

For clarity, below we list the referees comments in italics and our responses in normal font. Changes to the text are highlighted in blue. Page numbering refers to the ACPD manuscript.

We thank the referee for their remarks on the manuscript and for taking the time to review it. In the general overview, the referee makes reference to concerns on possible over-interpretation of the current work in terms of atmospheric implications, and also some of the strong statements made with reference to the assumptions on what can be expected to be the mineral ice nucleation activity. Specific instances where these issues arise have been pointed out by the referee, and we have aimed to rectify this in the revised manuscript.

Major comments

(1) *Please check the manuscript again for consistent use of the terms dust, mineral, biological, or organic material.*

We have carefully examined the manuscript, and identified cases where additional clarity is called for.

Our usage of the phrase mineral dust is now defined at page 20279 line 8: ‘*Since organic species can be internally mixed with mineral particles in dust aerosols, in the current manuscript we use the phrase “mineral dust” to refer to any dust which can be mobilized from soils, and may or may not contain organic matter.*’

We have identified two places where the phrase “mineral dust” was used in a way inconsistent with this definition: the title of the paper, and in the conclusions (page 20295, line 2). In the title, we have removed the word “dust”, and at page 20295, line 2, “mineral dust” is replaced by “*mineral component*”, to bring the use of the phrase throughout the paper into consistency.

With regards to the terms “biological” and “organic”, material from living entities (i.e. biological) undergoes decomposition in soils to the extent that the resultant material is no longer recognizable in terms of fragments of an organism/products of known biochemical pathway. The combination of all living and dead organic matter, regardless of the stage of decomposition is termed soil organic matter in the current manuscript, as in soil science (Stevenson, 1994). “Biological” is material which is recognizable in terms of fragments of organisms/products of known biochemical pathways. “Biogenic” is material which is derived from biological material, but the phrase does not imply an extent of decomposition. One perhaps unclear/improper use of the phrase “biological” was found in the current manuscript at page 20295 line 3, where the phrase “...results from the activities of biological residues” has been changed to “...*soil organic matter*” for clarity.

(2) Page 20276, lines 18-21 (Abstract): *This conclusion is very speculative and should be modified to just stating that agricultural activities can significantly contribute to the atmospheric IN concentrations.*

Addressed by a rephrasing here: Page 20276, lines 19-21 (Abstract): “*We conclude that dusts from agricultural activities could significantly contribute to atmospheric IN concentrations, if such dusts exhibit similar activities to those observed in the current laboratory study.*”

(3) *And what do you mean with "particularly at temperatures above 258 K" here? A few lines above you stated that at lower temperature the IN activity of the investigated soils approaches those of other mineral samples. How can a minor contribution to the total burden than have a special role in global IN activity? This enhanced IN contribution can at max be suggested for the higher temperatures where additional contribution from biological material was measured.*

What was meant here is that the relative contribution of fertile soil dust particles to the burden of atmospheric ice nuclei is likely to be largest at highest temperatures, as indicated in our charts. However, to avoid confusion here, we have removed the reference to 258 K as part of the rephrasing conducted in response to question (2).

(4) *On the other hand: was the IN activity in this T range really higher than published for e.g. desert dust material? And how relevant or representative are the four samples for soil dust in the atmosphere? Therefore be more careful with conclusions and implications, e.g. add some statements like "... if our laboratory studies are representative for the immersion freezing activity of aerosols originating from fertile soils ..".*

For desert dusts, we considered a comparison to the data of Niemand et al. (2012). However, in reference to temperatures above 258 K, there is only 1 data point in the Niemand et al. (2012) dataset. Consequently the validity of a comparison of our high temperature (>258 K) data to that measured by Niemand et al. (2012) is limited. Further studies at these higher temperatures would be useful before such comparisons can be made.

The reviewer is correct in questioning how representative four samples are in terms of soil dust in the atmosphere. Indeed, such a point could be made for the majority of laboratory studies of natural samples. Nevertheless, the results show that agricultural dust sources *may* be an important IN source. Clearly, more work needs to be done and this study will provide the motivation for that work. We acknowledge that there are limitations to how representative our samples are and accordingly we have drawn upon the cautious phrasing suggested by the reviewer here which forms part of the rephrasing at Page 20276, lines 19-21 (See response (2) above; i.e. "if such dusts exhibit similar activities...").

