

## ***Interactive comment on “Influence of particle size and chemistry on the cloud nucleating properties of aerosols” by P. K. Quinn et al.***

**P. K. Quinn et al.**

Received and published: 8 January 2008

Comments by the referee are in brackets followed by our response.

Response to Referee #2:

[The manuscript is very well written and all steps of the data analysis are clearly described. It contains many interesting and valuable points (e.g., comparison of chemical composition in PM<sub>1</sub> and CCN size range; relation of D<sub>c</sub> and HOA fraction). It definitely has the potential to make important contributions to the CCN literature, especially with further sensitivity studies (as suggested below). ]

We thank the referee for the recognition of the relevance and utility of the paper.

[However, I have some comments that should be addressed before publication. The most important ones revolve around the shortcomings of the current and the benefit of

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further sensitivity studies. In the former point there is some overlap with reviewers 1 and 2.

1) Instrument calibration: Please specify which theoretical model for calculating the critical supersaturations ( $S_c$ ) of ammonium sulfate was used in the calibration. In the literature many different ways are used to derive  $S_c$  (Rose et al., 2007 and references therein). It is therefore important to be specific to ensure comparability to other papers. Was the CCN counter also calibrated with respect to number concentration?]

We have added the following text to Section 2.2.

The critical supersaturation for a given particle size was calculated from Köhler theory (e.g., Fitzgerald and Hoppel, 1984).

In addition, CCN counter concentrations were compared to number concentrations from the WCPC for large diameter ( $> 70$  nm)  $(\text{NH}_4)_2\text{SO}_4$  particles and found to agree within plus or minus 15%.

[2) Derivation of  $D_c$ : The critical diameter in this work is not directly measured but derived from number concentration measurements. Therefore the uncertainty of  $D_c$  should be estimated based on uncertainties in size distributions and CCN concentrations, at least for a few representative examples. ]

As mentioned by the referee, the uncertainty associated with the calculated  $D_c$  is based on the uncertainty of the CCN and size distribution measurements. The uncertainty associated with the number concentration from the DMT CCN counter is estimated at less than 10% [Roberts and Nenes, 2005]. The uncertainty associated with the number concentration from the size distribution measurements is plus or minus 18% [Quinn et al., 2004]. The resulting error in the above ratio and, therefore, in  $D_c$  is plus or minus 20%. We have added the following statement of uncertainty to the text in section 3.2.1. Uncertainty in equation (1) and, therefore in  $D_c$ , is estimated at plus or minus 20% based on a quadrature of the errors in the number concentrations derived from the

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CCN counter (plus or minus 10%) and the measured size distributions (plus or minus 18%). The actual uncertainty in  $D_c$  will deviate from this estimate depending on the slope of the size distribution around  $D_c$ , i.e., whether  $D_c$  is greater than or less than  $D_{gn}$ .

In addition, we have added uncertainties to the sections describing the CCN counter measurements (Section 2.2) and the size distribution measurements (Section 2.3).

[3) Correlation of  $D_c$  and HOA This derived relationship between chemical composition and HOA fraction is an interesting result and could be very useful for parameterizations. However, HOA fractions are not very commonly measured. Therefore, it is important to present a similar correlation using the entire organic fraction. Maybe this would even give a better correlation. Or has this been tried and it did not work?]

We have included the results of the POM mass fraction versus critical diameter regression in Section 3.2.2 and Table 1. The added text in Section 3.2.2 reads as follows.

For comparison, a similar regression analysis (i.e., with the data segregated by measurement supersaturation) was performed on the sub-200 nm POM mass fraction and  $D_c$ . As for HOAMF versus  $D_c$ , a positive slope was found at each value of  $S$  with the magnitude of the slope decreasing with increasing  $S$  (Table 1). However, the slope and  $r^2$  values at each supersaturation were less than those for the regression between HOAMF and  $D_c$ . All  $r^2$  values were less than or equal to 0.2 indicating only a very weak correlation between POM mass fraction and  $D_c$ . Hence, the chemical properties of HOA that affect CCN activation are distinct from those of the bulk POM aerosol.

