Atmospheric Chemistry and Physics Discussions

Interactive Comment

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 #3

[The measurements presented here are very informative and useful. The measurements themselves are well presented and should be published. However, the analysis that follows is wrong. The analysis makes the assumption that the aerosol is a simple mixture of ammonium sulfate and insoluble organics. Although this is a reasonable scenario that many, including myself, have to some extent believed, the very measurements presented here fly in the face of such simplicity. It is the intercepts shown in Figures 4 and 5 that absolutely belie this simple picture. If the aerosol followed the simple picture assumed by the authors (and probably assumed by a number of atmo-

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Interactive Discussion

Discussion Paper

EGU

spheric scientists) then the zero HOA intercepts shown in these figures and in Table 1 should be the same as the ammonium sulfate dry (critical) diameters. The problem is that these intercepts are much larger than ammonium sulfate. This is starkly evident in Figure 4 where the ammonium sulfate size is displayed. There do not appear to be any data points with such low Dc at HOA zero. Most of the data at zero HOA is a factor of two greater than the 49nm size of pure ammonium sulfate. Therefore, there is either something wrong with the measurements or the simple assumption of ammonium sulfate and insoluble aerosol is incorrect. I suspect the latter. Unless the authors can find significant flaws in their data, which would undermine the manuscript to begin with, then the analysis must be completely changed. The data actually provide a very interesting result that there must be other soluble substances than ammonium sulfate. Most likely there are some soluble organics that are not as soluble as ammonium sulfate.]

Within the measurement error of the AMS and the error estimation of DC there are points in Figures 4 and 5 that correspond to a composition of (NH4)2SO4. We have made this clearer by adding the data points for (NH4)2SO4 test aerosol to Figure 5. For the Gulf-Southerly Flow regime, in particular, there are cases of very low HOAMF and Dc values near (NH4)2SO4. The y- intercepts in the figures, to which the referee may be referring, do not correspond to HOAMF = 0 and the Dc of (NH4)2SO4 because these points make up a small fraction of the data. In our model approach, we create of matrix of insoluble mass fractions and mean diameters and superimpose the Go-MACCS data upon it using the assumption that HOA is insoluble. We refer the referee to the Response to all Referees submission for further clarification and justification of our modeling approach.

[Even if the data could support the simple ammonium sulfate/insoluble model why is the pure ammonium sulfate aerosol set up as the straw man? Have there been articles that have deduced CCN concentrations from aerosol size distributions based on pure ammonium sulfate as the composition? If so the authors should cite such articles. It might be plausible to make such an assumption in clean maritime air masses but

to make such an assumption in the dirty air masses considered here would be too ignorant to suspend disbelief.]

A careful reading of the paper will reveal to the referee that marine air masses were sampled in the Atlantic before the ship entered the Gulf of Mexico. These marine aerosols contained relatively little POM. In addition, during the Gulf-Southerly flow periods, sulfate concentrations were high relative to POM. Again, we refer the referee to the cases of low HOAMF and Dc values near (NH4)2SO4 shown for the Gulf-Southerly flow periods in Figure 5.

The Köhler equation at the basis of our model requires input of the molecular weight and density of solute as well as a vant Hoff factor and epsilon which is the water soluble fraction of the dry particle. Since the precise chemical composition of atmospheric aerosol particles is variable and unknown, a model representation of a particle containing a defined number of soluble ions (thus having the same hygroscopic properties) must be chosen. We chose ammonium sulfate as the dominant compound analyzed. Another (or collection of) soluble compound(s) with average higher molecular weight and lower vant hoff factor could have logically been chosen to represent the soluble OOA. This approach would have increased the effect of HOA.

Many previously published papers have used ammonium sulfate as the fully soluble case for calculating CCN concentrations. A few of these include:

Rissler, J. et al., Atmos. Chem. Phys., 4, 2119 to 2143, 2004, Physical properties of the sub-micrometer aerosol over the Amazon rain forest during the wet-to-dry season transition: comparison of modeled and measured CCN concentrations, pages 2130 and 2139.

Svenningsson, B. et al., Atmos. Chem. Phys. Discuss., 5, 2833 to 2877, 2005, Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance. Table 1 includes various model chemistries with ammonium sulfate, nitrate and organic compounds.

Full Screen / Esc

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Interactive Discussion

Discussion Paper

Feingold and Kreidenweis, JGR Vol 107, No23, p 4687, 2002. Section 2.2 in particular, where the initial aerosol, which is assumed to be composed of ammonium sulfate.

[This was not what Dusek et al. (2006) suggested. They found something quite different, a very insoluble aerosol that they asserted to represent all global aerosol. But they also fell back to assert that if the size-Sc relationship (com-position) could be determined in various air masses then CCN could be deduced from size measurements. Therefore, a more important question is how much the observed composition variability would thwart efforts to deduce CCN from size measurements. The average composition within each air mass could be used as a basis for determining an ”error range” for CCN concentrations deduced from size distributions.]