(5) *Page 20280, lines 23/24: This sounds like you can quantitatively compare the particle fraction you extract in your laboratory with the one that would be found in the atmosphere, if the wind is dispersing particles from the region you collected your samples. A suspension-sieve-settling process is still somewhat different from a wind-driven dispersion and atmospheric settling process, therefore "atmospherically-relevant" is a strong word in this context. Please modify the formulation in the way of more describing what was actually done and less interpreting your lab methods for atmospheric relevance without further explaining the limitations of such interpretations.*

We did not intend to imply that one can simply extract an "atmospherically-relevant" fraction of dust which is both physically and chemically indifferent to natural windblown dusts, but rather that we wished to focus on a size fraction of soils which can be aerosolised by natural/anthropogenic processes.

Accordingly, we have rephrased Page 20280, lines 23/24 to “In order to focus our ice nucleation study on a size fraction which could become aerosolised in environmental samples, it was necessary to sieve and filter the samples”.

We have also added a discussion of potential artefacts of our soil dust extraction procedure in response to referee #2, comment 4.

(6) Page 20283, lines 18-21: What about the broad range of drop sizes in the pico and nano droplet spray experiments. Did they affect the interpretation of the freezing rate measurements? And can you be sure that the concentration of the suspensions is the same in the droplets of all sizes. This is a huge range of droplet sizes. What about surface tension or capillary effects to cause systematic shifts or separation of water and suspended material during aerosolization?

It is important to note here that during the data analysis of pico and nano droplet experiments, we confined the droplets to size bins with much smaller widths than that of the entire size distribution produced during nebulization (e.g. as was noted at page 20287, lines 1-10). Owing to the finite bin widths, this will result in an uncertainty in our droplet volume, and hence surface area per droplet. Although at page 20287 line 10 it was noted that this uncertainty, when propagated together with uncertainties in the surface area measurement, forms the error bars in figs. 4 and 6, we have now detailed more explicitly in the text the scale of the uncertainties generated by the binning procedure on n_s measurements. Accordingly, we have added during the data analysis section at page 20287 line 7: “The droplet size distribution is typically skewed towards smaller sizes, hence we estimate the bin centre with a median volume rather than a mean. Confidence limits are established in the range of droplet volumes enclosed in each bin, within which limits 68% of the droplets fall (which, were the droplet sizes distributed normally, would correspond to ± 1 standard deviation). The largest uncertainty produced by the finite bin width is less than $\pm 87\%$ of the bin median droplet volume for all nano litre experiments and less than $\pm 53\%$ for all picolitre experiments.”

Were there significant differences in the concentration of suspended material between droplets of varying size we would expect to see deviations between different size bins in the freezing activity. Given the good overlap between the n_s values calculated from multiple size bins, generally well within the uncertainties which stem from the finite bin width, any such effects if present must be small. This issue was also addressed in the supporting information of our recent paper on mineral dust (Atkinson et al., 2013).

(7) Page 20284, lines 14-19: I guess the pipette was operated in vertical orientation. How long did the drop formation step go on? Did you check if particle settling inside the pipette needle eventually enhanced the suspension concentration during drop generation?

Droplet settling within the pipette was an issue we considered during the method development of the microlitre assay. The pipette used is a handheld pipette, which during typical operation is held at an angle of 45° . $10\ \mu\text{L}$ of suspension is withdrawn from a vigorously stirred vial containing the suspension, and to pipette $10 \times 1\ \mu\text{L}$ droplets takes less than 15 seconds. The height of the column of suspension within the pipette is 1.5 cm.

