriate.
Done.

Specific Remarks:

p. 1 l.6: "lignite" is only mentioned in the abstract. If it is important to know it should be mentioned in the main paper body, if not it can be deleted.
We added that the coal ashes stem from lignite burning but will be referred to as brown coal ashes according to the generic term. This can be found on P6 L8-9.
p. 2 l. 3: Is "Pruppacher and Klett, 1997" truly the primary source? Give the original reference otherwise.
We now cite Szyrmer and Zawadzki, BAMS 78, No. 2, 1997 on P2 L5.

p. 2 l. 24: What is the chemical composition of mineral dust and ash that is very similar? Be more precise.

We added that “both include several common mineral components such as Si, Na, Ca, Fe and oxides” (P2 L29-30).

p.3 l.5ff: What other factors could determine the found differences between the two ashes? I can’t think of any other factors, assuming same sized particles were used. Thus this sentence does not yield new information.

We included this sentence to point out to the reader that no clear reason for the differences in the IN ability of different ashes had been found in the earlier study. Nothing was changed.

p.4 l.13 “second to last section” is this correct? Is last section referring to the second topmost or lowermost section? What is the residence time in the ice nucleation part if droplet activation only takes place in the second to last section?

Here we do mean the second to last section counting from top to bottom, i.e., section 6 of 7. The nucleation time is 1.6 s. This was added in the manuscript (P5 L15-16).

p. 5 l. 12: delete “(quartz)” as the chemical composition analysis does not yield information on the lattice structure which defines the mineralogy.

Done.

p. 5 l. 12: How much is “more SiO_2”? Be more precise!

Done.

p. 5 l. 15: Why is K in biomass burning ash water soluble in but not in coal ash? Shortly state the chemical reason behind that.

We added the following explanation on P14 L15-17: “K in wood ashes is present in the form of soluble salts and oxides, whereas coal ashes contain K in clay minerals with low solubility”, citing Steenari et al., 1999, Fuel, 78. In the course of this, we changed the previous citation of Andreae et al., 2004, Science, 303 (original manuscript P5 L16) to Steenari et al., 1999, because the reasoning is presented more clearly in the latter.

p. 6, Figure 1: Do the mass fractions add up to 100 %? It appears to me that not. What is the composition of the remaining material? If this is not known, the exact amount of how much is unknown should be stated, given that the frozen fraction often is for most samples below 10 %.

In addition to Fig. 1 the manuscript now includes a table with the corresponding values (Tab. 3), where the sum of the analyzed components is shown. You correctly observed that the given values do not add up to 100 %. This is due to the analysis procedure: It is standard to recalculate the concentrations of the ten major ions into the mass of their most common oxide forms, even though they may have had other counterions in the original sample. In some cases the compounds are indeed oxides, but we do not know the counterions in each case. K for example would be more likely to occur as KCl, K_2CO_3 etc., than as K_2O. Any missing percentage is due to other than these ten elements and the fact that other counterions would have been involved. This has been added to the manuscript (P7 L2-P9 L2).

p. 6: caption Figure 1: Replace “minerals” by “oxides”. Again – what is shown is only chemistry, no lattice structure information which is needed for statements on the mineralogy.

Done.

p. 7 Figure 2/3: Why aren’t images shown of non-US treated particles? To understand what the US treatment does to the particles it would be helpful. Also, is the chemical composition the same? This goes into the same direction as above – does the composition change with size? If it does than the US could lead to differences due to breaking up larger particles. Also the crystal ratio for non-US treated particles could be determined and a better comparison would be possible.

We do not expect to see a visual difference due to the treatment with the ultrasonic bath, while surface charges might have changed, which will be difficult to detect with chemical analysis. We added to the manuscript “that the chemical composition of fly ash particles with aerodynamic diameters between 0.2 µm and 4.8 µm is remarkably consistent (Kaufherr and Lichtman, 1984)” (P4 L27-28). Therefore, a change in chemical composition for the fly ash is not to be expected, which would also imply that a breakup of larger particles would not lead to a change in chemical composition for this sample.

p. 8 l.24: The original publication is Vali (1971). It should at least be given in addition to Hartmann et al. (2013) if not replacing it.

Done.

p. 8 l.26: What does “saturation range” refer to in this case? The temperature range in which f ice saturates? Please be more precise!

We changed the formulation to “… with f_ice* being the ice fraction in the temperature range in which f_ice saturates.” (P12 L8).

p.9 Figure 4 and p.13 Figure 5: I appreciate that the color code is mostly consistent throughout the paper. However, it would be helpful to use in addition different marker symbols and not only circles. Also, “Fly ash from brown coal burning susp. +US *4.54” is in Figure 4 given as open circle with dot and in Figure 5 as open circle without dot. Please change that.

