

*We would like to thank the Reviewers for taking the time to read through our manuscript and for the useful feedback on the manuscript. Our responses to the Reviewers' comments are presented in italicized blue text beneath each comment. The page and line numbers referred to are that of the ACPD version. All changes and corrections are on the revised manuscript that is submitted alongside this response.*

## **Anonymous Referee #1**

Received and published: 19 December 2014

The study presented by Umo and co-authors is a timely work about the ice nucleation activity of different kinds of ashes. Ashes are one of the open issues as far as ice nucleation is concerned, and not many studies exist on this topic, so far. The study gives a good overview of the basics concerning the topic, and then gives a solid description of the examinations which were done. The examined ashes were not only analyzed with respect to their ice nucleation ability in immersion freezing, but also characterized in other aspects as e.g. surface area, size distribution, mineralogy and composition.

The emerging picture is, that ashes in general are ice active in a comparable manner to the ice activity of some mineral dusts, and that particularly coal fly ash as produced and emitted by power plants is ice active already at comparably high temperatures.

This study might be seen as a starting point for future research on the topic of the ice activity of ashes. It is well written, and besides a few technical comments I give below, I have no concerns and would, after the below mentioned issues are removed, suggest this study for publication in ACP.

*Firstly, we thank the referee for the succinct summary of our work and for the positive recommendation for publication in ACP pending clarifications to the technical comments that are addressed below.*

Technical comments:

p. 28847, line 11: The citation of "Vali et al., 2014" relates to the discussion version of this paper, and I generally recommend to refrain from citing these versions as they are not peer reviewed, yet. Moreover, it was discussed in the discussion of this paper that particularly condensation freezing was not well defined. There is a paper by Wex et al. (2014), which, in its appendix, provides a short overview of the variety of definitions of condensation freezing present in literature.

*We have taken out Vali et al., 2014 reference and added Wex et al. 2014 as suggested.*

*This section now reads: 'Ice nucleation can occur via various pathways: deposition nucleation entails formation of ice from water vapour onto a solid particle; contact freezing occurs when a particle comes in contact with an interface of a supercooled water droplet; immersion ice nucleation happens when a particle is fully immersed in a water droplet and freezes upon further cooling; condensation freezing is more poorly defined, but involves the condensation of water prior to freezing (Vali, 1985; Wex et al., 2014).'*

p. 28847, line 13: replace "(0 - - 36°C)" with "(0 to -36°C)"

*Done.*

p. 28849, line 13: add "identified as" in front of "carbonaceous-mineral"

*Changed.*

p. 28851, line 6: When reading "known mass" twice in this sentence, I wondered how much that might have been. Later I understood that the concentrations are given in the respective figures. Please mention already here that different concentrations were examined and that these values will be given later.

*We have added that 'The ash particle concentration was varied and the concentrations corresponding to specific experiments are indicated in the respective figures'.*

p. 28851, line 23: Mention explicitly how many droplets were examined.

*The number of droplets placed on each hydrophobic glass slide in each experiment varied between 45 and 65 droplets.*

p. 28852, line 9 -15: You mention sieving the samples, prior to further analysis. Were also those samples sieved, that were used for the suspension examined in the freezing experiments? Please state explicitly, somewhere in the text dealing with preparations of the suspensions, if they were or were not sieved. This also connects to the values given in Table 2, where the data for the CFA bulk was different from that of the sieved CFA. I can only imagine that this is the case if some material is lost through sieving, but you make it sound (see also the following remark), that all of the CFA passes through the 40 micrometer sieve. Please explain clearly somewhere, where the difference in the composition of bulk and sieved CFA came from.

*To respond to the first question - yes, all the ash samples used in preparing suspensions for the freezing experiments were sieved. We have added that 'Also, the ash samples that were used in the preparation of the suspensions were sieved beforehand' to the revised article'. About Table 2 – CFA data is from the same sample the only difference between the two is that CFA (bulk) was not sieved while the other was sieved (i.e. CFA (sieved to  $\leq 40 \mu\text{m}$ )). This is stated in the Table 2 caption. CFA (bulk) is the only ash sample that was not sieved before the BET and mineralogy test.*

*For the CFA sample, not all the ash particles passed through the sieve - this was stated in the manuscript that 'A fraction of the CFA particles were larger than  $40 \mu\text{m}$  and did not pass through the sieve' (page 28852, line 13 -14). The differences in composition between the bulk and sieved CFA is very minor (see the new analysis).*

p. 28852, line 13: It is clear what you want to say here, with "that at least two dimensions of the particles were smaller than 40 micrometer", but I had to think about this sentence twice before I got it. Maybe you can find an alternative way of phrasing it?