While inevitably there will be some settling within the pipette from this procedure, the question arises if this a significant effect in terms of the measured ice nucleating activities. By using a well characterised standard (potassium feldspar), which has a similar size distribution to the soils investigated here (full size distribution for the feldspar can be found in the supplementary information of Atkinson et al. (2013)), we can compare the activities using the above procedure (i.e. 10 μL dispensed in $10 \times 1 \mu\text{L}$ droplets) against the case of only $1 \times 1 \mu\text{L}$ droplet being pipetted at a time. Accordingly, this removes the potential for settling in the pipette needle to result in significant changes to the surface area per droplet. As indicated in Discussion Figure 1 below, the results between the two methods are well within the margins of error of our measurement, and practically indistinguishable, demonstrating that such settling effects are not significant.

(8) Page 20287, lines 21/22: As mentioned above, I'm not in favor of such general statements and conclusions from selected lab and simplified modeling studies. Changing "the dominant ... component" to "a dominant ... component" or, even more appropriate in my view, to "a major ... component" would be more appropriate here. Well, of course you are correctly citing the Atkinson et al. (2013) work which includes such strong statements even in the abstract, so at this place it is up to you to change this formulation or leave it as is.

This has been changed to the referee's preference of "a major...component".

(9) Page 20287, lines 22-24: Such important data treatment should be mentioned and discussed in the plain text and only shortly be mentioned in the figure caption (see also my comment for caption of Fig. 4).

The data treatment has been removed from the caption of Fig.4 and placed in the main article text in section 3.1. In its place in the caption the following text has been inserted "The K-feldspar n_s has been scaled down according to the feldspar mass fraction in each of the soils (see section 3.1)".

(10) Page 20290, lines 5/6: What is the background mineral ice nucleation activity? I really do not see a robust data base for such a statement with regard to the ice nucleation activity of the soil samples investigated in the present work. Each sample can be different, samples you compare here are treated much differently, and concerning the IN results for the nanoliter droplets shown in Fig. 4 I do not even see a systematic trend of the IN activity with the feldspar content: samples B and C seem to follow the postulated "feldspar fraction rule", but samples A and D do not, though they contain a similar feldspar amount as sample B.

We appreciate here that the phrase "background mineral ice nucleation activity" is unclear. We have changed the sentence to make it more accurately reflect our observation, i.e. *Page 20290, lines 5/6* ".....above about 258 K, the ice-nucleating activities of the fertile soil dusts tested here result from the presence of a thermally labile, carbonaceous component, suggesting that biogenic residues are likely responsible for the observed activities."

In relation to what the referee refers to as the "postulated feldspar fraction rule", an important point is raised. While we do find that the order of magnitude of activity does seem to correlate well to what would be expected on the basis of the feldspar content of the soils for all soils tested here, it is important to note that this is a first order approximation. The key assumptions are that the feldspar in our feldspar sample and the soil samples have the same size distribution and also that the feldspars are

not chemically altered in soils in such a way that affects their ice nucleating ability. Nevertheless, the feldspar mass fraction is a reasonable first order predictor of the ice nucleating ability in this temperature range which is consistent with Atkinson et al. (2013). In the past other researchers have used clay mineral samples in order to compare to the IN activities of environmentally relevant samples (e.g. Mortazavi et al., 2008; Conen et al., 2011; Attard et al., 2012). In light of Atkinson et al.(2013), where it is shown that clay minerals are much less effective ice nuclei than the feldspars, using feldspar for this comparison would now seem much more reasonable.

We have modified the pertinent section which now reads: ‘The K-feldspar n_s data in Fig 4. have been scaled down to the feldspar content in each of the soils ($\leq 11\%$, see Table 1) for the purpose of comparison. In the absence of a mineral resolved size distribution for our soils we make the approximation that the K-feldspar mass fraction in the soils can be used to estimate the available surface area of this mineral able to nucleate (i.e. wt% K-feldspar = % of total SSA attributable to K-feldspar in the samples). It is important to note that, in this feldspar scaling approximation, it is assumed that the K-feldspar component of the soils has a similar size distribution as that measured for the bulk soils here and also that the feldspar in soils has not been chemically altered in a way which would change its ice nucleating ability. Inspection of Fig.4 shows that despite these assumptions the feldspar scaling approximation is a first order predictor of the ice nucleating ability of these soil samples in this temperature range, predicting n_s within an order of magnitude.’

(11) Page 20291, line 5: Again speculation, see above.

In line with our response above, we have removed the phrase “tended towards the estimated mineral dust activities” as it is too vague.