The model results presented in the revised paper address the issue that the referee raises here, i.e., how much the observed composition variability impacts CCN concentrations. We direct the referee to changes made in Sections 3.3 and 3.4.

[Abstract L2. Composition and mixing state are redundant.]

Composition and mixing state are not redundant in that they refer to distinctly different properties of the aerosol. Composition refers to the chemical components of which a particle is composed. Mixing state refers to how all the components are distributed among the particles [Seinfeld and Pandis, 1998]. Seinfeld and Pandis describe two extremes of mixing state as one extreme is termed an external mixture, where, in the aerosol population, each particle arises from only one source. An example of an external mixture is a collection of pure $(NH_4)_2SO_4$ particles mixed with a population of pure soot particles. The other extreme is an internal mixture, in which all particles of a given size contain a uniform mixture of components from each of the sources.

Seinfeld, J.H. and S.N. Pandis, Atmospheric Chemistry and Physics, John Wiley & Sons, Inc., 1998.

[Abstract L2. Supersaturation is a characteristic of the clouds not the aerosol. Sure the

aerosol is characterized according to critical S (Sc) of the particles but this is a way of classifying the combined effects of composition and size].

The reviewer states that supersaturation is characteristic of the clouds not the aerosol. On lines 1 to 3 of the abstract it is stated that:

The ability of an aerosol particle to act as a cloud condensation nuclei (CCN) is a function of the size of the particle, its composition and mixing state, and the supersaturation of the cloud. Hence, it is not clear what the reviewer is arguing against.

[L10. Insert ”potential” before ”activation”]

Done.

[L12. Insert ”to warm clouds” for ”for particle”]

Changed to:

Measurements were made of CCN concentrations, aerosol chemical composition in the size range relevant for particle activation in warm clouds, and aerosol size distributions.

[L15. This is not marine. It is only ”marine” relative to the more polluted aerosol.]

Marine aerosol was sampled over the Atlantic Ocean during the transit to the Go-MACCS study region. We clarify this in paper by adding the following text:

In Section 1:

The NOAA RV Ronald H. Brown encountered a wide variety of aerosol types ranging from marine over the Atlantic Ocean near the Florida panhandle to urban and industrial in the Houston-Galveston area.

Figure 1 caption:

The portion of the cruise track from Charleston, SC to the GoMACCS study region is not shown.

Interactive
Comment

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Interactive Discussion

Discussion Paper

EGU

[L18. This is the Sc not S. S is something in the cloud. Sc is a property of the particle.]

It is stated on lines 16 to 18 that:

Combining all data from the experiment reveals that composition (defined by HOA mass fraction) explains 40% of the variance in the critical diameter for particle activation at 0.44% supersaturation (S).

Here, S is referring to the supersaturation of the CCN counter, not the critical supersaturation (Sc) unique to a particle of a given size and composition. We have changed the text to clarify this point.

[L22. Insert ”variability in particle” in front of ”composition.]

Done.

[P14173 L13. Delete ”that impact the climate system” as all clouds impact the climate system not just some of them as this statement implies when the restrictive clause (that) is used.]

Done.

[L18. Delete ”as well as the supersaturation of the cloud parcel.” CCN ability is characterized by Sc not the other way around.]

A particle will not activate to form a cloud droplet unless the supersaturation of the surrounding air or cloud parcel is sufficient.

[L19 and beyond. You have defined S as the abbreviation for supersaturation but it is never used. Critical S (Sc) should also be defined and used when appropriate].

We define supersaturation, S, as the instrumental S of the CCN counter. We have made this clearer with the change made on line 18 of the abstract. We have added the definition to Section 2.2 where we describe the CCN concentrations measurements as follows.

A Droplet Measurement Technologies (DMT) CCN counter was used to determine CCN concentrations at supersaturations, S, of 0.22, 0.44, 0.65, 0.84, and 1.0%.

[L21 and 22. Density is another very important property of substances with respect to size and Sc.]

The sentence has been changed as follows.

Composition affects CCN activity by determining molecular weight of the solute within a cloud droplet, density, solubility, degree of dissociation, and surface tension.

[L27-. Why focus on modeling studies? There have been many observational studies showing this, and these are much more valuable than modeling studies.]

Frankly, cloud-scale, regional scale, and global modelers would be offended by this comment. In any case, we summarize results from both model and measurement studies in Section 1.

[P14174 L10. Density.]

This sentence refers to the results of a model comparison study performed by Ervens et al. [2005] who reported that variability in the predicted changes in droplet concentration due to the presence of organics was due to specific composition parameters (solubility, molecular weight, and surface tension). Density is not listed here because it was not one of the composition parameters found to be most influential.

