Atmospheric Chemistry and Physics Discussions

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.

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

Response to Referee #1

[Generally the paper is well written and understandable. It is a valuable contribution to aerosol-cloud research and fits well into the scope of ACP. I encourage publication after the major comments (see below) have been addressed.]

We thank the referee for the positive overall review.

[1] The CCN measurements are not size resolved. Therefore, the method to infer the critical diameter as is explained in section 3.2.1 relies on the assumption that the CCN/CN ratio (the activation efficiency) is an ideal step function that jumps from 0 to unity at the critical diameter. In reality this is usually not the case: Firstly, the activa-

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tion curve is broadened around Dcrit, and secondly, the activation curve sometimes lies below unity for larger particles (due to measurement uncertainties or due to incomplete activation), sometimes also above unity (due to measurement uncertainties). Size resolved CCN measurements usually define the critical diameter as D50, i.e., the point where the activation curves reaches 50% of the maximum value. What is the uncertainty for Dcrit induced by the method presented here?]

In our analysis, we chose to define the critical diameter for CCN activation, Dc, as the diameter at which

CCNmeasured = CNCintegrated

where, CCNmeasured is the measured CCN concentration and CNCintegrated, the integrated condensation nuclei concentration, is found by integrating the number size distributions from the largest measured diameter down to the diameter where the above equation is satisfied. We chose this method because submicrometer aerosol was fed to the CCN counter rather than size selected aerosol. As a result, we did not have any information about the slope of the activation curve which is required in order to assume a ratio of 0.5.

In any case, whether a ratio of 0.5 or 1.0 is used, the overall result is the same, i.e., an increasing Dc corresponds to an increasing HOAMF. In Figure 4, a slope of 43 is shown for the linear regression between HOAMF and Dc corresponding to a CCN/CN ratio of 1. If, instead, HOAMF is plotted vs. Dc for a CCN/CN ratio of 0.5, the slope remains equal to 43 while the y-intercept decreases to 34.

The uncertainty associated with the calculated Dc 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 uncertainty in the above ratio and, therefore, in Dc is plus or minus 20% based on a

quadrature of the CCN and size distribution number concentration errors. We have added the following statement of uncertainty to the text in section 3.2.1.

Uncertainty in equation (1) and, therefore in Dc, is estimated at plus or minus 20% based on a quadrature of the errors in the number concentrations derived from the CCN counter (plus or minus 10%) and the measured size distributions (plus or minus 18%). The actual uncertainty in Dc will deviate from this estimate depending on the slope of the size distribution around Dc, i.e., whether Dc is greater than or less than Dgn.

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).

[2] The method used to infer the geometric mean diameter Dgn needs to be discussed in more detail. The authors fit lognormal distribution to the Aitken mode and to the accumulation mode und take Dgn of the accumulation mode, if an accumulation mode is present. In cases without an accumulation mode, they use Dgn of the Aitken mode. To my understanding this leads to two problems: 1) an overrepresentation of small accumulation modes. 2) A "jump" of Dgn from the accumulation mode to the Aitken mode at the moment when the accumulation mode disappears. Thus, I expect that the geometric diameter in Figure 3 is biased in favor of larger diameters. Wouldn’t it be more useful to "force" a monomodal distribution through both Aitken and accumulation mode?]

We thank the reviewer for helping us find an error in the description of the fitting method. We stated incorrectly in the text that

If the size distribution contained both an Aitken and accumulation mode, the fit was performed on the larger accumulation mode.

Instead, if both an Aitken and accumulation mode were present we fit the Aitken mode. The results of this fitting approach can be seen in Figure 3a where it is shown that the

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majority of the Dgn values are in the Aitken mode size range (< 100 nm). We have corrected the text in Section 2.3 to the following.

If the size distribution contained both an Aitken and accumulation mode, the fit was performed on the smaller Aitken mode. If only an accumulation mode was present in the submicrometer size range, it was used to determine Dgn.

[3] The comparison with the Dusek 2006 data is not correct: Dusek 2006 did not differentiate between HOA and OOA. Assuming all POM in the Dusek 2006 study to be HOA leads to a HOA fraction that is too high. If one assumes the same HOA/OOA ratio as the present Quinn manuscript (HOA/OOA ca 2:1 for sub-200), the HOA fraction is overestimated by approximately 33%. This would shift the Dusek box to 40 - 60%, into a range where the CCN concentrations are higher and the errors are lower. In this range "size matters more than chemistry". Furthermore, how was the range of Dgn of Dusek estimated? The simulations in Dusek 2006 were made for the whole campaign, not only for the 4 case studies plotted in Fig 2 of Dusek 2006. The range of Dgn used for the simulations is not given in Dusek 2006.]

We have removed the comparisons to the Dusek et al. and Hudson data sets from the paper. The comparisons appeared to have caused concern because the Dusek and Hudson data were not completely compatible with the GoMACCS data set (e.g., Dusek did not report an HOA mass fraction or the full observed variability in the size distribution, Hudson only reported the solubility parameter, B, and not composition).

[4] Please give the time period when the measurements were performed. Only in Figure 2 the reader can learn that two measurements were made on 8/5 and 9/11 (which I assume to be month/day). The times of the measurements should be noted in the introduction (e.g., on page 14174), and also indicated in Figure 1. Are the presented data (in terms of meteorological conditions and air mass trajectories) representative only for summer/fall or also for the rest of the year?]

We thank the reviewer for pointing out this deficiency. We have added the following

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statement to the introduction.