(12) Page 20293, lines 1-3: You may also add other literature results like the desert dust related curve by Niemand et al. (2012).

We have added a curve derived from the Niemand et al. (2012) data here. We have also modified the discussion of this figure in order to make it consistent with the revised figure. Most of the changes involve a change of order and the conclusions from this plot are the same. The section now reads: ‘The result is plotted in Fig. 9 (red line) together with measured IN concentrations from between 500-800 hPa ((DeMott et al., 2010)). For comparison, also shown is the IN number estimated for 100% of the dust burden (dashed blue line), assuming that 5% of the dust surface area is K-feldspar. At temperatures greater than about 255 K, the enhanced activities of fertile soils results in ice nuclei concentrations greater than those predicted for the entire dust burden based on feldspar alone. This is consistent with the study of Atkinson et al. (2013) who found the K-feldspar component of mineral dust was one of the most important IN below 258 K, but above this temperature other IN types are increasingly important.

A calculation assuming that 100% of atmospheric dust has the activity of dusts from desert region as reported by Niemand et al. (2012) is also plotted in Fig. 9 (dark red line). The Niemand et al. data has a more shallow slope compared to that for feldspar, which results in enhanced nucleation at higher temperatures. This is intriguing since it implies that such dusts may also display enhanced nucleation at warmer temperatures, which may be consistent with Creamean et al. (2013) who found that biological material co-located with dusts from arid regions may be important IN. More work clearly needs to be done to assess if organic material in arid region dusts can enhance its ice nucleating activity.

It should also be noted that the soils investigated during this study are at the lower end of the wide spectrum of ice-nucleating abilities previously reported for fertile soil dusts. For instance, the most active soil dust examined to date was collected from Western Yakutia (Conen et al., 2011). As an upper limit to the potential number of ice nuclei possible from soil dusts based on current available data, this case is plotted in Fig. 9 (black line) using this enhanced ice-nucleating ability, with the same assumptions as used for the soils in current study. This shows that the organic content of soils has the potential to dominate the IN population at temperatures above 258 K.

(13) Page 20294, lines 15-18: Again, this is a very speculative statement. I agree that it is interesting to compare such rough estimates based on globally averaged aerosol concentrations from highly idealized and simplified model runs with field measurements of IN concentrations. But, on the other hand, one should not argue that such estimates can explain or "account for" actual measurements at certain locations and for certain time periods. To my opinion, this is not more than an order of magnitude estimate, if at all useful to get significant additional information about the relation between aerosol properties and ice nuclei concentration. A more thorough and meaningful study should compare model results at the point and time of measurement and should also include measurements of aerosol properties together with the IN measurements.

Agreed. On reflection and in light of the referee's comments, we have removed the entire discussion of this point. We have also reduced the amount of field data in Fig 9 in order to simplify the graph. Data from ground level have now been removed, and it now only contains IN concentrations measured from between 500-800 hPa.

(14) Page 20294, lines 19-29: This section also is rather speculative and does not include extra information other than repeating that a certain amount of primary ice nuclei is needed to trigger the ice multiplication process in clouds. Therefore, this section should be removed.

We have removed this section.

(15) Page 20311, Fig. 4: This figure should be enlarged, in particular in the y-axis direction, in order to better identify agreement or disagreement between the different data sets and so better identify sample to sample variability.

In final version figure has been enlarged by 50% in the y-direction.

(16) Page 20313, Fig. 6: This figure should be larger in the final version. In the caption you mention that the Atkinson et al. (2013) data have been scaled down to simulate the mass fraction of the feldspar in the soil samples. I think, this is not a simulation, it is just a scaling factor which not even needs to be representative for the different IN activity in the respective sample. There are other factors like completely different pre-treatments of the feldspar and soil samples which may affect the IN activity even more than just the different feldspar content (see other comments above).

The figure is enlarged in the final version. With regards to the use of the phrase "simulate", this may perhaps imply that what has been done is more complex than just a simple scaling. The pertinent line

in the caption now reads: ‘The K-feldspar n_s has been scaled down according to the feldspar mass fraction in each of the soils (see section 3.1).’.

