Response to reviews

Reviewer comments are in **bold**. Author responses are in plain text. Modifications to the manuscript are in *italics*. Line numbers in the responses correspond to those in the revised text showing tracked changes (Word document).

Reviewer #1

(1)This paper relates the CCN-derived hygroscopicity of organic-rich particles, composed either of pinonic acid, a C6 -C9 diacid, or secondary organic matter (SOM, either isoprene or α-pinene precursor), to the bulk water solubility of the OM. Many previous studies have dealt with this issue, and the major contribution of this paper is to relate the transitions between insoluble, slightly soluble, and highly soluble compounds to O:C ratios of 0.2 and 0.6. This subject will be of interest to ACP readers, and this data set and analysis are sufficiently extensive to allow more firm conclusions to be drawn than in previous studies of the relationship between solubility and CCN activity. I recommend publication in ACP after the following concerns are addressed.

We thank the reviewer for the careful reading, and acknowledging the usefulness of the manuscript.

(2) Major comments: The authors found that pimelic acid was more CCN-active than predicted. In lines 16-27 on page 31839, the authors hypothesize that an increase in solubility with temperature accounts for this difference. I had several issues with this paragraph. First, due to its speculative nature, I feel it belongs in the discussion section (if anywhere), and not in the results. Furthermore, and more importantly, the authors cite similar results from Hartz et al. (2006) and Frosch et al. (2010)- but both of these studies used a static thermal-gradient CCN instrument, which involves active cooling and therefore temperatures at activation below room temperature. For example, for the Wyoming CCN instrument used in Frosch (2010), the temperature at activation is < 293 K (Snider et al., 2010). Therefore it seems that the enhanced CCN activity of pimelic acid occurs at lower temperature as well. This is in contrast to the actively heated CCNC used in this work, which as the authors point out involved activation at T=303K. This difference in temperature between static and continuous-flow CCN instruments has been used in a previous study to constrain the influence of T on CCN activity (Asa-Awuku et al., 2009). Finally, as the authors point out, temperature effects were not observed for other compounds, and it is not clear why if temperature effects are important. Given all this, I feel that the authors should either test their hypothesis by presenting results taken at a lower temperature, for example 293K instead of 303K, or omit this paragraph.

We acknowledge the reviewer for this comment, which is based on strong technical background. We agree with the reviewer that the discussion is based on hypothetical ideas because systematic experiments to investigate the temperature dependence have not been conducted (Christensen and Petters, 2012). As pointed out by the reviewer, the Wyoming type CCNC is actively cooling the instrument to create supersaturated environment. Differences in both particle generation methods as well as CCNC would need to be considered in comparing experimental results. Both Hartz et al.(2006) and Frosch et al. (2010) employed atomization of aqueous solutions to generate particles, unlike our present study. As clarified in the revised manuscript, particles generated by atomization are frequently contaminated by trace amount of impurities such as ammonia, which also affects solubility of organic materials. Therefore, systematic experiments on temperature dependence using pure pimelic acid particles will need to be conducted in the future for this issue. We have revised the text to accommodate this input.

'*Some technical issues associated with CCNC instrumentation, as well as particle production methods, must be considered in elucidating possible reasons for the discrepancy among the theoretical prediction and experimental observations. There are temperature gradients inside the instruments that can significantly influence CCN activation for compounds that have high sensitivity with respect to temperature-dependent solubility (Asa-Awuku et al., 2009; Christensen and Petters, 2012). Apelblat and Manzurola (1989) reported a significant temperature dependence for the solubility of pimelic acid, more so than for the other studied acids (Appendix A1). The highest temperature in the CCNC during the measurement of pimelic acid particles was 303 K, corresponding to the lower section of the instrument. At this temperature, the value of C = 0.06 borders between highly and slightly soluble, leading to a hypothesis that the elevated temperature in the instrument altered the CCN activation regime of the pimelic acid particles. CCN activity of pimelic acid particles is in particular sensitive to temperature because the solubility at room temperature is on the border between slightly and highly soluble cases. Temperature dependences in solubility have also been investigated for other organic compounds, yet such regime shifts were not observed for these cases (Appendix A1). A systematic experiment on the temperature dependence is motivated for confirming this explanation for pimelic acid (Christensen and Petters, 2012). Another possibility is that impurities such as ammonia could affect solubility, as in the case of adipic acid (Hings et al., 2008; Kuwata and Martin, 2012b). Other factors, such as particle morphology, changes in surface tension at elevated temperature, or non-ideality of solution, might also influence the activation.*'

We retained this section in the results section of the manuscript rather than the discussion section because we think the manuscript flows better and is clearer to read in this case. To the reviewer's concern, we think the clarifications pointed out by the reviewer are important and, with those in place, this section can still be adequately presented in the results section.

