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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.

**Anonymous Referee #3**

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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 atmospheric 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.

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. 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 (composition) 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.

Abstract

L2. Composition and mixing state are redundant. 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.



ACPD

7, S7307–S7312, 2007

L10. Insert ”potential” before ”activation”
L12. Insert ”to warm clouds” for ”for particle”
L15. This is not marine. It is only ”marine” relative to the more polluted aerosol.
L18. This is the Sc not S. S is something in the cloud. Sc is a property of the particle.
L22. Insert ”variability in particle” in front of ”composition.

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.
L18. Delete ”as well as the supersaturation of the cloud parcel.” CCN ability is characterized by Sc not the other way around.
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.
L21 and 22. Density is another very important property of substances with respect to size and Sc.
L27-. Why focus on modeling studies? There have been many observational studies showing this, and these are much more valuable than modeling studies.

P14174
L10. Density.
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.
L16. Insert ”variability” after ”composition.”
L21. Insert ”knowledge of” in front of ”size.”
L22. Insert ”without using CCN measurements” after ”concentrations.”

P14175
L3-4. Delete ”in the size range where cloud drop activation is particularly sensitive to



ACPD
7, S7307–S7312, 2007





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

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

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

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

P14184.
L2. Insert "cloud" in front of S. What sensitivity?
L6-19. Especially informative.
L25. CNintegrated is a very bad term. CN refers to all particles. And when "integrated"



ACPD
7, S7307–S7312, 2007





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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.

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 determining 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 practical 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 determined 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-defined Dc) to Sc. This makes comparisons difficult if possible.
L26-27. A useful statement.

P14186.
L2. Insert ”75-115 nm” to make this more clear.
L15-16. Why would composition become ”less critical” (poor word choice) with increasing 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.
L17-25. This is incomprehensible to all but specialists in this type of analysis.

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



ACPD
7, S7307–S7312, 2007





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

P14189.
L5. S does not affect calculated CCN. Calculations are a function of S or Sc. 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.
L8. Why would this be expected?
L9-10. How can both size and composition become less important? What would determine CCN at high S (or any S) besides size or composition?

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.

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 "critical" 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 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.

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7, S7307–S7312, 2007

Interactive Comment



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