Table 1 now includes the slope,  $y$ -intercept, and  $r^2$  values for the sub-200 nm POM mass fraction vs.  $D_c$  regression.

[4) Sensitivity study First part: The first part of the sensitivity study assumes an idealized aerosol consisting of a single lognormal mode and a composition of ammonium sulfate and insoluble material. CCN concentrations are calculated as a function of

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mean diameter (20-140nm) and soluble volume fraction (0-1), which covers a wide range of conditions. The problem is relating this idealized study to actual data, i.e. where to place the boxes on the graph. This is made obvious by the comparison with the data of Dusek et al.: The presented simplified sensitivity study suggests roughly equal changes in CCN concentration with variation composition and size distribution for the Dusek et al. data set. However, the actual data in Dusek et al., (full size distributions, size resolved spectra) show that CCN concentrations vary much more with changes in the size distribution than with changes in chemical composition. The assertion of the authors that this sensitivity study overestimates the influence of the size distribution does therefore seem questionable. I think there are many reasons why it is problematic to superimpose actual data on this plot.]

We have changed the model study and removed the Dusek et al. and Hudson data from the paper.

[As reviewer 2 pointed out, the author's own results show that soluble volume fractions cannot simply be equated with HOA fraction. Soluble volume fractions can also not be equated with the total organic fraction as is done in the comparison with Dusek et al.. And especially to equate it with HOA fraction for one study and with OC fraction for another study will lead to inconsistencies, as also noted by reviewer 1. One of these inconsistencies is that the cut-off diameters at  $S=0.44\%$  for this experiment lie most frequently between 60 and 100nm (Figure 3b grey area). This overlaps well with cut-off diameters at 0.4% in Dusek et al., so it is hard to understand why the respective boxes are not overlapping in Figure 6.]

Assuming that the soluble volume fraction can be equated with the HOA mass fraction requires assuming that HOA is insoluble and all the other chemical components that are present are either fully or highly soluble. As we discuss at several points in the paper (Sections 3.1.1 and 3.3), what little information that is available about HOA (e.g., mass spectra, CCN activity and combustion particles) suggests that it is fully or highly insoluble. The difference in the relationship between HOAMF and  $D_c$  and the

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relationship between POM mass fraction and  $D_c$  that is now shown in Table 1 provides evidence that HOA has soluble properties very distinct from the bulk POM aerosol. The result of the factor analysis ( $D_c$  being proportional to the HOAMF and inversely proportional to the sulfate and OOA mass fractions) indicates a similarity between the solubility of OOA and sulfate while HOA was distinctly different. Finally, measurements of marine aerosol when HOAMF were near zero and  $D_c$  values were near that of  $(\text{NH}_4)_2\text{SO}_4$  (Figure 5 Gulf-Southerly Flow) indicate that highly soluble aerosol was encountered during the experiment. This paper presents the first attempt (that we are aware of) of relating HOA mass fractions to critical diameters. The assumptions we make are simplifying but, in the absence of a full knowledge of the solubility of chemical components present, this analysis serves as a good starting point and leaves room for refinements in subsequent studies.

We have removed the Dusek et al. data from the paper and, therefore, eliminated the contradiction between using HOA fraction from one study and the POM fraction from the other.

[In summary, why use epsilon at all and not just  $D_{gn}$  on one axis and  $D_c$  on the other axis (now epsilon)? Then the comparison to the data would be much more straightforward.]

The major goal of the paper is not to compare the Dusek and Hudson data to the model output but rather to determine the influence of composition on cloud droplet activation. The measurements indicate that there is a relationship between HOAMF and  $D_c$  such that an increase in HOAMF leads to an increase in  $D_c$ . We use the model to estimate the impact of neglecting variability in the composition observed during GoMACCS on calculated CCN concentrations. Hence, restricting the analysis to the  $D_{gn}$  vs.  $D_c$  relationship is not sufficient to address the overriding goals of the paper. It may, however, be useful in future analyses.