*We have now rephrased it as '...that at least two dimensions of the particles were smaller than  $40 \mu\text{m}$  and the third could conceivably be larger.'*

p. 28854, line 4 and line 14: You mention size distribution measurements in this chapter, and in Fig. 3, these are shown. From Fig. 3 it seems that these size distributions are expressed in terms of volume

fractions per channel. Please mention this explicitly in the text, as it makes a large difference if it is shown related to particle diameter or surface area or volume.

*We modified the text to read: 'The results in Fig. 3 are volume fraction size distributions for ash suspensions agitated and stirred in the same way as for the ice nucleation experiments.'*

p. 28854, line 11: Are the average volume diameters you derive here compatible with what is shown in the SEM pictures? There you gave a value of 5 micrometer for CFA, and the difference likely originates in the different reported values (where it is the average volume diameter for the laser diffraction measurements), but this should be discussed in a sentence or two.

*We stress that we did not attempt to use the SEM images to establish a full size distribution, but the sizes were consistent. We have added a sentence to section 4.2 to discuss this difference. 'The SEM images for CFA particles were consistent with the size distributions determined by laser diffraction.'*

p. 28855, line 2: The ";" should be a ","

*Changed.*

p. 28855, line 6 (5): Insert "in" between "used" and "this study"

*Done.*

p. 28856, line 25: To might want to explain here that this experimental limitation originates from the fact that there is a larger amount of material (ash in this case) present, per droplet, in the micro-liter experiments, increasing the probability of ice nucleation and hence already causing all droplets to freeze at higher temperatures, compared to droplets that contain less material.

*We have added that 'The heterogeneous freezing temperatures for the nL-NIPI are lower than those for the  $\mu$ L-NIPI, because nanolitre volume droplets with the same concentration of ash contain less ash and hence, have a lower probability of freezing at a given temperature.'*

p. 28857, line 18-20: The citations given here are in parenthesis (opening in line 18, closing in line 20), and these parenthesis should be removed.

*Removed.*

p. 28860, line 25: It would be interesting to see the parameterization by Augustin-Bauditz et al. (2014), which you mention in the text, in Figure 8, too (the "clay base- line"). Please add the line mention it in the caption and the legend.

*We have added the suggested line to Figure 8.*

p.28866, line 23 and line 27: DeMott needs a capital "M". There are also other occurrences of this name in the references, sometimes with a capital "M", sometimes without. Just go through the whole list and correct it.

*Corrected.*

Figures: Often the legends and other text (e.g. elements in Fig. 4) are MUCH too small to be decipherable (e.g., I had to blow Fig. 7 up to 300% before I could see the concentrations). Please check all of your plots and change them such that they will be readable when printed, and while doing so take into consideration if you want a particular plot to have a single or double column width.

*We will work with the publishers to make sure that the final figures are clearer and easily readable.*

Figure 6: You mention a run done with pico-liter droplets which I can't find mentioned in the legends. Please correct.

*Corrected – the reference has been removed.*

Figure 8: You'd have done me and future readers a favor if you had sorted the entries in the legend following their "appearance", e.g., from "top to bottom", at least within each category (e.g., within the mineral dust measurements), mentioning first the K-feldspar, then the Na/Ca-feldspar, then quartz, ... - particularly for those datasets that are all close to each other, this helps to identify the symbols.

*Rearranged.*

Literature:

Wex, H., P. J. DeMott, Y. Tobo, S. Hartmann, M. Rösch, T. Clauss, L. Tomsche, D. Niedermeier, and F. Stratmann (2014), Kaolinite particles as ice nuclei: learning from the use of different kaolinite samples and different coatings, *Atmos. Chem. Phys.*, 14, 5529-5546, doi:10.5194/acp-14-5529-2014.

## **Anonymous Referee #2**

Received and published: 19 December 2014

The authors present a thorough study of the heterogeneous ice nucleation behavior of four different bottom and fly-ash samples and make the case of missing information on the emission strength of Coal fly ash from different combustion sources as far as their ability to nucleate ice, hence their influence on climate, is concerned. They combine the droplet freezing experiments with physical characterization of the fly ash and classical (bottom) ash samples in order to better understand the relationship between freezing behavior and surface composition of these complex materials, which represents a laudable effort in itself. Apart from a few required clarifications and questions I have not found a major "show stopper" in this report, which would prevent me from withholding recommendation to publish.