Minor points and typos

(1) Page 20276, lines 8/9 (abstract): *What about mentioning the particle size range and concentration already in the abstract?*

Done.

(2) Page 20276, lines 13/14 (abstract): *If possible indicate if the ice nucleation from biological material contributes all, a major fraction or just a minor fraction.*

We have added the phrase “...demonstrating that a major fraction of the ice nuclei stem from biogenic components in the soil”.

(3) Page 20276, lines 18 (abstract): *“We conclude that, although only . . .”*

This sentence has been changed (see response to major comment (2) above).

(4) Page 20276, lines 23-25: *I wondered why you cited these recent papers here. The freezing behavior of pure water was investigated much earlier and was investigated by some more recent papers since then for several reasons. This, and also the statement of the following sentence is text book knowledge.*

We agree that there is a large list of literature on the topic, however, the more recent work highlights the discrepancies in the literature. For such a fundamental process there remains a lot of uncertainty and the new references reflect and discuss this in some detail. The value we chose of 237 K is based on the more recent work with the spread in temperatures (for the same nucleation rate) over several degrees.

(5) Page 20283, line 10: *Please also mention respective range of drop diameters. A 1 μ l droplet already has a diameter of more than 1 mm, I think.*

Droplet diameter “(d=8 μ m - 1.45 mm)” added here

(6) Page 20285, line 28: *I would prefer replacing "stochastic approach" with "nucleation rate approach", because this refers to what the approach really is, namely another approximation to measured freezing rates, just using rate equations from classical nucleation rate theory, which in turn of course assumes stochastic freezing behavior.*

Changed to “stochastic nucleation rate approach”. We wish to retain the phrase “stochastic” here in order to help distinguish from a singular approach, which does not assume stochastic behaviour. Furthermore, we wish to avoid confusion between different uses of the word “rates” e.g. as defined by Vali (1994) the “nucleation rate” and the “freezing rate”, which are different quantities.

(7) Page 20285, lines 28: “. . . that nucleation behaved like a time-independent process

. . .

Inserted “. . .that nucleation behaves as a time-independent process”

(8) Page 20286, lines 7/8: *I preferred to see only those work cited here that gives direct evidence of time-dependent freezing going on in nature, like the one by Westbrook and Illingworth (2013), though, as far as I can see, also this work gives only indirect evidence on time-dependent freezing mechanism*

Yes, the references didn't quite match the statement made here. We have modified the sentence to read: ‘although it should also be noted that there may be situations in nature and in the lab where the time-dependent behaviour of nucleation becomes important’ and have retained the original references.

(9) Page 20287, lines 1-3: *You may more explicitly mention that in microliter experiments the droplets appeared to be of more similar or monodisperse size, whereas in the nano and picoliter experiments the droplets appeared to be more polydisperse.*

Done. Added at page 20287 line 3: “In microlitre experiments this size binning was not necessary as the droplet population is monodisperse ($1 \pm 0.1 \mu\text{L}$).”

(10) Page 20289, line 5: *Add year of publication*

Done.

(11) Page 20289, lines 10/11: *And what about the uncertainty of the optical technique for a-spherical particles? Which equivalent diameter is actually measured? And which surface area is then available in a model to apply lab result for ns parameterization?*

Uncertainties originating from the optical technique itself (e.g. those due to variations in the refractive indices chosen for the analysis) have been highlighted in section 2.2.. Uncertainties due to particle shape effects have now also been detailed in response to referee #2 comment (5).

We have changed the phrase in brackets at 20289 lines 8-9 to “(the fundamental quantity measured in laser diffraction is the volume equivalent sphere diameter)” in order to clarify what equivalent diameter is measured. Similarly, in the experimental section it is now explicitly stated at 20282 line 8 that it is the “volume equivalent sphere” diameter and also on page 20282 line 11: “We have used the manufacturers standard analysis model for samples containing irregular particles in order to determine volume equivalent spherical diameters”.

