

## ***Interactive comment on “Slower CCN growth kinetics of anthropogenic aerosol compared to biogenic aerosol observed at a rural site” by N. C. Shantz et al.***

**N. C. Shantz et al.**

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Response to Referee #2: First of all, we would like to thank Referee #2 for the detailed review of our manuscript, with constructive comments and suggestions. Below are our replies to the specific comments provided by the Referee. Please note that section numbers have changed in the newest version of the manuscript and the new section numbers are referred to below. All page and line numbers below refer to the original manuscript in ACPD.

Referee general comment: The authors measure and simulate droplet growth rates of aerosol of anthropogenic and biogenic origin. Organics affect two parameters neces-

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sary to model droplet growth, the accommodation coefficient,  $\alpha_c$ , and the hygroscopicity parameter,  $\kappa$ . Below 20% organic aerosol mass fractions, droplet growth behaves like pure ammonium sulfate. Lowering  $\alpha_c$  for constant liquid water content, increases cloud droplet numbers.  $\alpha_c$  increases when the liquid water on the droplets increases. These findings can have significant consequences for the aerosol-indirect-effect. The subject matter is relevant and of interest to the greater scientific community. However sometimes insufficient details and or a lack of references do not appear to support conclusions. Subtle changes in syntax and organization will improve the clarity of the paper and are suggested by the reviewer below.

Response: We have now added the following references to the manuscript in hopes of providing some clarity:

Albrecht, B. A., Science, 1989.

Chang, R. Y.-W. et al., in preparation, 2009.

CRC Handbook, 2004.

Cross, E. S., et al., Aerosol Sci. Technol., 2007.

Feingold, G., and Chuang, P. Y, J. Atmos. Sci., 2002.

Fountoukis, C., and Nenes, A., J., Geophys. Res.-Atmos., 2005.

Fountoukis, C., et al., J. Geophys. Res.-Atmos., 2007.

Gunthe, S. S., et al., Atmos. Chem. Phys., 2009.

Johnson, G. R., et al., J. Geophys. Res.-Atmos., 2005.

Leaitch, W. R., et al., Tellus, 1986.

Liou, K. N., and Ou, S. C., J. Geophys. Res.-Atmos., 1989.

Petters, M. D., and Kreidenweis, S. M., Atmos. Chem. Phys. Discuss., 2008.

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Ruehl, C. R., et al., *Geophys. Res. Lett.*, 2009.

Twomey, S., *Atmos. Environ.*, 1974.

Vesna, O., et al., *Atmos. Chem. Phys.*, 2008.

Voigtländer, J., et al., *J. Geophys. Res.-Atmos.*, 2007.

Wang, J., et al., *Atmos. Chem. Phys.*, 2008.

Wex, H., et al., *Atmos. Chem. Phys.*, 2009.

Referee major concerns: One finding suggests that oxygenated compounds may not correlate to a more soluble and or higher droplet growth uptake. Can you show evidence of this? How was the oxygenated state determined? No figures and current analysis in the text indicate this. Furthermore, nowhere in Slowik et al 2009 is droplet growth shown and the droplet growth work of Shantz et al, 2008 applies to a different study.

Response: This is an excellent point, thanks for bringing it up. We have added Part (c) to Figure 2 including the oxygenated fraction of the organic components measured with the AMS. This was determined using PMF analysis, as outlined in Slowik et al 2009 (currently in ACPD) and further explanation has been added to the Section 4.1 page 13780 line 15 about this analysis. This paragraph, starting on page 13783 line 9, has been moved to the end of the following Section 4.3.

Referee major concerns: The relationship between  $\alpha_c$  and  $\kappa$  is unclear. Is it linear? How strong is the correlation? Is it consistent? There appears to be an infinite number of simulations of the combination of the two parameters that could fit the experimental data. The paper would be of greater relevance to others if the authors could expound on the correlation and or provide a sensitivity study of the two parameters for this data set.