However, Sections 6 and 7 are way too wordy and lengthy for the (trivial) content that the authors want to convey to the readers at the end whereas the core results on the droplet freezing experiments are not discussed at length. They should essentially concentrate pages 28862 to 28864 to at most two succinct paragraphs as the conclusions are really quite simple and not especially earthshaking, namely that (a) CFA (Coal fly-ash) has an ice nucleating (IN) ability comparable to most mineral dust samples, (b) whose IN ability falls short of K-feldspar, and (c) that therefore one may (perhaps) make a case for additional measurements of these materials on a global scale. However, this last point is by no means uncontested,

for what error would we be making if the ice nuclei budget of CFA and mineral dust were confounded?

*We have gone through sections 6 and 7 again, we do not find irrelevant material that should be removed, rephrased and restructured for the revised manuscript. Other Reviewers are happy with them and one even suggested we add more detail to a particular section. We do understand that there might be some eminent pieces of information that people in the ice nucleation community may consider trivial, but readers outside the ice nucleation community will find them very beneficial. This work has the interest of the engineering researchers in the energy sector and they find these pieces of information really useful for their better understanding of this research. Our strong preference is not to shorten these sections.*

*Regarding the referee's final comment on 'what error would we be making if the ice nuclei budget of CFA and mineral dust were confounded?' In order to estimate man's impact on clouds, we need to be able to make estimates of what the INP loading was pre-industrially as well as in the present day atmosphere. To do this we need a quantitative understanding of the different sources of INP, coal fly ash for example is anthropogenic and was not present pre-industrially. If it turns out that fly ashes (or bottom ashes) are important INP now, then we need to know this. In response, we have adjusted the pertinent sentence in section 6 to read 'This sort of quantification can give an insight into the importance of INPs from different sources and potentially allows us to assess changes in INP concentrations due to human activities'*

Here are my critical remarks that I would like to see answered before publication of the present paper:

- Regarding the use of Millipore water in the preparation of the ash suspension I think that the authors took the worst possible solution: Millipore water has a minimum of ionic impurities, but is not specified as to the number of floating insoluble nanoparticles. Owing to the fact that Millipore water flows through a bed of solid ion exchange material the flow periodically "breaks off" chunks of that material. The authors may easily convince themselves by atomizing pure (Millipore) water, evaporating and counting the particles using a CNC (Condensation Nucleus Counter). Using doubly-distilled water (our "best" solution) we have found a particle count of 10 to 50 particles per cc occurring in a broad mode centered around 50 to 60 nm, varying from day to day, which is not very satisfying. This most probably does not influence the nL-NIPI, but could affect the subtraction scheme of the microL-NIPI results.

*We do not contest the fact that Milli-Q ultra-pure water (18.2 MΩ.cm resistivity, TOC < 10 ppb) may contain some solid nano-scale impurities as mentioned by the Reviewer. We stress that we have quantified the INP content of the water. As the Referee points out, the concentration of impurities is negligible for the nL-NIPI, but is important for the μL-NIPI. In order to be confident in our reported measurements of ice nucleating activity we compiled the results of 23 experiments with the same water source on different days and these results were used to establish an experimental baseline and the variability is used to define the quoted uncertainties (which were small, because most experiments were well-above the baseline). Hence, the presence of impurities in the Milli-Q or on the surfaces was well defined and accounted for.*

*In an ideal world, we would be able to cool microliter-sized droplets to homogeneous freezing by eliminating all INPs or active sites on the surfaces. In practice, this has proven to be a challenge and we are not aware of any data in which microlitre droplets have been repeatedly cooled to homogeneous freezing. We have tried water from multiple sources (e.g. HPLC grade water and water which we filtered ourselves with KDa centrifuge filters) and also tried various substrates without a reproducible shift to*

*lower freezing temperatures. While the Milli-Q water is perhaps not ideal, it is of a consistent quality which allows us to use it. Pushing the  $\mu\text{L-NIPI}$  to lower temperatures remains a challenging area of work, but does not detract from the results presented in this paper.*

- Considering Figures 2 and 3 one must be careful when taking the results of Figure 2 as an illustration of the particle size distribution function: Taking row A, middle panel for CFA in Figure 2 as an example, one gets the impression that the number of large spheres are important in the CFA size distribution. It ain't so because these large particles of approx. 8-10 microns represent the tail-end of the distribution. A disclaimer is in order when comparing or illustrating Figures 2 and 3! They cannot be compared because one is a geometric diameter derived from an optical measurement, the other is based on the particle mobility in an electric field.