For use in model simulations, we would expect that the surface area determined from techniques which estimate the distribution based on equivalent spheres to be the most appropriate to use in this case, rather than the use of gas adsorption techniques, as the former more closely resembles how surface area distributions are typically measured for atmospheric aerosols. For instance, in Fig. 9, we use the surface areas determined from spherical equivalent diameters and our n_s values (also determined using spherical equivalent diameters from laser diffraction) to estimate IN concentrations.

(12) Page 20289, line 14: *to which experiments do you refer to herer?*

Inserted “In microlitre drop freeze assay experiments”

(13) Page 20291, line 27: *“ . . . makes it difficult . . . ”*

Corrected

(14) Page 20292, line 29: *Why did you assume only 20% of the soil dust related aerosol particles to be ice-active?*

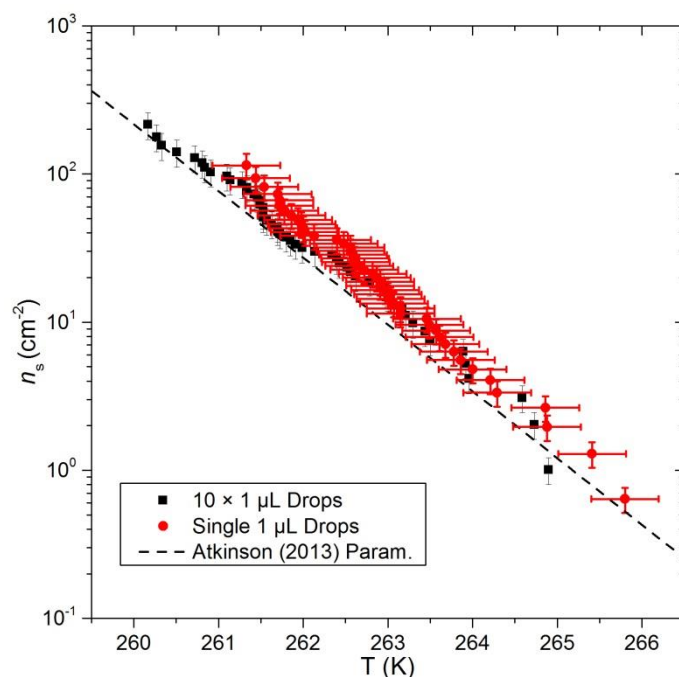
We did not assume that only 20 % of the soil dust had IN activity, but rather that if the 20 % of dust emissions which can be attributable to agricultural emissions (page 20292 lines 21-23) had the same activity as the fertile soil dusts studied here in order to examine the potential contribution of fertile soil dust sources to the overall IN burden. To avoid confusion, we inserted: “...assuming a 20 % portion of soil dust aerosol particles had the same activity as the soils we sampled.” For additional clarity, at page 20293 line 2, rather than using the word “total” to detail the dust loadings used for the feldspar and Niemand data estimates for arid mineral dusts, we have changed to “100 %” of the dust burden.

(15) Page 20315/316: *Any reason for reversing the temperature scale in Figs. 8 and 9?*

We have revised the figure to make it consistent with the previous figures.

(16) Page 20317, Fig. 9: *Figure could be larger, caption should be shorter. In caption, publication year of Hoose et al. reference is missing. You may also mention in thecaption for which pressure range you selected the model dust load as input for the IN calculations (I think you mentioned this in the text somewhere).*

Figure is enlarged in revised version. We realise that the caption is quite detailed here, although given the complexity of the figure, we wished to have as informative a caption as possible, so that the reader didn't have to keep flicking forward and back to the text to be able to understand the graph. Please note the caption has been updated for the presence of the Niemand et al. (2012) data as requested (major comment 12 above) and to clarify what percentages of the dusts loads were used for the various samples (minor comment 14 above). The publication year of Hoose et al has been added, along with the pressure range from which the dust loads were taken (600 hPa).



Discussion Figure 1: Examination of the possibility of settling effects in pipetting technique using K-feldspar as a standard. For clarity, x-error bars are only shown for one series. Illustrated are results from when a suspension of K-feldspar is pipetted to form 1 μL droplets from a 10 μL suspension reservoir in the pipette (10 \times 1 μL Drops), and when each 1 μL droplet is withdrawn and pipetted individually (Single 1 μL drops).

References

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