[A last problem is that a single lognormal mode is not a good representation of the

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actual size distribution. In the case of a bimodal size distribution, a lot of the site distribution variability can lie in the relative fraction of Aitken and Accumulation mode particles. In this case a shift in D<sub>gn</sub> is not necessarily representative of the variability of the whole size distribution. This might contribute to the observed underestimate of the role of the size in Dusek et al. by the current study. If the first part of the sensitivity analysis is retained (with D<sub>c</sub> instead of epsilon), this potential shortcoming should be discussed in the text. ]

We realize that a single lognormal mode does not always accurately represent the actual measured number-size distribution. Inclusion of more complicated size distributions over the CCN diameter range is beyond the scope of the model discussed in the paper. The unimodal distributions we use in the model are representative of those observed during GoMACCS and serve to illustrate, via the model, the effect of composition on CCN concentration for a given number-size distribution.

[Second part: In a second part of the sensitivity study, the  $\pm$  error of using ammonium sulfate to predict CCN concentrations is assessed. In my opinion this should only be a first exploratory step. It is obvious from Figure 6 that the  $\pm$  errors are always positive, which indicates that the model is biased. Therefore this sensitivity study says mainly that pure ammonium sulfate is not a good model of the aerosol in this region. This is a valid result, but definitely not the most interesting that could be obtained with this data set. The beauty of these data is that they cover a very complex region, where marine air and extreme pollution can be found in close proximity. From the data of Dusek et al., it seems that if marine air is advected over Germany for one day the cut-off diameters are already more  $\pm$  continental than  $\pm$  marine. This is not the case here. A very important question is how much detail in chemistry is needed to predict CCN concentrations in such an environment. I therefore suggest to repeat this sensitivity study using the mean cut-off diameter for the whole region as a reference (instead of ammonium sulfate). Further sensitivity studies could use mean cut-off diameters of the four sub-regions and the dif-

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ferent air mass cases. The results could simply be summarized in a table, because the comparison with Dusek et al., and Hudson et al., would of course not be meaningful. (It was already not very convincing to present the errors these authors would have made, had they chosen to model their aerosol with ammonium sulfate, which they obviously never did). ]

We do not use the mean cut-off diameter as a reference because it is really the influence of composition on particle activation that we are interested in. Instead, we use the mean HOAMF of 0.4 as the base case. We then calculate CCN concentrations for plus or minus 1 sigma standard deviation about the mean and determine the impact of neglecting the observed variability in particle composition. This approach directly addresses the question of how much detail in chemistry is needed to predict CCN concentrations. As reported in Sections 3.3 and 3.4, neglecting the observed variability in HOAMF can result in an under- or over-prediction of CCN concentrations by 50% at  $S = 0.22\%$ .

Please see our comments in the General Response to all Referees submission for more information about the model approach in the revised paper.

[In any case, I encourage the authors to use  $D_c$  instead of epsilon to avoid the problems raised by me and the other reviewers. If they choose not to do this, I second the view of reviewer 2 that some entirely different sensitivity study should be done. In my opinion the data and analysis are also publishable without any sensitivity study at all, but I would find it a pity because of the great potential of this data set. ]

As stated above, using DC instead of epsilon obscures any information obtained in the model analysis concerning the sensitivity of particle activation to composition.

[Specific comments: p14184, line 1-5: It is important not to mix CCN activation in an instrument where the supersaturation is fixed and droplet activation in an actual cloud. In the present study the supersaturation is fixed in the instrument as well as in the calculation of CCN. If these CCN concentrations are modeled using a size distribution

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with constant sigma they will be less variable than otherwise. Therefore holding sigma constant will underestimate the impact of particle size on CCN at a certain S, as used in this study. ]

We no longer are considering the impact of the variability in the size distribution on particle activation so modeling the size distribution with two modes and a variable sigma is not as crucial.

[p14186, line 24: Is this loading significant? What would be a possible reason that Dgn could be related to Dc]?

We refer the referee to the new discussion of the factor analysis in Section 3.2.2.

[p14189, line 20-25: It is not correct to superimpose the Dgn determined at 60% on this plot, because as far as I can tell the modeled size distributions were assumed to be dry. Instead of correcting the data of Dusek et al, and Hudson et al., Dgn of this study should be shifted to lower diameters].

The Dusek and Hudson data have been removed from the paper.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14171, 2007.

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