*We did not make a direct comparison of both figures in our discussion for a number of reasons: (1) As rightly pointed out by the Reviewer, one is a geometric diameter and the other is based on particle mobility (2) one measurement is with dry ash particles while the other was measured in a suspension (3) SEM looked at a limited portion of the ashes whereas the laser sizing considered a large volume of the ashes during measurement. For instance, for the bottom ashes where the particle shapes/sizes are undefined based on the SEM pictures, it will be difficult to analyze the particle size distribution; but by the laser particle sizing method, we saw a clear particle size distribution.*

*CFA is a unique case where we were able to use Image J software to measure some of the sizes of these particles because they are spherical. That was the information that we use in discussing the morphology of CFA and not the particle sizing. We have added an explanation to section 4.2 regarding this: 'The SEM images for CFA particles showed a slightly smaller average diameter of  $\sim 5 \mu\text{m}$ , but only relatively few particles were imaged in the SEM compared to the laser diffraction method, which looked at a large volume of the material'.*

- Regarding the symbols in the formalism there is a certain inconsistency with Whale (2014) in that "sigma" in equation (1) corresponds to "A", the total surface area in a droplet used in Whale (2014), whereas A in equation (4) is the specific surface area in units of square cm per g. Why use two different symbols in publications written in the same year? This is confusing.

*We have corrected the equation 4 and now the symbol 'A' has the same definition.*

- Regarding the experimental results the authors do not really undertake an in-depth discussion.

*We feel that there is a thorough discussion of the results and address the specific concerns raised below.*

Why haven't there been repeat freezing experiments? How do sequential freezing curves look like when performed with the same droplet suspensions in place?

*Repeating the freezing of the same droplets is not the focus of the paper and would involve a huge amount of additional work. This sort of experiment yields information on the stochastic nature of freezing, which we have focused on extensively in other papers (e.g. Herbert et al. (2014)). This could be interesting future work now that we have established that this material may be important. The key conclusion of this paper is that combustion ashes nucleate ice and we anticipate more work on these materials in the future.*

What is the reason for the sometimes significant difference of the fraction of droplets frozen vs. average

droplet diameter?

*Each of the panels is made of multiple freezing experiments of 0.1 wt% of the ash suspension. Because of the nebulization method of making droplets the droplet size distribution varied between experiments, hence the fraction frozen curves were different. This is clearly described in the third paragraph of section 5.1.*

See results in Figure 6 (nL-NIPI results) for CFA (upper left panel, green symbols). Is there a systematic contribution of the "pure" water to the freezing behavior of the ash IN?

*We have modified the pertinent paragraph in section 5.2 to read: 'In the determination of ns from nL-NIPI results we assumed that the background INP concentrations were negligible. In general, this appears to be a reasonable approximation, but it is possible that for runs employing the largest droplets (> 100 μm) there may have been a significant number of background INPs present in the droplets. Accordingly, this could lead to an over-estimation for the highest temperature nL-NIPI ns values when compared to the equivalent μL-NIPI ns values. Note that some pure water droplets freeze above -36 °C (Fig. 6). Even with this potential contribution of background INP in some nL-NIPI experiments, the agreement between the various experiments shown in Fig. 7 is reasonable.'*

- In the display of Figures 5 to 8 the authors managed to sneak in some ophthalmological eye charts: Both the graphic material as well as the legends are impossible to read as submitted!! Please make sure the reader finds itself in a position to read and understand these Figures.

*This ACPD specific typesetting issue will not be an issue when the figures are published full sized..*

- Regarding the results of the number of interaction sites (ns) as a function of temperature displayed in Figure 7: What is the reason for the "saturation" behavior of CFA compared to the bottom ashes as well as with respect to mineral dusts displayed in Figure 8? The authors should advance a plausible reason as the results displayed in the upper left panel of Figure 7 (and 8) are distinct from all others. Any reason for the systematic deviation off the common parametric line for the bottom ashes in Figure 7? Somehow, the points from the two frozen droplet experiments (nL and microL-NIPI) do not want to overlap as they deviate from one another!

*The Reviewer's question is a good one and we have mentioned some possibilities that we think could be related to the unique behaviour of CFA compared to the other bottom ashes or natural mineral dusts. Please see section 5.2 and the paragraph beginning with 'Inspection of the various plots in Fig. 7 reveals a striking difference in temperature dependence of ns between the CFA and the bottom ash samples'*

- A last point of contention concerns the relationship between the EDX mineralogical results and the expected freezing behavior of the bottom and fly-ash samples. EDX addresses one to a few nanometers of matter, especially in this case because carbon is a light and low-density material from which X-rays may escape from some depth. In contrast, the freezing behavior depends only on the composition of the interface, in the case of crystalline material embedded in amorphous carbon probably from one or two molecular monolayers. It is outrageously simplifying when the authors just compare the EDX signals of the ash samples and derive the surface composition, thus freezing behavior. A robust disclaimer or additional explanations are in order here.

