

## **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<sub>2</sub>. 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 1.27ff 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).
- 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.
- One could also add motivation from field observations of biomass burning, e.g.: Prenni et al. 2012, GRL; McCluskey et al. 2014, JGR

#### *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?
- 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?
- 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?

#### *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.
- 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.

#### *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.

*Language:*

It seems to me that there is an overuse of “could”. If 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.

**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.

p. 2 l. 3: Is “Pruppacher and Klett, 1997” truly the primary source? Give the original reference otherwise.

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

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.

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?

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

p. 5 l. 12: How much is “more SiO<sub>2</sub>”? Be more precise!

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.

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 %.

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.

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.

p. 8 1.24: The original publication is Vali (1971). It should at least be given in addition to Hartmann et al. (2013) if not replacing it.

p. 8 1.26: What does “saturation range” refer to in this case? The temperature range in which  $f_{ice}$  saturates? Please be more precise!

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 as open circle without dot. Please change that.

p. 10 1.3: Which exact temperature range are you referring to “where effects of homogeneous nucleation can be rules out”?

p.10 1.7: How is “start nucleating ice” defined? In Figure 4  $f_{ice}$  data points are shown at temperatures warmer than  $-33^{\circ}\text{C}$  and  $-29^{\circ}\text{C}$ , 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.

p.10 1. 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.

p. 10 1.18 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

p. 11 1.1: 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.

p. 11 1.13: Is it possible to give a rough estimate by how much  $f_{ice}$  would be reduced if multiple charge correction was applied?

p. 11 1.30: The sentence about  $n_s$  does not belong here and should be moved further to the back.

p. 12 1.25: “increase” compared to what? I assume in comparison to LACIS. Then state that.

p.13 1. 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?

**Technical Remarks:**

General: SBM has been several times spelled SMB. Please check.

p.1 1.8: replace “effect” with “influence”

p.2 1.31: insert “alone” after “insoluble fraction”

p.8 1.2: replace “could be” by “was”

Figure 4: Grey and black as colors for the two SBM fits from the literature are hard to differentiate.

p.11 1.22: typo in “homogeneous”

p.11 1.31: New paragraph before “In the plateau...”

p.14 1.21: insert space between “at” and “the Leipzig”