With respect to the comments of the other referees, Fig. 4 (now Fig. 3) was changed to a 4 panel figure for better clarity. We think that the use of further marker symbols is not necessarily needed now. The suggested change in the case of “Fly ash from brown coal burning susp. +US *4.54” has been made.

p. 10 l.3: Which exact temperature range are you referring to “where effects of homogeneous nucleation can be ruled out”?

We detect effects of homogeneous nucleation at temperatures as cold as -38 °C. This limit was determined measuring the IN behavior of highly diluted ammonium sulfate droplets which should freeze due to homogeneous nucleation only (data is now included in Fig. 3d). We changed the cited sentence to: “In case of the wood ash particle, f_ice does not exceed 10 % between -35 °C and -37 °C.” (P12 L13-14).

p.10 l.7: How is “start nucleating ice” defined? In Figure 4 f ice data points are shown at temperatures warmer than -33°C and -29°C, respectively, indicating that freezing is taking place also at warmer temperatures. You seem to refer only to the plateau regime. Please write this explicitly, as this is different to other experiments.

With “start nucleating ice”, we mean that we detected an ice fraction that is above our detection limit. This was added in the manuscript (P14 L2). The given values are simply wrong and were corrected to -27 °C and -32 °C (P14 L2-3).

p.10 l. 18: “ice active sites on the particle surface might affect the ice nucleation ability of a substance.” is not very meaningful as ice active sites are defined by the ice nucleation ability of a particle. This sentence can be deleted.

Done.

p. 10 l.18 ff: The whole discussion on active sites is hardly based on observations but mostly speculative. It may well be that the statement given here is correct but since the mineralogy is not even known talking about crystallographic dislocations

You are right, there is a lot of speculation in this sentence. However, we wanted to mention a possible reason for the differences in IN behavior of the ashes, even though this was observed for mineral dust and even though we do not know anything about the mineralogy. We clearly state that the given explanation is mere speculation in saying that this “might” be a factor.

p. 11 l.1: What type of amorphous material are you referring to? What could this material be based on the chemical composition information that you have? This sounds extremely vague.

From previous studies we know that the amorphous material in fly ash is mainly aluminosilicate glass (Ramsden and Shibaoka, 1982, Atmos. Environ., 16, 9; Querol et al., 1996, Atmos. Environ., 30, 21). This was added in the manuscript and related to the high content of SiO2 and Al2O3 in our fly ash sample (P14 L22-24).

p. 11 l.13: Is it possible to give a rough estimate by how much f ice would be reduced if multiple charge correction was applied?

As we selected 300 nm particles which is far to the right of the maximum of the size distribution, we made sure 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.

We must mention that crystals will probably have occurred during the size distribution measurements as well and we are not sure how the size distributions look like for the insoluble only. 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).

p. 11 l.30: The sentence about n_s does not belong here and should be moved further to the back.
Done.

p. 12 l.25: "increase" compared to what? I assume in comparison to LACIS. Then state that.
Done.

p.13 l. 4: How could the extended time of the ash particles in suspension lead to changes in n_s? Just a short comment what you ascribe it to? Reference that supports this suggestion?
We can only speculate what leads to the observed change in n_s. The extended time the samples spent in water could possibly lead to the dissolution of more material. Peckhaus et al., ACPD (2016, see Suppl. Fig. 6) observed dissolution of different elements from feldspar samples continuing for weeks. This has been added to the manuscript (P18 L1-5).

Technical Remarks:

General: SBM has been several times spelled SMB. Please check.
Corrected.
p.1 l.8: replace "effect" with "influence"
Done.
p.2 l.31: insert "alone" after "insoluble fraction"
Done.
p.8 l.2: replace "could be" by "was"
Done.
Figure 4: Grey and black as colors for the two SBM fits from the literature are hard to differentiate.
As we did not want to introduce yet another color, we used a lighter grey for the SBM fit of the clay mineral base line.
p.11 l.22: typo in "homogeneous"
Corrected.
p.11 l.31: New paragraph before "In the plateau…"
Done.
p.14 l.21: insert space between "at" and "the Leipzig"
Done.

References cited in our answers:

Andreae et al., Science (2004)
Damle et al., Aerosol Science and Technology (1981)
Flagan and Seinfeld, Fundamentals of Air Pollution Engineering (1988)
Kaufherr and Lichtman, Environ. Sci. Technol. (1984)
Murray et al., Phys. Chem. Chem. Phys. (2010)
Peckhaus et al., ACPD (2016)
Petters et al., GRL (2009)
Querol et al., Atmos. Environ. (1996)
Ramsden and Shibaoka, Atmos. Environ. (1982)
Steenari et al., Fuel (1999)
Szyrmer and Zawadzki, BAMS (1997)
Umo et al., ACP (2015)
Whale et al., AMT (2015)
Wiedensohler, Journal of Aerosol Science (1988)