

Interactive comment on “Competition between water uptake and ice nucleation by glassy organic aerosol particles” by T. Berkemeier et al.

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Referee comment 1:

First of all, I am very sorry for the delay with sending these comments. This paper presents model calculations and conceptual analysis of the competing effects of particulate phase diffusion vs. ice nucleation, commenting on the ways that organic aerosols can interact with clouds. The paper makes useful points and is probably a good starting point for further studies, although a lot needs to be done still to resolve the different processes through which organic aerosols interact with clouds. I think this paper can be considered for publication in ACP once the following points, along with the points raised by the other reviewers, have been addressed by the authors.

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Response:

We gratefully thank anonymous referee 3 for her/his review of our manuscript and appreciate the suggestions she/he made to improve the quality of the paper. In the following, we will address the comments individually.

Referee comment 2:

Major/general comments: 1. If I understand correctly, you assume constant hygroscopicity parameter for your mixtures. As you probably know, however, the hygroscopicity parameter depends on the RH/supersaturation in case the organic material is not completely dissolved. Now the authors limit the discussion in the main paper to kinetic transport vs. ice nucleation, while the organic solubility is not discussed at all. I think the authors should add a discussion on how the solubility of organic compounds and its dependence on external conditions (water content, temperature) would affect the results / play into the conceptual scheme.

Response:

The model calculations in this study assume that water and oxidized organics are perfectly miscible over the observed humidity range (55 – 95 % RH). For the model system sucrose, which is described first in this paper, this assumption certainly holds and also a full, multi-parameter water activity parameterization has been used to describe sucrose hygroscopicity. For simplification of the very complex system of secondary organic aerosol (SOA), water activity of SOA is parameterized using a constant hygroscopicity parameter κ_{org} . We note that κ_{org} is not well known at these low temperatures, which is why we neglected a composition/RH dependence of it. While this is certainly not a perfect description of such a complex system, we think that the generality of our approach (SOA mixtures are derived from marker substances bundled into classes of same precursor origin) justifies the use of such a rather simple measure. A recent paper by You and Bertram (Atmos. Chem. Phys. Discuss., 2014) did not observe any temperature dependence of liquid-liquid phase separation, suggesting no

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major changes in the thermodynamic solution properties of those organics. To clarify the origin of our hygroscopicity estimates, we added a clarifying sentence to section 3.3, which reads as follows:

Hygroscopicities of the various SOA were taken from Lambe et al. (2011), who suggested that κ_{org} can be parameterized independently of SOA type as function of O/C ratio.

In fact, in our modelling studies, uncertainty in κ_{org} is among the stronger uncertainties, which will be evident from a new Fig S6. Moreover, we add a subsection on limitations and uncertainties of the model to section 3 of the manuscript that addresses the problem of uncertain thermodynamic parameters.

While a measured κ_{org} value in principle considers insoluble fractions, the model does not resolve them numerically and doesn't assign ice nucleation activity to them. To clarify this point we added the following sentence to the discussion in Sect. B2:

Possibly, insoluble products from Naphthalene OH oxidation remained solid in the otherwise fully deliquesced particle and nucleated ice heterogeneously with lower efficiency. Such a process is not considered the model, which does not resolve single compounds and treats Naphthalene SOA as homogeneous mixture at all times.

Referee comment 3:

2. Besides the solubility, another thermodynamic parameter that is likely to be strongly influenced by the water content as well as temperature is the volatility of the organic material. I think this too deserves some discussion on the paper. This paper seems to focus on the importance of the phase state on the kinetics of water in the organic matrix, but I think the importance of the phase state for the energetics/thermodynamics of the organic system (manifested in solubility and equilibrium vapour pressures) deserve some discussion as well.

Response:

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In this study, we looked at organic aerosol under cirrus conditions, i.e. at temperatures below 240 K. While volatility plays an important role in gas-to-particle partitioning of SOA in general, volatilization of organic compounds is expected not to be significant during our model simulations under these low temperature conditions. We thus find it reasonable to neglect volatilization effects for our study. We have added this information to the new section 3.4:

Volatilization of organic material has not been included in the calculations presented above since vapour pressures of typical SOA marker compounds are low under the low temperature conditions employed in this study (Huisman et al., 2013; O'Meara et al., 2014).

Referee comment 4:

3. I would have appreciated a discussion on the potential limitations of the model and what kind of experiments the authors would need to constrain it better.

Response:

The largest uncertainty in the simulations presented in this paper arises from the uncertainty in input parameters. In particular, the model would benefit from accurate parameterizations for the water diffusion coefficient inside SOA particles. Until now, these values are practically unknown. This paper makes a first attempt to estimate diffusivities of water within such complex organic mixtures. Additionally, the heterogeneous ice nucleation process on glasses needs more detailed understanding and investigations so that accurate and reliable nucleation onsets are available for a larger number of different compounds and also mixtures of these compounds. We agree that such a discussion might be worthwhile and added a full section 3.4 to discuss model uncertainties to the revised version of the manuscript.

Referee comment 5:

Minor/specific comments: 4. Abstract, p. 16452, line 20: I find the concluding state-

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ment of the abstract a bit too general and vague. Please be a bit more specific here. What kind of formalisms are needed? What would be the first, most critical, improvements in the atmospheric models that one should start with?

Response:

In our opinion, atmospheric models should, after further careful studies have been conducted, implement organic aerosols as ice nuclei. This study suggests upper temperature limits below which these particles can act as ice nuclei at a certain ice supersaturation. We also show that a potential parameterization of a heterogeneous ice nucleation onset must include air parcel updraft velocity and particle size to account for the competition between water uptake and ice nucleation on these particles. We will thus add the following sentence to the abstract:

For the incorporation of ice nucleation by organic aerosol particles into atmospheric models, our results demonstrate a demand for model formalisms that account for the effects of molecular diffusion and describe ice nucleation onsets not only as a function of temperature and relative humidity, but also include updraft velocity, particle size and composition.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 16451, 2014.