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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Organic matter matters for ice nuclei of agricultural soil origin" *by* Y. Tobo et al.

Anonymous Referee #2

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Review of Tobo et al., Atmos. Chem. Phys. Discuss., doi:10.5194/acpd-14-9705-2014: "Organic matter matters for ice nuclei of agricultural soil origin"

This work looks at the ice nucleation activity of different dust particles examined with a continuous flow diffusion chamber (CFDC) in the laboratory. Examined samples comprise two different agricultural soil dust samples, a China loess soil dust sample and a mineral dust sample for comparison, and particles are additionally treated with either H2O2 or heat to obtain information about the nature of the ice nucleating entity on the particles. Particle analysis with SEM/EDX was also done.

The results show that the soil dusts contain organic materials which dominate the ice nucleation ability increasingly towards higher temperatures in the temperature range

from -36°C to -24°C. These results are in line with other recent studies which point out the importance of biological particles for atmospheric ice nucleation, and carry our current knowledge forward. The work is on the cutting edge of research in the respective area and hence has a high value for the community. Still, below I have comments and questions which the authors should consider. Once this has been done, the work definitely should be published in ACP.

I also want to add that deciding between minor and major revisions was a close call, and I only chose the latter due the amounts of comments I made. But it should all be easily done.

Specific comments:

page 9706, line 2-3: Is the importance of desert soil dusts for ice nucleation really relatively well understood? “Relatively” in that context could be misunderstood, and I’d recommend weakening the statement a bit more.

page 9706, line 22: It is textbook-knowledge that IN are required to trigger ice nucleation at temperatures warmer than about -36°C, and instead of citing these three newer publications, I recommend citing the Pruppacher and Klett book (e.g. already the version from 1978 or any of the newer prints, and the knowledge as such has been around even longer).

page 9706, line 26: The work by Hoose et al. (2010) you cite here and a second paper by Hoose et al. (2010b) both came to the conclusion (based on modeling), that there is only a marginal / negligible contribution of biological material to global ice nucleation and hence to not support your statement here. The Hoose et al. (2010) cite should be removed, or you have to discuss that it comes to a controversial conclusion. However, there is literature around which explicitly dealt with the importance of soil dust for ice nucleation (Conen et al. (2011) and O’Sullivan et al. (2014)) – you cite this later, but please cite these two here, too.

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page 9707, line 2-3: “has not been taken into account” – this contradicts the previous sentence, where you stated that “suggest that soil dusts are the most important IN sources at temperatures between about −36°C and −15°C”. This sentence needs to be rewritten, also based on the fact that I suggest changing the citations in the previous sentence.

page 9707, line 13: “The chemical composition of individual particles capable of nucleating ice has remained uncertain.” More work than you suggest here has been done in this respect. E.g. Szyrmer and Zawadski (1997) list a variety of biogenic IN (fungi, bacteria, pollen, etc.). A recent publication by Hartmann et al. (2013) summarizes exemplary work of the past 4 decades, describing that it is a protein complex which causes the ice nucleation activity for bacteria. There, it is also argued that these complexes can occur separated from the original bacteria, attached only to some membrane fragment, and that those were found to be preserved and maybe accumulated when being connected to mineral surfaces (Kleber et al., 2007). Furthermore, Pummer et al. (2012) and Augustin et al. (2013) both examine pollen washing water, showing that there is a small macromolecule (likely a polysaccharide) which is the ice active entity in case of pollen. All of this should be included / discussed in your text.

page 9708, line 6: When reading the text the first time, I thought China loess soils were thought to represent an agricultural soil dust sample, too, as arid regions can be irrigated. Therefore, please clarify here if the China loess soil is or has been used for agriculture or not.

page 9709, lines 1-5: From what I remember from measurements made with your CFDC as shown in literature, immersion freezing is the most active heterogeneous freezing process of those mentioned here and hence should overwhelm all others? If you agree with me on that point, please mention this here or change the sentence accordingly.

page 9709, line 8: Some more information on the sampling by the impactors is needed

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(e.g. impactor type, how they were operated, lower size cut, ...) Also mention explicitly that you sampled behind the CFDC and in parallel to it. Also, when sampling behind the CFDC: How were IN distinguished from droplets and non-frozen dry particles, and how did you make sure that ice crystals in the CFDC did not evaporate prior to sampling?

page 9709, line 21: Motivate why you think that H2O2 treatment most likely destroys organic matter, or else remove the statement.

page 9709, line 25ff: In some of your own work (Wex et al., 2013) it was shown that kaolinite from Fluka changed its ice nucleation activity when coated with H2SO4, while the kaolinite you chose for your study (KGa-1b) did not. This difference is argued to occur due to the presence of K-feldspar, which is not present in the KGa-1b kaolinite. Hence it is possible that this mineral is also not present in the China loess soil dust but in both agricultural soil dust samples you examined, and that it is not biological material but K-feldspar which you destroy by H2O2 treatment. Can you argue against that? However, it helps that you also did a heat treatment, because with this you can argue that the K-feldspar is heat resistant (work from your lab (Sullivan et al., 2010) showed in the past that Arizona Test Dust did not decrease in ice nucleation activity when heated up to 250°C, so you could use that as an argument) while the organic matter likely is not heat resistant. Rewrite this part of your text according to the points I raise in this comment.

page 9710, lines 19/20 and lines 22/23: It is not entirely clear what you mean by "examples of the other elements". Do you mean "some of the elements which were present only in smaller amounts"? Please rephrase!

page 9710, line 25: The caption of Fig. 5 does give the number of particles you examined, but I suggest you also give this information in the main text.

page 9710, line 26: This refers to a point I already made earlier (page 9709, line 8, concerning the impactor sampling): How exactly did you isolate those particles which

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are IN active at the different temperatures for separate examination? Please describe the method used in more detail somewhere in your text.

page 9710, line 28ff: As mentioned before, in the literature (Hartmann et al. (2013) and many older references therein, Pummer et al. (2012), Augustin et al. (2013)) it has been shown that the ice nucleation by biological entities such as bacteria, pollen and fungi is caused by single very small INA-MM (size of a few 10nm) (for fungi this so far has only been shown in Fröhlich-Nowoisky et al., (2014)). Can you exclude that such a small macromolecule is present on those particles you define as "mineral particle"? Again, the heat treatment might help you, but you should discuss this explicitly in your work.

page 9711, line 8-10: Hint towards Fig. 5b, where you show the respective results.

page 9711, line 12: Again: Referring to H2O2 treatment here might be too weak – you might want to mention that the heat treatment more certainly only affected the organic ice nuclei and resulted in a similar decrease of the ice nucleation activity.

page 9712, line 3-4: As mentioned before, more is known about this than you suggest here, and you should discuss this accordingly (see my comment to page 9707, line 13).

page 9713, line 18ff: You argue that the contribution from biological IN to the overall IN population is small. This might be misleading as SOM might consist of ice active macromolecules (see my respective comments above). It might be argued that the contribution from whole bacteria or pollen is small, but it might be wrong to extrapolate that to biological IN in general.

page 9714, line 16: Typo: The author of the paper is Santl-Temkiv (i.e. an “l” instead of an “i”)

Appendix A, equation A5: Could it be that the nominator misses a “ + N_IN[inorganic]”?

Figure 4: Do you really mean “representative”, or rather “exemplary”. Just think about

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it and choose which term fits better.

Figure 4 and 5: The print in both figures is rather small, particularly for Fig. 5. If you can assure that the figures will be printed in the final version using two columns, you can leave it as is, but if they are thought to be printed in a single column, a copy of your paper when printed on paper will be indecipherable.

Literature:

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