Response: Thanks for your comment. Both are adjustable parameters and indeed

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there are many possible combinations. We have provided some sensitivity work for each parameter but have not attempted to find a correlation. More cases with different air masses would be required for a relationship to be found.

Referee major concerns: The authors should emphasize that a soluble sulfate and insoluble organic model,  $\kappa = 0$  and  $\alpha_c = 0.044$  can be used to describe droplet growth. This finding is consistent with previous works (e.g, Fountoukis et al., 2007).  $\alpha_c = 0.044$  is very close to previously reported optimal values,  $\alpha_c = 0.042$  (e.g, Fountoukis and Nenes, 2005). Please cite relevant works.

Response: The 2 suggested references have been added to the manuscript thanks to the reviewer's suggestion. Fountoukis and Nenes (2005) was added to page 13782 line 21 and Fountoukis et al. (2007) has been included on page 13777 line 12. It has been emphasized on page 13782 line 21 that a low solubility organic and lower  $\alpha_c$  describes droplet growth for polluted cases. However, we found that an increasing  $\alpha_c$  with increasing LWC on the droplets may better capture the droplet growth as was previously discussed on page 13785 lines 9-11 and is now discussed in more detail in Section 4.2 page 13782 line 10-11, line 13-15. Please keep in mind that the findings in this paper refer to CCN counter observations and not necessarily real clouds. Fountoukis et al. (2007) attempted closure of aerosol and cloud droplets in a polluted environment using a value of  $\alpha_c = 0.06$ , but this closure also depends significantly on how the updraft speed is treated and this result is not a proper comparison with the present observations. We don't think that " $\kappa = 0$  and  $\alpha_c = 0.044$  can be used to describe droplet growth" in terms of the biogenic aerosol. The point of this manuscript was to show how different these 2 scenarios are.  $\kappa = 0.07$ ,  $\alpha_c = 0.04$  may be suitable for anthropogenic aerosols, such as Stroud et al 2007 and our manuscript (7 June, 11 June) but not necessarily for biogenic aerosols (11 June).

Referee major concerns: How will incorporating nitrate salts affect the models? Nitrates contribute to the regional aerosol population (Fig 3.) and can increase particle hygroscopicity. How sensitive are the models if nitrates are incorporated?

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Response: Figure 3 shows the nitrate is very low during this period. We wonder if you meant to write "Figure 5" which does show a nitrate component to the aerosol. In any case, we ran simulations for both scenarios including ammonium nitrate at your request. We ran the following simulations: (a) 7 June 100% ammonium nitrate (monodisperse), (b) 7 June 2% ammonium nitrate, 60% ammonium sulphate, 38% organic (with  $\kappa=0$  or 0.07,  $\alpha_c=1$  or 0.055) (monodisperse), (c) 1 June 100% ammonium nitrate (polydisperse), and (d) 1 June 11% ammonium nitrate, 49% ammonium sulphate, 40% organic (with  $\kappa=0$  or 0.07,  $\alpha_c=1$  or 0.06) (polydisperse). We found that since ammonium sulphate has  $\kappa=0.61$  and ammonium nitrate has  $\kappa=0.67$  (Petters and Kreidenweis, 2007), these  $\kappa$  values are really close enough that changing from one to the other makes very little difference in the simulations. This is the reason we simply grouped all inorganics together and used  $\kappa=0.61$  (ammonium sulphate) to simulate all inorganics. The fact that sensitivity tests for ammonium nitrate show little difference from ammonium sulphate has been added to the manuscript (new Section 3 about the Model on page 13780).

Referee major concerns: Fig 5a and 6a. For  $\alpha_c=1$  and  $\kappa=0$ , Figure 5 shows that 3.5 volts are measured at 3 seconds and Fig 6 shows that 1.5 volts are measured at 5 seconds. Also the simulations for pure sulfate are not the same on a daily basis. Why are the simulations between the two figures different? The observed voltage sulfate droplets are not the same (Figs 3. And 4). What has changed between experiments? What  $\alpha_c$  and  $\kappa$  values reproduce the ammonium sulfate growth observed in these figures?