*EDX gives information about elemental composition and we state that the elemental composition is*

*consistent with the mineralogy determined by X-ray diffraction. EDX does not give direct mineralogical information. The reason for doing the EDX analysis was to characterize these samples. In section 5.3 we discuss how our samples compare to various minerals and desert dusts. In this section, we make some suggestions as to which component of the ash is causing it to nucleate ice. No firm conclusions are drawn, but we do make some reasonable suggestions.*

- Reference “(Wilson (et al.), 2012)” is missing (as is (Connolly et al., 2009) in (Whale et al., 2014)).

*Wilson et al., 2012 has been added and we think Connolly et al., 2009 will be added in the revised manuscript of Whale et al., 2014.*

- The English is OK in most parts, but must be checked by a native English speaker. Frequent use of double plurals are distracting. “Warmer” temperatures? Top of pg. 28859: “. . . a cumulative nucleation site density. . .”Pg. 28847, line 11: “. . . as a CCN activates” (What is the meaning?).

*The ‘double plurals’ such as ‘warmer temperatures’ have been removed or corrected. The term ‘a cumulative nucleation site density’ is commonly used and must remain. ‘as a CCN activates’ means when a cloud condensation nucleus (CCN) takes up water to become a cloud droplet. We have removed the reference to CCN from this section.*

### **Anonymous Referee #3**

Received and published: 26 December 2014

Review Umo et al. (2014) Ice nucleation by combustion ash particles at conditions relevant to mixed-phase clouds

Summary of the presented work

This study investigated different combustion ashes regarding their potential atmospheric relevance as ice nuclei. To motivate the study, the authors emphasize the injection into the atmosphere. However, ice residual measurements do not distinguish ashes from minerals yet, so that the atmospheric presence remains unclear. Additionally, the ice nucleating behavior of combustion ashes was also not investigated until now.

The study distinguished two different combustion ash types with respect to their sources. The first class is bottom ash coming from complete combustion processes of coal in households and power plants. The second class is fly ash, which is emitted during combustion processes like wild fires, biomass burning or domestic combustion and may include other materials.

As an example for the bottom ash particles the authors used first wood and coal solid fuel combustion ashes and second combustion ash from wood combustion in a typical household. For the fly ash class the authors used a filter sample from a power plant. The samples were characterized regarding their surface and morphology, their size distribution and their mineralogical composition and finally their ice nucleating ability. To this end, they used the  $\mu\text{L}$ - and  $\text{nL}$ -NIPI experimental setup.



The coal fly ash (CFA) sample shows compared to the bottom ashes a smaller BET specific surface area. Regarding the size distribution show the bottom ash samples a much narrower distribution with a smaller mean diameter than the CFA. Also in the mineralogy the CFA clearly separates from the bottom ashes. The results for the ice nucleating properties show that the CFA has higher  $n_s$ -densities than the other samples. The reason suggested in this study for that could be the difference in the combustion process or the morphology. The parameterization of the  $n_s$ -density for CFA has a temperature dependency similar to biological particles. In comparison to other aerosols the combustion ashes have an  $n_s$ -density comparable to clays and minerals.

The authors call for future studies to improve the separation of ash particles from the mineral class in ice residual measurements. Furthermore the differences between the ash samples have to be investigated in more detail.

#### General comments

This study is technically impeccable and original. Most parts of the article are well written. The main problem which I have with this work is its relevance for the atmosphere. Although the authors go to great lengths to justify the atmospheric importance of these particles and cite a lack of suitable analysis methods as the reason for why they haven't been in focus until now, it could also simply be that they occur only very locally and in small number concentrations. The size of the particles investigated here (after artificial disaggregation!) is simply too large to keep them aloft in the atmosphere for significant times. Nevertheless, I support the publication of this paper subject to a number of corrections and clarifications and hope that future research in the field will elucidate the questions raised in this study.

*We are pleased the referee wishes to support the paper. The issue of the atmospheric relevance of the size of the particles is an important one. Yes, the atmospheric lifetime of the 10  $\mu\text{m}$  particles will be limited, but the size distribution of the particles in our experiments extends into the sub-micron range, which will have a substantial lifetime. Much like desert dusts, only the smaller particles in the distribution will remain in the atmosphere for lifetimes of days. In applying the derived  $n_s$  values to a population of atmospheric ash particles we would need to assume that  $n_s$  are not size dependent. This assumption has been made for other materials with some experimental justification.*

Detailed comments Section 1: - Is any information available on the size distribution of ambient ash samples?

*We cannot answer this question because there is no data in the literature on the ambient measurement of combustion ash in the atmosphere. As stated earlier, we have made a strong proposal in our manuscript for this aspect of measurement to be carried out.*

- What number or mass concentrations of ash are found in ambient air? If this information is not available for ash specifically, what are the total aerosol concentrations close to ash sources?