(3)The authors use small inorganic seed particles when generating SOM. However, they report κ_{CCN} without making it clear if this value is for the mixed particle or if they have used, e.g., the ZSR rule to isolate the organic fraction of the particle. Please include the details of how (if at all) the calculations accounted for the inorganic portion of the dry particles. Table 2: Along with observed κ, the volume fraction organic in the dry SOM particle (or alternatively, the diameters of the SOM-coated particles) would be of interest. I recommend adding it to this table. The text mentions SOM diameters from 30 to 300 nm, but I'm assuming this wide range was not used for each experiment.

We assumed ZSR approximation (i.e., inorganic and organic compounds uptake water independently) to obtain κ_{CCN} of organic aerosol particles, as described in our previous publication (Kuwata et al., 2011). The particle diameter for the CCN measurement ranged from 80 to 150 nm, meaning that volume fraction of SOM was larger than 0.95. The following statement was added to address the reviewer's comment.

'*The volume fraction of the SOM was greater than 0.95 for the analyzed particles (i.e., > 80 nm), and a correction was included in the analysis based on volume additivity between sulfate (<5%) and SOM (Kuwata et al., 2011)*'

(4)Table 4: The water activities at deliquescence ($a_{w,D}$) cited from Chan et al. (2008) are actually the water activities of saturated macroscopic solutions (a_{sat}), so it is not correct to say that "Chan et al. (2008) measured $a_{w,D}$". The authors explain for some of the other $a_{w,D}$ values how they were calculated from bulk solubility data; they should add that Chan et al. (2008) used the same approach. There are other places in the manuscript that imply that Chan et al. (2008) measured ($a_{w,D}$) directly (see below); they should also be corrected.

According to our understanding, in the absence of Kelvin effects the two quantities can be equated because deliquescence is a statement of free energy balance (Seinfeld and Pandis, 2006), which leads to the following statement: 'first, that the molality of the solution at the deliquescence point is the same as the solubility of the salt at that temperature. Second, the deliquescence relative humidity is consequently the same as that over the saturated solution.' (http://www.aim.env.uea.ac.uk/aim/tutorial/lesson2c.htm). The implication is that a_{sat} of bulk solution synonymous with $a_{w,d}$. This approach has been used experimentally, for instance, by Chelf et al. (1999)or Brooks et al. (2002). We added the following statement in the revised manuscript to clarify this point.

'*Chan et al. (2008) measured aw,D at 23 C for a stated uncertainty of 0.003 by the experimental approach of measuring the water activity of saturated aqueous solutions.*'

Minor comments:

(5)P 31835, L 21: Recommend that "highly soluble" be changed to "NaCl" or "salts with high ion densities", since "highly soluble" has already been used (on page 31834) to describe organic compounds with aqueous saturation concentrations greater than 0.1 v/v. Such highly soluble organic compounds have κ much lower than 1.3.

We updated the description, following the comment. The word 'highly soluble' was still left in the text because sodium chloride is highly water soluble.

'*The value of κ varies from 0 for insoluble materials (e.g., oleic acid) to 1.3 for highly soluble materials (e.g., sodium chloride).*'

(6) P 31839, L 3-4: As stated above, Chan et al. (2008) did not directly measure $a_{w,D}$, but rather estimated it based on bulk solubility data. The authors should change the text to indicate this.

Chan et al. (2008) actually measured water activity over saturated aqueous solutions'; therefore, those values are not estimated from bulk solubility data. As described in the response to question (4), we would like to use $a_{w,d}$ because those two variables (e.g., deliquescence water activity of particles and water activity of saturated solution) are thermodynamically equivalent.

(7)P 31840, L 7-11: the authors state that for azelaic acid, the measured κ of 0.02 to 0.03 is "close to the theoretic result for limiting solubility", but then that it is "higher than the theoretically predicted value of 0.001-0.002". This seems contradictory, please clarify.

The intention was to indicate 'κ value is significantly lower than that predicted for highly soluble case, demonstrating that azelaic acid particles are not highly soluble.' The statement was clarified in the revised manuscript to address the reviewer's point.