Response: We apologize but it seems there is some confusion on this point. We have attempted to clarify these points below and in the manuscript.

The model simulations, where we perform sensitivity tests to  $\alpha$  and  $\kappa$ , refers to the model cross section on the right axis. The  $\alpha$  and  $\kappa$  tests do not refer to the voltages on the left axis, which is the raw voltage measured with the CCN counter (observations, not simulations). This was explained in the figure caption for figures 3,

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5 and 6 but we have now added it to page 13781 lines 16-18.

Next point of confusion/clarification: Figure 5 shows 6 volts at 5 seconds, 2.2 volts at 3 sec. Figure 6 shows 7 volts at 5 seconds, 1.2 volts at 3 sec.

About why the simulations for pure sulphate is different: Although the chemical composition in each of these cases is the same (ammonium sulphate), the size distributions are different. The size distributions for each case is shown in Figures 5b and 6b. The voltages (observations) and cross section area (simulations) will change according to the initial dry size distribution. In fact, the observed voltage depends on number concentration, size of particles and chemical composition, which is why we felt that Section 4.2 was useful, where we controlled the size and concentration and thus limited it only to the affects of the chemical composition (this was mentioned on page 13779 line 17, and line 21-23 but we have added additional explanation to 13779 line 23 and a paragraph to page 13781 line 5). Section 4.3 is complicated by the polydisperse size distributions, but ammonium sulphate is different in each case because the polydisperse size distributions are different.

About the observed voltage for sulphate not being the same for Figures 3 and 4 and what has changed: In Figure 3, the number concentration is 215-225  $\text{cm}^{-3}$  and size is 0.1 microns (page 13781 line 15, Figure 3 caption) and Figure 4 has a number concentration of 35-45  $\text{cm}^{-3}$  and size of 0.12 microns (page 13782 line 24 and Figure 4 caption) and as stated above, the voltages depend on the size and number concentration of the particles. These are the differences between the observed detector voltage for the ammonium sulphate experiments. Clarification has been added to page 13781 line 7-8 and page 13782 line 22-23.

About what  $\alpha_c$  and  $\kappa$  values reproduce the ammonium sulfate growth observed in these figures: Figure 3b, Figure 5a and Figure 6a have been modified to include the  $\kappa$  values. In the simulation for ammonium sulphate, we assumed  $\alpha=1$  (Davidovits et al., 2004; Laaksonen et al., 2005; Mozurkewich, 1986; Voigtlän-

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der et al., 2007) and  $\kappa=0.61$  (Petters and Kreidenweis, 2007). This was also mentioned previously on page 13782 lines 1-2 and page 13781 lines 20-21. We have added it to the new Section 3 about the simulations.

Overall, the number concentration, dry particle size and composition all affect the raw measured CCN counter voltage. By holding the number concentration and size constant between the ammonium sulphate and ambient, we can eliminate the concentration and size effects and concentrate on the composition alone by directly comparing the ambient case with the complementary ammonium sulphate case. It varies from case to case due to the different number concentrations (monodisperse) and polydisperse size distributions. We have added clarification to a new first paragraph in Section 4.2 about this point.

Referee major concerns: P13783 L16. How do the authors infer the organic molecular weight? Is there any evidence that suggests molecular weight is higher?

Response: Thanks for pointing this out, it may not have been previously clear, we have attempted to make this clearer in the manuscript. We have included on page 13778 line 1 that the  $\kappa$  value includes parameters such as molecular weight, density and ionic dissociation factor. We have also added clarification to the new Section 3 about the model description on page 13780. In our work, the assumed organic molecular weight is incorporated in the  $\kappa$  value that is tested throughout this manuscript. We therefore did not need to infer an organic molecular weight. On page 13783 line 16, we are providing suggestions about the type of organic that may be present and did not intend to infer any organic molecular weight, apologies for the confusion.