*Ash concentrations are not known and we do not think that total aerosol concentrations near ash sources are relevant. The INP concentration may be dominated by a minor component of the aerosol population and they may have very little relation to the total aerosol concentration.*

- It seems likely that the composition of what is termed "ash" is size-dependent, and that at the smallest sizes there is a transition to soot. Please comment.

*Soot is entirely a different material with different formation mechanism to combustion ashes. Whereas soot is mainly a carbon-based fractal combustion by-product, combustion ash is a distinct class of combustion product. As far as we know, there is no transition of smaller sizes of combustion ash material to soot.*

- It could also be that the ice nucleation ability is size-dependent. Was any indication for this observed in the experiments?

*No, in our experimental design, we did not size-separate the combustion ash before performing the ice nucleation tests beyond removing very large particles. It is not possible to say at this point if its ice nucleation ability is size dependent - this will require further investigation. This is something we would like to investigate in the future.*

- page 28848 line 20ff: The study by Block and Doms (1976) which is cited to underline the atmospheric relevance of fly ashes is quite old. During the last 40 years the inefficiencies within the collection systems in power plants have certainly improved.

*There is no doubt that the collection systems in power plants have certainly improved in the last 40 years but we dare to say that these facilitates do not function at a 100 % capacity, hence, these substances still get into the atmosphere. In addition, we did not just present the sources of these material as being only from direct emission but during other processes as presented in page 28848, lines 16 - 23. Our argument here is that the collection systems do not function at 100 % efficiency; hence, they are bound to emit some into the atmosphere. Also, there are emissions from the biomass burning - which is an open source emission, household emissions, or during transport.*

- page 28849 line 13/14: when citing the McCluskey et al (2014) paper, please add the conditions (T and RH) under which ice nucleation was measured.

*We have added that - The measurement was performed activation temperatures of between -5 to -23 °C at water supersaturation (SSw) of 5 (±2.5)% at each temperature.*

Section 2: Sources and generation of combustion ashes:

- It did not become quite clear to the reviewer what “solid fuel” is, as the term is ambiguous (at least to non-native speakers). A better description of the material and where it was bought would improve the understanding of this section.

*Solid fuel is defined as solid materials, such as wood or coal, that are used as fuel which through a combustion process can produce energy for various uses. We have added ‘(e.g. wood or coal)’ after the first mention of solid fuel. In terms of specific sources of material, our suppliers asked us not to reveal their identity. This is frustrating, but we are using commercially sensitive materials.*

- Furthermore the question arises whether the domestic ash was produced in a typical stove in a kitchen or in a stove in a living room. When it was produced in a kitchen stove the authors have to justify whether this kind of cooking is really relevant these days (or in which parts of the world it is relevant).

*The domestic ash was produced from a typical stove used in a in a living room in the UK. The specifications of the stove have been described in the text. “The stove used here was a type approved by*

*DEFRA (the UK's Department for Environment, Food & Rural Affairs) for use in UK smoke control areas for the purpose of household heating, hence, typical of modern domestic stoves with similar standard as the one mentioned earlier". The one earlier mentioned here refers to the multi-fuel stove rated at 6.5 kW (BS EN 13240:2001 and A2:2004) – see page 28850, line 6.*

Section 3: Preparation of ash suspension and freezing experiments:

- The samples were preprocessed before the freezing experiments were done. The question is whether the samples are representative of atmospheric particles after the processing. This applies in particular to the stirring which breaks down the aggregates.

*The stirring breaks up loosely bound aggregates of particles, which increases the stability of the suspensions and ensures that the material is homogeneously distributed between droplets. It is not anticipated that this relatively gentle stirring processes alters the individual particles and in fact, we did not observe any effect on the particles when they were re-examined with SEM.*

- page 28853 line 12ff: For a better comparison between fractal agglomerates the indication of the fractal dimension or the size of the primary particles as for soot agglomerates would be better. Additionally the used software Image J should give this information.

*We agree that Image J software can give information on the fractal dimension of soot, however, that comparison is not possible here because they are entirely two different materials. While soot exists as fractals, ash particles are distinct and this analysis is not appropriate.*

Section 4.2: Size distribution of combustion ash particles:

- Why show all 4 samples 2 modes in the size distribution?

*We feel it is important to show the full size distribution for each material in order to provide information on the range of sizes of the particles we are studying.*

- From these size distributions you can get the geometric surface area. Therewith a direct quantitative comparison of the BET surface area and the geometric surface area is possible and also of interest for further studies.