GoMACCS took place in 2006 from the end of July to the middle of September. Photochemical pollution and regional haze are common during this time of year in Texas. Between July 27 and September 11, 2006, the NOAA RV Ronald H. Brown encountered a wide variety of aerosol types ranging from marine near the Florida panhandle to urban and industrial in the Houston-Galveston area.

We have also added the dates to the caption of Figure 1.

[Minor Comments: Abstract: p. 14172, lines 2-5: Move first two sentences to introduction p. 1763, lines 5-9: These sentences are almost exactly repeated in the introduction, they can be omitted here.]

We think these sentences are necessary to put the results listed in the abstract into the context of the scientific question being addressed. Since many readers only look at the abstract, we think it is important to leave these sentences in place.

[Introduction: p. 14173, line 18: Replace "cloud parcel" with "air parcel"]

Done.

[p. 14175, line 19: It should be noted here that a vacuum aerodynamic diameter of 200 nm can correspond to roughly 300 nm mobility diameter (assuming density 1.5, shape factor 1)]

A mobility diameter can be derived from vacuum aerodynamic diameter by dividing by the particle density. For a spherical particle having a density of 1.5, a vacuum aerodynamic diameter of 200 nm corresponds to a mobility diameter of 133 nm. We have added the following sentence to this section.

A Dvaero of 200 nm corresponds to a geometric diameter of 133 nm for a spherical particle with a density of 1.5.

[Methods: p. 14177, line 20: Are the DMA columns custom built? In not, give type and

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anufacturer or reference.]

They are custom built.

[p. 14177, line 25: "Stratmann" (also on page 14196, line 33)]

Corrected.

[p. 14180, line 14: Why was 1000 mBq/m3 used as a threshold? Are there any references]?

If the goal were to discern remote marine air from continental air, we would have to use a Rn threshold much lower than 1000 mBq m-3. In this case, however, we are considering separating air masses that had immediately come from the continent from those that have recently been over the Gulf of Mexico. In the Gulf of Mexico air masses, radon had not decayed away to the extent it would have in remote marine air.

[Section 3.1.2 p. 1483, lines 22-25: These statement is a repetition of page 14178, lines 4-8].

The lines on p. 14183 have been removed.

[Section 3.2.2 p. 14186, lines 17-25, also Table 2: The results and the methods of the PCA needs more explanation. Is this a more qualitative analysis or does a number like "0.76" in Table 2 mean that 76% of the variation in critical diameter can be explained by the sub-200nm mass fraction? A reference for the method is needed. What is "factor 2"? What is "CCN activation factor"? In the text it is only stated that "Table 2 shows the factor with the highest loading for the critical diameter. "]

We appreciate the comments offered by the reviewer and have significantly revised this section of the paper. We have added more information in the text (Section 3.2.2) about the factor analysis as follows.

A multivariate factor analysis was performed to further assess the correlation between critical diameter and composition. Factor analysis often is used to separate chemical

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species and other relevant parameters into different groups based on their degree of covariance [e.g., Sweet and Vermette, 1992; Millet et al., 2005; Quinn et al., 2006]. Parameters with a high degree of covariance are grouped together into factors. The analysis results in a loading matrix that reveals the strength of the association between parameters within and between factors. The analysis performed here was done using a principal component method with varimax rotation (SYSTAT 11, SYSTAT Software, Inc.). The goal was to test for the degree of covariance between aerosol component mass fractions (SO4=, NH4+, OOA, and HOA) in the submicron and sub-200 nm size ranges and Dc and, in particular, to determine with which variables Dc was most strongly correlated.

Five factors explained 91% of the total variance. Factor one, which contained a high loading for Dc (-0.84), explained 27% of the total variance in the parameters included in the factor analysis. Also highly loaded on this factor were the sub-200 nm HOA (-0.90) and SO4= mass fractions (+0.64), indicating a strong covariance between them and Dc. A high HOA mass fraction forced a larger Dc value for a given supersaturation because the particle, as a whole, had fewer water soluble molecules or ions. The positive loading for the sub-200 nm SO4= mass fraction indicates an increase in soluble mass led to a decrease in Dc. Hence, the multivariate analysis confirms the strong relationship between composition and critical diameter within this data set. Factor four, which explained 15% of the total variance had a high loading for only Dgn (+0.92) indicating it was independent from all other parameters included in the factor analysis.

[p. 14186, line 24: Why "negatively" instead of "negative"?]

Corrected..

[p. 14187, line 6: Equation 2 is usually referred to as "Kohler Equation" or "Köhler Equation" (e.g. Equ. 2 in McFiggans 2006).]

We have added Köhler Equation to the description of Equation 2.

[Replace in Equ. 2 the second "=" by " " since this is an approximation (see McFiggans 2006).]

Done.

[Figures and Tables: Figure 1: I would suggest to plot the insert in the same size below the main figure]e

Done.

[Figure 2: - Make plot sizes of c + d uniform]

Done.

[- Indicate error bars in AMS size distributions]

The purpose of the plot is to convey general information about the extremes in the size distribution of POM, HOA, and OOA for different sampling locations. Since we have an extensive discussion of AMS uncertainties in the methods section, we have refrained from adding error bars here as it would make the plot unnecessarily busy.

[- Legend: sub -$>$ d $<$ 1 μm, sub 200 -$>$ d $<$ 200 nm]

Done.

[Table 2: replace "subum" by "submicron"]

Done.

[Table 3 and 4: The sentences "calculated using a growth factor of 1.3" that are marked with an asterisk should be in the footnote.]

This portion of the analysis has been removed from the paper.

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