[L13-14. This is misleading. Insoluble material does not ”reduce CCN activation.” It is essentially material that is inert with respect to CCN. It has no effect on the CCN material itself. It can fool fools perhaps, but it does not affect CCN. There is speculation that some organics might inhibit CCN but no proof of such is offered here or elsewhere.]

The sentence has been changed to:

Petzold et al. (2005) investigated carbonaceous particles produced by combustion and

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Interactive Discussion

Discussion Paper

EGU

found that only a small fraction activated to CCN. Furthermore, a high fraction of non-volatile organic matter in the particles caused a considerable increase in the activation diameter.

[L16. Insert ”variability” after ”composition.”]

Done.

[L21. Insert ”knowledge of” in front of ”size.” L22. Insert ”without using CCN measurements” after ”concentrations.”]

The sentence has been changed to:

Measurements of a broader range of aerosol composition during several aircraft campaigns indicated that a knowledge of both size and composition are required to accurately deduce CCN concentrations in the absence of CCN measurements [Hudson, 2007].

[P14175 L3-4. Delete ”in the size range where cloud drop activation is particularly sensitive to particle composition.” There is no such size range as Sc always depends on composition and composition can vary over all size ranges. Even if this phrase were correct ”particularly” is a poor word choice. Moreover, this begs the question of this manuscript.]

Done.

[L5-12. I agree that this is essentially the size range relevant to atmospheric clouds but the sensitivity to composition is not limited to this size range. Although I will not quibble with 40-200nm, I would broaden this range to 20-400nm. The lower limit is due to the maximum updrafts, which can be several meters per second and in cleaner air (not relevant to this study) S can be 2% or higher. The lower limit is due to the low concentrations of the larger particles that make them irrelevant to cloud droplet concentrations. Even large particles will not activate if they are totally or very insoluble.]

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

The reviewer must mean that the UPPER limit is due to the low concentrations of the larger particles that make them irrelevant to cloud droplet concentrations. In any case, we chose the 40 to 200 nm size range because this is the size range with a uniquely large mass fraction of HOA and, as we state in the following paragraph and as was well said by McFiggans et al. (2006), most particles greater than 200 nm diameter with moderate amounts of soluble material will activate under reasonable supersaturations.

[L15-17. This is a misleading and unnecessary statement.]

We have changed the sentence to:

HOA in the smaller size range may lead to fewer particles activating to form CCN compared to the case where the POM is composed only of OOA.

[P14181. L21-22. If this is true then how can you say that chemistry is less important at small sizes?]

To what statement of chemistry being less important at small sizes is the reviewer referring? On page 14175 it is stated that :

It is significant, then, that this size range (< 200 nm) often contains a large mass fraction of particulate organic matter (POM) indicating the importance of chemistry at small sizes.

We do state on the same page that:

Regardless of composition, smaller diameter particles will not activate under these conditions while larger diameter particles will.

but this is well known for the size range of < 40 nm that this statement is describing.

[P14182. L1. The vessels would probably also emit organics (HOA and OOA).]

True but irrelevant as this sentence is referring to marine vessels as a source of the measured sulfate.

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Interactive Discussion

Discussion Paper

[P14183. L16-17. Again this size range is no more composition-sensitive than any others. More-over, such a statement begs the question of this analysis of whether and how sensitive Sc is to composition.]

See comments above.

[L17-18. Again insoluble material does not impact CCN activation. It merely provides material that is essentially inert to CCN and thus increases size without affecting the CCN.]

The sentence has been changed to:

In the following analysis, the mass fraction of HOA for Dvaero $<$ 200 nm was used to represent the variability of aerosol composition during the GoMACCS experiment because of its prevalence in this size range and its limited solubility which is expected to impact the critical diameter for particle activation.

[P14184. L2. Insert ”cloud” in front of S. What sensitivity?]

The sentence has been changed to:

The decrease in supersaturation may lead to fewer particles being activated to CCN, especially in polluted air masses dominated by larger particles.

[L6-19. Especially informative.

L25. CNintegrated is a very bad term. CN refers to all particles. And when ”integrated” is attached to ”CN” it is redundant rather than restrictive. What is meant here has nothing to do with CN; it is just the integrated particle concentration up to specific values.]

We have changed the term to CNCintegrated which refers to the integral of the number-size distribution.