'*The measured value for κ was 0.02 to 0.03 for azelaic acid, in agreement with the literature (Hartz et al., 2006). This value characterizes a slightly soluble material. It is higher than the theoretically predicted value of 0.001-0.002 based on solubility data.*'

(8) P 31840, L 12-13: the authors state that $a_{w,D}$ for azelaic acid is "0.999 as reported in the literature and as predicted from solubility data". Please include a citation if this has in fact been measured directly. If it has not, I recommend omitting the phrase "as reported in the literature" and leaving "as predicted from solubility data."

We added Chan et al. (2008) as a reference. Further related information is provided in response to the comment #4.

(9)P 31840, L 24: "$a_{w,D}$ = 0.999 as reported in the literature" ? again, if this has been reported in the literature, please provide a citation.

We added Chan et al. (2008) as a reference. Further related information is provided in response to the comment #4.

(10) P 31845, L 10-13: I don't think this is a satisfactory explanation, for reasons given above. I recommend either addition of pimelic acid CCN data at lower temperatures, or that these lines be removed.

We updated the corresponding description, following the reviewer's suggestion.

'*Pimelic acid behaved with respect CCN activation as a highly soluble compound, in agreement with reports in literature, though contrary to expectation as a slightly soluble compound.*'

Reviewer #2

(11) Kuwata et al. report new CCN data to better understand how the atomic O:C ratio controls transition between solubility limited and molecular weight limited CCN activation regimes. The results quantify how O:C relates "insoluble", "slightly-soluble", and "soluble" regimes and the work may serve as a basis to explain observed empirical relationships of O:C with CCN activity. The manuscript is well-written, easy to follow, and suitable in scope on content for publication in ACP.

We acknowledge the reviewer for recognizing the worth of the manuscript.

(12) I would like to add to the excellent comment made by referee #1 on the speculated temperature dependence for pimelic acid. Christensen and Petters (2012) have demonstrated that the solubility vs. temperature curve for adipic acid shown in Figure A1 can be retrieved from temperature dependent CCN data using a very similar instrument configuration as was used in this study. Their data demonstrate 1) that solubility quantitatively controls CCN activation for adipic acid, and 2) that that temperature can indeed lead to the regime change between slightly soluble and soluble as suggested in Section 4.1.2. The above cited study may be used to corroborate the authors' conjecture.

As suggested by the reviewers #1 and #2, we updated the description as follow.

'*A systematic experiment on the temperature dependence is motivated for confirming this explanation for pimelic acid (Christensen and Petters, 2012)*'

References

Brooks, S. D., Wise, M. E., Cushing, M. and Tolbert, M. A.: Deliquescence behavior of organic/ammonium sulfate aerosol, *Geophys. Res. Lett.*, 29: 1917. doi: 10.1029/2002gl014733, 2002.

Chelf, J. H. and Martin, S. T.: Water activity and equilibrium freezing temperatures of aqueous NH4HSO4 solutions from-30 to 25 degrees C, *Geophys. Res. Lett.*, 26: 2391-2394. doi: 10.1029/1999gl900436, 1999.

Christensen, S. I. and Petters, M. D.: The Role of Temperature in Cloud Droplet Activation, *J. Phys. Chem. A*, 116: 9706-9717. doi: 10.1021/jp3064454, 2012.

Frosch, M., Zardini, A. A., Platt, S. M., Muller, L., Reinnig, M. C., Hoffmann, T. and Bilde, M.: Thermodynamic properties and cloud droplet activation of a series of oxo-acids, *Atmos. Chem. Phys.*, 10:

5873-5890. doi: 10.5194/acp-10-5873-2010, 2010.

Hartz, K. E. H., Tischuk, J. E., Chan, M. N., Chan, C. K., Donahue, N. M. and Pandis, S. N.: Cloud condensation nuclei activation of limited solubility organic aerosol, *Atmos. Environ.*, 40: 605-617. doi: 10.1016/j.atmosenv.2005.09.076, 2006.

Kuwata, M., Chen, Q. and Martin, S. T.: Cloud condensation nuclei (CCN) activity and oxygen-to-carbon elemental ratios following thermodenuder treatment of organic particles grown by α-pinene ozonolysis, *Phys. Chem. Chem. Phys.*, 13: 14571-14583. doi: 10.1039/c1cp20253g, 2011.

Seinfeld, J. H. and Pandis, S. N. (2006), Atmospheric Chemistry and Physics, Wiley-Interscience.