Referee major concerns: Fig 3. What sizes do the voltages correspond to? Can you provide the conversion? Droplet sizes are more relevant to readers with different optical sizing techniques and would be of greater use and reference to future works.

Response: The voltages measured with the CCN counter depend on the size distribution and chemical composition of the dry particles as well as the size of the growing

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droplets. Often people working with this counter convert the maximum voltage reached to a number concentration of CCN based on ammonium sulphate or sodium chloride calibrations. We do not have a reliable way of pulling the droplet size out of this voltage information. We have added to the manuscript that at 5 seconds, droplets formed on pure ammonium sulphate are 1.4 microns in the simulations (page 13781 line 21).

Referee major concerns: Fig. 4. Why do the droplets grow again after 9 seconds? The text suggests that droplet measurements are impacted by gravitational settling and diminish in size after 5 seconds (P13781 L18). So again, what is happening at 9 seconds? Is this droplet coalescence in the instrument? Does this effect occur before 5 seconds? Unfortunately, the authors may have opened "a new can of worms." with this figure. Why is data shown up to 10 seconds? The authors suggest only the first 5 seconds are relevant for analysis but some unexplained measurement behavior is shown for larger times.

Response: The first activated particles will begin to fall out of the detection region as the particles that have activated from above fall into the detection region and will then grow more in the higher supersaturation near the detection region. This phenomenon is often observed with this type of counter. They do not diminish in size but fall out of the detection region so they are no longer detected. We do not simulate > 5 sec because of these complicated effects. We left 10 seconds in Figures 3a and 4a because of the maximum peak comparison between the ambient and AS. This is the value that is used to calculate CCN number concentration from this counter. In the anthropogenic case, AS grows more overall at 10 seconds than the ambient (which, if you believe the CCN number concentration calibration, means a higher number of CCN in the AS case than the ambient). BUT the biogenic case grew more than the AS, which was completely surprising. There are so many uncertainties in this but we thought it was interesting to include the graphs at the very least. We have added this explanation to a number of sentences starting on page 13781 line 5 and 1 additional sentence on page 13782 line 28.

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Referee minor comments: P13781 L15. Replace “of the particles” with “of the dry particles”

Response: Thank-you for the suggestion, the word “dry” has been added in 2 places on page 13781 line 15.

Referee minor comments: P13781 L21. Are there references for the particle densities? PS. Cross et al measure 1.27 g as an average organic particle density close to 1.3.

Response: We have added references for the particle densities, including the CRC manual and the Cross et al reference to page 13781 line 24, as suggested.

Referee minor comments: P13783 L17. HOA is not defined in text. How much looks like HOA? Is this data from Slowik et al, 2009?

Response: Thanks for pointing out this mistake, HOA is now defined in the text on page 13780 line 15 and Figure 2c has been added to demonstrate the results from Slowik et al., 2009 (in response to your first “Referee Major Concern” about the oxygenated components) and to show how much HOA was found with the PMF analysis.

Referee minor comments: P13786, L25. “. . . the oxidation of forest emissions are soluble”. References Please. (like those already cited e.g., Engelhart et al, 2008; Hartz et al 2005)

Response: This has been added to the manuscript on page 13786 line 25.

Referee minor comments: Fig 3. 4. 5. 6. Captions. Average particle densities are calculated from organic and sulfate AMS composition assumptions. This is mentioned in the text but not the figures. Please clarify. Suggestion: replace “assuming a particle density of” with “assuming an organic and sulfate composition particle density. . .”

Response: This has been changed in the figure captions as suggested.

Referee minor comments: Fig 3. Does 0.1 um refer to the dry particle size? Please clarify in caption.

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Response: Thanks for mentioning this. The text has been changed accordingly.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13775, 2009.

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