[P14185 L1-2. Nevertheless this determination of Dc again begs the question of this

manuscript. It assumes that all particles are CCN and that size is the only factor in de-termining Sc. This is far from the truth. First of all there are probably some even large particles that are totally or almost totally insoluble that will not be CCN at any practi-cal S. Moreover this would seem to assume that all particles have the same relative concentrations of soluble and insoluble components, which is probably not the case. The Dc so de-termined would be a minimum value that would be correct only if the particles were completely soluble or had identical mixing states or if solubility always decreased with particle size. Dc was not determined by Dusek et al. (2006) or Hudson (2007). Here the entire size range and CCN spectrum is considered whereas the other two related various narrow dry particle sizes (not the so-de.ned Dc) to Sc. This makes compar-isons dif.cult if possible.]

We have removed the Dusek and Hudson data from the paper.

[L26-27. A useful statement.

P14186. L2. Insert ”75-115 nm” to make this more clear].

Done.

[L15-16. Why would composition become ”less critical” (poor word choice) with in-creasing S? Composition is always important and it can vary at all sizes. Perhaps this is meant in a cumulative sense, but this requires more explanation even if it is correct.]

The section has been changed to:

The HOAMF and Dc relationship is a strong function of supersaturation. Segregating the data set by measurement supersaturation reveals a positive slope at each super-saturation but the magnitude of the slope and the r2 values decreases with increasing supersaturation (Table 1). As the supersaturation increases, more smaller particles will activate. Hence, the change in slope may be due to a less variable particle composi-tion (number of soluble molecules or ions per unit mass) in the lower end of Aitken size

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Interactive Discussion

Discussion Paper

EGU

range. This response may also be due to non-linearities in the Köhler equation.

[L17-25. This is incomprehensible to all but specialists in this type of analysis.]

We have added more details which should make it understandable to those with even the most basic understanding of statistics. Changes made to this section include the following. 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 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 ($SO_4^=$, NH_4^+, 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 $SO_4^=$ 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 $SO_4^=$ 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,

Interactive
Comment

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Interactive Discussion

Discussion Paper

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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.

[P14188. L4-6. This is circular. Dc was determined from a measured CCN concentration already.]

The reviewer seems to be confusing the measurement portion of this paper from this section which is titled MODELED Sensitivity of CCN Concentration to Observed Variability in Composition and Particle Size. In this section we are describing how CCN concentrations were calculated from the simulated size distributions.

[L6-15. This needs a lot more explanation. For instance what are the increments of the matrices? But this point is moot since the assumption that this analysis is built upon is inconsistent with the data that it attempts to explain. A different analyses needs to be done.]

We now state in Section 3.3 that :

CCN concentrations were calculated for a matrix (201 x 201) of insoluble mass fractions ranging from 0 to 1 and mean diameters ranging from 20 to 140 nm.

[L21-22. I agree that carbonaceous particles are poor CCN, but perhaps not completely inert as assumed.]

Perhaps, but given the likely composition of HOA (long-chain hydrocarbons) the assumption of insolubility in an aqueous phase is reasonable.

[L24. ”Reduced CCN activation” is another misleading statement. It only appears to reduce CCN activation if one makes the ridiculous assumption that all particles are ammonium sulfate.]

The sentence has been changed to:

Saxena et al. [1995] reported that for urban aerosol, organic compounds decrease water adsorption by the inorganic fraction of the aerosol which, presumably, would

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Interactive Discussion

Discussion Paper

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lead to fewer particles being activated to CCN.

[P14189. L5. S does not affect calculated CCN. Calculations are a function of S or Sc.]

The supersaturation of a cloud (or CCN instrument) will impact whether a particle of a given composition and size will activate or not.

[L6-8. This is true all other things being equal. But all other things are seldom equal. When CCN concentrations are high there is usually a lot of less soluble material. There are seldom high CCN concentrations with pure ammonium sulfate as the composition.]

We have changed this sentence as follows:

As expected, relatively few particles are activated to form CCN for small diameter aerosol with a large insoluble mass fraction. Conversely, most particles are activated to form CCN for large aerosol that is composed primarily of soluble species.

Remember, these are normalized CCN concentrations.

[L8. Why would this be expected? L9-10. How can both size and composition become less important? What would de-termine CCN at high S (or any S) besides size or composition?]

As S increases, more particles are activated since S becomes greater than Sc.

[P14190. Comparing Dusek et al. (2006) and Hudson (2007) with this study is more complex, if even possible. I do not understand what is done here (Fig. 6) and it is not worth more effort.]

We have removed the comparisons with the Dusek and Hudson data.

[P14192 L25-27. Composition or variability of composition is not less important at higher S. This is apparently a result of the false assumption. Moreover ”criti-cal” is a poor word choice. There are not firm conclusions probably because of the wrong assumption. I cannot agree with any of the specific conclusions because

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Interactive
Comment

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Interactive Discussion

Discussion Paper

EGU

they are based on an assumption that is inconsistent with the data. I do agree that composition is important for determining Sc. The conclusion here is an underestimate of the importance of composition.]

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

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