

Interactive comment on “The effect of organic compounds on the growth rate of clouddroplets in marine and forest settings” by N. C. Shantz et al.

N. C. Shantz et al.

Received and published: 29 July 2008

First of all, we would like to thank Referee #1 for the detailed review of our manuscript, with constructive comments and suggestions. Below are our replies to the specific comments provided by the Referee.

Referee general comment: The paper includes two different concepts that should be distinguished more clearly: (1) The water uptake is a dynamic process and the organics are slowly dissolved and, according to Köhler theory, the hygroscopicity (κ) changes over the course of particle/drop growth (kinetic approach). (2) The organics have a defined hygroscopicity (κ) that is lower than the inorganic fraction (thermodynamic approach) (Section 5). Whereas the second approach has been used in many previous studies, the effect of 'delayed growth' by organics has not been discussed in many studies yet. However, it has been shown that mixed inorganic/organic particles

usually have a very low efflorescence relative humidity (ERH), e.g., [Marcolli et al., 2004]. Even at a few % RH all organic might have been dissolved even though in a pure state they might have a lower solubility. Given such results, I am not sure whether reporting the solubility of organics (even though the authors point out that it probably does not reflect the 'true solubility'; anyway) is a useful parameter. The comparison of figure 7 and 13 suggests that assuming either a dissolving organic compound or a organic compound with a smaller kappa leads to the same result in terms of the predicted growth rate. It should be made clear why the predicted solubility might be a better/equally useful parameter to represent organic properties.

Response: We agree completely with these comments. We have clarified the difference between these 2 concepts in the introduction, in Section 3.2 and in the conclusions. Actually, we have rewritten Section 3.2 in the hopes of clarifying these issues and those of the next general comment. We have also included the suggested reference and a discussion of the concept of "effective solubility"; in Section 3.2. We agree that modelling solubility has its problems, but we wanted to compare the original code with gradual dissolution of the slightly soluble organics to the kappa-CCN model. Also, solubility provided a reference that we could use to compare the CCN growth rates between different organic cases. We hope this is all clearer in the manuscript now. Thanks very much for the suggestions.

Referee general comment: The difference between 'solubility' and 'hygroscopicity'; should be made clearer throughout the paper. Whereas inorganic salts (and possibly some organics) are very soluble, their hygroscopicity (proportional to kappa and the solute term in the Koehler equation) and, thus, CCN ability can differ significantly.

Response: We have made this distinction in the manuscript, especially in Section 3.2. Minor corrections to this regard were also made in Sections 4.1.4 and 4.2.2.

Referee general comment: The water soluble organic carbon (WSOC) measurements have been used as a measure to determine the soluble vs. insoluble OC fraction. How-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

ever, recent CCN studies suggest that WSOC might not be dissolved at the relatively small amounts of water as present in the CCNc [Ervens et al., 2007]. Only at high dilution as used in order to dissolve filter samples, this OC fraction might be really dissolved. Can you give an estimate of the water on the activated particles? I.e. organics of which solubility can be dissolved in this water volume?

Response: We agree with the reviewer on this point. Indeed we discussed this with respect to our model in Shantz et al. (2003). What we said there was that there can be a kinetic limitation to dissolution that is not what we describe with our model. That is, our model assumes a new equilibrium at each time step based on the total amount of condensed water. However, there can be a kinetic limitation to dissolution such that the solute does not dissolve that quickly. This is a concept that is equivalent to the WSOC issue that the reviewer describes. WSOC represents a total amount of solute that is dissolved in a relatively large volume of water, but it neither reflects the small amounts of water accumulating on solution droplets during cloud activation nor does it reflect the kinetic aspect of dissolution. Here, we made two sets of simulations for the Golden Ears cases; the first used an assumption that the entire organic component had a specified solubility, and a range of solubilities were used (Sections 4.2.2 and 4.2.3). In the second set of simulations, the organic was split between an insoluble section and a soluble component, where the latter was based on the WSOC measurements (the new Section 4.2.4 concerning only WSOC from Golden Ears). The solubility of the soluble fraction was again varied in the second case. This was done more to represent the potential mix of water active organics, which the WSOC fraction can reasonably represent.