*We agree that geometric surface area information can be estimated from the size distribution, but in the case of laser diffraction there are some significant uncertainties. Uncertainty can be introduced by the values of absorbance, density and the refractive index used for such calculation. We used values from Jewell and Rathbone, 2009, but these values are material dependent. We also note that deriving surface area from such measurements tends to under predict surface area (discussed in Atkinson et al., 2013). This is in part because the bottom ashes are irregular shaped so it is difficult to estimate the geometric surface area.*

- Volume mean diameters of 8-10  $\mu\text{m}$  are very large compared to typical atmospheric aerosol particles sizes. This should be mentioned.

*It is important to bear in mind that these size distributions are volume distributions, the peak number distribution would be a lot smaller, but laser diffraction is sensitive to volume, not number. As mentioned*

*above, the distribution does go into the submicron, atmospherically relevant range.*

Section 5.2:

- page 28858 line 21 to page 28859 line 3: This section is difficult to understand. A more detailed description is necessary. Please comment on how large the difference is to the previous method and whether the published results change when the new calculation is applied.

*On re-reading this section there was key information missing. We have adjusted it to read:*

*“For the nL-NIPI experimental results, the determination of  $n_s$  needed to take into account the broad size distribution of the droplets (20 – 450  $\mu\text{m}$  diameters). In the past, we have used a method where we bin droplets into narrow size ranges as described above and then apply Eq. (1) using the average surface area per droplet (Murray et al., 2011). However, this method relies on the assumption that we can take an average surface area per droplet in each bin. This is an appropriate assumption only when the size bin is narrow and was found to be justified in previous work e.g. Murray et al. (2011) and Broadley et al., (2012). In the case of the nL-NIPI experiments presented here the size distribution is very broad and it is not possible to bin the limited number of droplets in sufficiently small size bins. This leads to an under-prediction at lower temperatures.*

*Instead, we have used a moving average method similar to that used by Vali (1971). In this analysis the average surface area per droplet is defined as:*

$$A = S_{\text{liq},T} / n_{\text{liq},T} \quad (5)$$

*Where  $S_{\text{liq},T}$  is the total surface area of the ash in liquid (unfrozen) droplets at  $T$ , and  $n_{\text{liq},T}$  is the number of liquid droplets remaining at  $T$ . Hence,  $A$  generally decreases through an experiment as the largest droplets tend to freeze first and therefore provides a better approximation of  $n_s$  than the standard method.  $A$  is used to determine differential nucleus spectrum  $k(T)$ :*

$$k(T) = -\ln\left(1 - \frac{n_i}{n_{\text{liq},T}}\right) (A \cdot \Delta T)^{-1} \quad (6)$$

*Where  $n_i$  is the total number of frozen droplets in the temperature step ( $dT$ ). This can be used to derive the cumulative value,  $n_s$  (Vali, 1971):*

$$n_s = -\int_0^T k(T) dT \quad (7)$$

- The use of different fit functions for the different samples is not well justified. In particular, the domestic bottom ash appears to have very similar temperature dependence as the other bottom ashes, but the fit function includes a third free parameter. Of course this improves the quality of the fit, but it does not add any information or does not aid the physical interpretation. How much worse would the fit be with just two parameters?

*We stress that these fits are simply parameterisations to describe the data and carry no physical significance other than representing the data. The polynomial fit to domestic ash is necessary because the data is not well represented by a straight line.*

Section 5.3: Comparison of ice nucleation activities of combustion ashes to INPs with varied mineralogies:

- It should be mentioned that the study from Niemand et al. (2012) used geometric surface areas to determine the  $n_s$ -density whereas the other studies used BET specific surface areas. Therefore, a direct comparison is not possible. Furthermore you have to mention which parameterization (BET or geometric  $n_s$ ) from Hiranuma et al., 2014 you used.

*We have now specified the surface areas (either BET or geometric) used for each reference material in the figure 8 caption.*

- A comparison with volcanic ash immersion freezing experiments e.g. by Welti et al, 2011 and Steinke et al., 2011 would also contribute to the study.

*$n_s$  was not reported in both of these papers, but was estimated by Murray et al, 2012. The resulting parameterization is plotted.*

Section 7:

- There is some work on pyroconvective clouds (e.g. Sassen and Khvorostyanov, 2008, doi:10.1088/1748-9326/3/2/025006) which could be mentioned here.

*We have added in the text: 'In addition, Sassen and Khvorostyanov, (2008) report that particles associated with boreal fire smoke could nucleate ice and influence altocumulus clouds. They suggested that these particles could have been soil/dust particles, coated soot aerosol or organic material; we suggest that fly ash should also be considered as a possibility.'*

Technical comments: - page 28863 line 19 “in the this category” - either the “the “or the “this” is too much.

*Corrected.*

#### **Anonymous Referee #4**

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#### **General Comment**

This manuscript makes a fairly concise and straightforward assessment of the ice nucleating potential of various ash particles from combustion. The assessment includes a variety of ash types, and characterizes the particles in detail, so that comparison to mineral dusts can be made on an equal basis (surface areal site density). The point that these types of ice nucleating particles have not been often or readily distinguished from dust particles in the atmosphere, and that they require such assessment as potentially important atmospheric contributors is well taken. The statement that these particles could play an important role in primary ice formation in mixed phase clouds is not supported as yet on the basis of

actual atmospheric measurements. It is enough to say that this deserves investigation. The basic findings can stand alone as an excellent paper that will stimulate further research. All specific comments are rather minor.

#### Specific Comments

Page 28847, lines 6-7: The definition of deposition nucleation includes a statement that it occurs in a regime where bulk water cannot exist. I am not certain that the term bulk is appropriate in this case. Certainly aerosol water can exist and it can even potentially create an encapsulated particle in the regime below water saturation. I suggest to be clearer.

*We have simplified the definition to remove any mention of bulk water: “deposition nucleation entails formation of ice from water vapour onto a solid particle”*

Page 28850, lines 8-10: One could infer from the statements here that 300C is a representative temperature for a wildfire. While that may be the flash point of wood, I believe that literature supports that this is far less than the high temperatures encountered in the flames of a wildfire.

*This was a typo – it has been corrected to 800 °C.*

Page 28859, discussion of Figure 7: I am not sure exactly where the discrepancy between some of the experiments that amounts to 1.5 to 2 orders of magnitude in the temperature regime from -20 to -25C is discussed. Is this what the discussion of larger droplets is about here? I do not consider these to be slight deviations. It would help if Figure 7 were more easily readable. Although there are a lot of experiments shown, the labels are just far too small.

*We discussed on these discrepancies in the ns values in Page 28859, lines 10 - 18. We suggest that these deviations may be due to background freezing issues in the nL-NIPI experiments. We have removed the word ‘slight’ and changed the sentence to read “Accordingly, this could lead to an over-estimation for the highest temperature nL-NIPI ns values when compared to the equivalent  $\mu$ L-NIPI ns values”.*

*We have modified figure 7 to be easily readable.*

Page 28861, lines 4 to 6: I found this to be a strange statement, suggesting that the lower activity of the ashes compared to mineral dusts is due to the absence of feldspar. It seems to be made as some kind of indirect support that feldspars are vitally important to ice nucleation by mineral dusts, but this paper is really about ash particles, which of course are not desert dusts.

*Unambiguously, the article is about combustion ashes and not desert dusts but they do share some common mineral components hence it is worth comparing their activity with available data for minerals. We have concluded in the past that feldspars are some of the (if not the) most ice active mineral hence it is a useful benchmark. We go on to suggest that it is the quartz component which may control the ice nucleating ability of combustion ashes, but more work is needed. We have modified the section to make*

*this discussion more balanced: 'X-ray diffraction analyses (Table 2) shows that there is no detectable feldspar present in the ash samples, but there was a detectable amount of quartz in all samples. In fact, the  $n_s$  values for the ashes ranges from roughly 30 to 1 % of that of the available literature data for quartz at  $< -26$  °C. This suggests quartz could be important in the ice nucleating activity of combustion ashes, but further work is required to explore this hypothesis.'*

Page 28861, line 12-14: The Wilson reference seems missing. Also, Archuleta et al. (Atmos. Chem. Phys., 5, 2617–2634, 2005) may be relevant for mention here due to inclusion of study of amorphous silicate particles. Studies were at cirrus temperatures, as were the others listed here.

*We have now included the Wilson et al., 2012 reference. We have also added and rephrased our sentence as: "...and aluminium-silicates also nucleate ice under cirrus cloud conditions (Archuleta et al., 2005), but the ice nucleating ability of the amorphous silicates in ash at mixed-phase cloud conditions remains unknown". Archuleta et al. (2005) has been added to the reference list.*

Page 28864, line 2: Back trajectory correction is an awkward term since back trajectories have large uncertainties associated with them. Perhaps say back trajectory attribution? That at least does not suggest anything about the correct nature of the assigned trajectory.

*Changed to '..... back trajectory attribution'.*

Page 28864, last sentence: If persisting in making this statement, which is not needed, perhaps be more explicit about what work is needed, such as defining atmospheric concentrations in likely situations such as biomass burning.

*The last statement has been taken out.*