We have added some words of clarification about the WSOC issue as we perceive it, and we think that our perception is not at odds with this reviewer (or reviewer #3 of this paper). In the early stages of cloud droplet formation, particularly prior to activation, there is insufficient water to completely dissolve many organic compounds with small solubilities that would still be recognized as WSOC. Therefore, we feel that the WSOC

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

measurement is not a good surrogate for solubility of the organic aerosol, and as stated above, we use it here only as a means of looking at differences between potential organic CCN components and those (such as straight alkanes) that would not participate in water uptake.

Clarification and further explanation has been included with respect to the fact that WSOC may not be entirely dissolved. The reference to the Ervens et al. paper has been included in Section 4.2.4. Solubilities that may dissolve at 5 seconds into the simulation have been added to the Section 4.2.4.

Referee specific comment: p. 8206, l. 11: What is the range of assumed solubilities?

Response: Thank-you for the suggestion, we have added to Section 4.1.3 the range of solubilities, from insoluble (solubility=10⁻⁶ g L⁻¹) to soluble (solubility=200 g L⁻¹), as well as Section 4.1.2, where these solubilities were also missing.

Referee specific comment: p. 8208, l. 9-11: Is the conclusion here that the organics only act as 'carrier'; and increase the size of particles? Do larger particles grow faster than smaller ones?

Response: Yes, we found that the organic increases the size of the particles into more CCN active size range. Yes, the large particles grow faster than the smaller particles but the key here is that there are a larger number of particles at sizes that activate at these supersaturations. Clarifications have been added to the text.

Referee specific comment: p. 8209, l. 20: Are the 17% and 4% the sulfate fractions? If so, you should reword this sentence as you talk here about sulfate/organic ratio.

Response: No, these numbers are average sulphate/organic ratios for the period. The word 'average' has been added and these values are now expressed as fractions (0.17 and 0.04).

Referee specific comment: p. 8210, l. 8: Is the molecular weight of the insoluble (BC) fraction used at all? In the Koehler equation usually only the insoluble fraction is used.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Response: Thanks for mentioning this. You are right; molecular weight of BC is not used. The text has been changed accordingly.

Referee specific comment: p. 8210, l. 19-22: Where would be the activation diameter if you assumed purely inorganic particles? Can mode 1 ever be activated at these S?

Response: The upper edge of mode 1 would activate if we assume pure ammonium sulphate particles (minimum activation diameter=0.0492 microns). This note has been added to the manuscript.

Referee specific comment: p. 8210, l. 22: You should remind the reader here (once more) that the observed growth rates are a combination of particle number, and size (and composition).

Response: This has been corrected.

Referee specific comment: p. 8210, last line: Replace 'insoluble curves' by 'curves representing insoluble organics' or something like that (check also the remainder of the manuscript for this term).

Response: This correction has been made.

Referee specific comment: p. 8214, l. 25: Mixing processes usually increase the CCN ability of particles since any soluble material added to a previously insoluble particle increases its hygroscopicity. Thus, mixing is unlikely to be the reason of decreasing kappa. The argument you give at the end of the 'summary and conclusion section', i.e. increased organic mass fraction seems more reasonable.

Response: Clarification has been included and the reference to the 'mixing processes' has been removed.

Referee specific comment: p. 8215, l. 10: Replace 'the organic is of no consequence' by something like 'organics do not contribute to water uptake and appear to be insoluble'.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Response: This correction has been made.

Referee specific comment: p. 8215, l. 23-26: You should also add 'molecular weight' to the list of these assumed parameters since it determines also the organic hygroscopicity.

Response: This correction has been made.

Referee specific comment: Figures 2, 4, etc: Add either in the caption or in the figures itself that the numbers on top of the plot are the supersaturations.

Response: This correction has been made.

Referee specific comment: Additional references

Response: The two additional references have been added. Thanks for all of the detailed suggestions.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8193, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper