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Atmospheric
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Discussions

Interactive comment on "Effects of aerosol organics on cloud condensation nucleus (CCN) concentration and first indirect aerosol effect" *by* J. Wang et al.

Anonymous Referee #3

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The authors present data from an airborne field campaign that measured aerosol size distributions, size-resolved aerosol major species mass concentrations (using an AMS), and CCN number concentrations at 0.22% supersaturation. A major finding of the paper relates to the treatment of the organic fraction of the aerosol. The authors show that assumptions regarding organic species' hygroscopicity are not too important to the computations of CCN activity if the organic species are not the dominant component in the particles. When they are dominant, then calculations of CCN number concentrations are more sensitive to such assumptions.

I have a few suggested modifications. This is a nice study and the paper should be

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published after review comments have been addressed.

1. I echo the suggestion of Diana Rose and Uli Poeschl regarding including more details about the CCN counter calibrations. At the very least, the kappa that has been assumed for the calibration aerosol (ammonium sulfate) should be noted. As Rose et al. note, various commonly-applied assumptions for ammonium sulfate can lead to significant offsets in the reported critical supersaturations among various studies.

2. I liked the calculations shown in Figure 8. This view of uncertainty seems useful for discussions of forcing.

3. Although the authors do allude to its role, the importance of the aerosol mixing state is not as clearly delineated as it might be. The arguments for assuming internal mixtures for two of the aerosol types and external mixtures for the above-cloud type are reasonable, but of course the AMS data cannot indicate anything definitive about the mixing state of individual particles. It would be illuminating to compare predicted CCN number concentrations for both extreme assumptions (fully external and fully internal mixing). I think this property (mixing state) is really key in closure studies. If the aerosol is internally mixed, then as indicated by the results here and in other published studies, the average value of kappa does not vary that widely (because the internal mixing comes about by condensation of mostly inorganic species, and kappas tend to similar averages; e.g., in the range kappa˜0.2-0.3 for continental aerosol and ˜0.6 for marine, according to Andreae and Rsenfeld (2008). Hence the effects on the closure calculations, of various assumptions that change the average kappa values somewhat, are not so great. In contrast, for an externally mixed aerosol, the particle to particle variation in kappa can be larger, and when coupled to variations in size between particle types, the effect on derived critical supersaturations and hence on the computed CCN spectrum can be more substantial.

4. I am not sure I completely understand the treatment of the AC aerosols. Within each mode, does the composition vary with particle size, in proportion to the volumes of each

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component in a particular diameter subrange? This is what I assumed, although the paper says "For each mode, the volume fractions were calculated from fitted mass fraction" from which could also be inferred that composition was assumed uniform across particle size in each of the two mass modes.

5. In Figures 2-4 the number distributions are shown along with AMS-observed component mss distributions. I wondered about showing the volume distribution derived from the SMPS number distribution so it could be compared with the AMS data. How were vacuum aerodynamic and mobility diameters related to each other?

6. I don’t think I agree with the statement in the Abstract (and at the top of page 9802) that "a detailed knowledge of organic hygroscopicity is required to accurately predict CCN concentrations". After all, the authors achieved closure with a single assumption (kappa=0.12) applied to the organics as a whole (this same value worked for all 3 aerosol types, in fact; although for the other aerosol types it is hard to distinguish between kappa=0.12 and kappa=0 just from fitting to the CCN data). From this, one may conclude that it is not necessary to understand the individual properties of all organic components, but to know this overall best-fit kappa_org or, if more data were available, to know for example a gross split of the organic into two fractions (kappa=0 and kappa=hygroscopic) from which one can calculate the appropriate overall kappa_org. I suggest that in some cases, especially when organic species dominate the submicron aerosol mass, a more appropriate statement is "a detailed knowledge of the mixing state of the aerosol is required to accurately predict CCN concentrations". The authors can conduct some sensitivity calculations (as suggested above) to determine if this statement is in fact correct and outweighs the importance of other assumptions.

7. P. 9785, line 25 ff and p 9787, lines 16-21: The text implies that the major limiting factor in prediction of N_CCN for ambient aerosols is that we don’t know properties of the organics and cannot completely speciate the organic components. As noted from my comments above I tend to believe this is less of a problem than (1) lack of size-resolved composition and (2) lack of data on mixing states of particles within each size

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class.

8. p. 9787, line 27: the measurements in this study were made at 0.22% supersaturation. This corresponds to: kappa = 1, Dc=66 nm; kappa=0.5, Dc=81 nm: kappa=0.1, Dc=140 nm. The choice of supersaturation for the measurements, combined with the size distributions and composition, can lead to more or less sensitivity to assumptions made for the closure calculations. For example figure 4a shows that the size distribution decreases very sharply from ˜70 to 100 nm so CCN number concentrations might vary quite a bit for assumed kappas between 0.5 and 1 for this case. This sensitivity is captured in equation 17 with the term n(lnDp)/N_CCN, which is stated "depends on the shape of the particle size distribution and Dpc". I think this is an important point that might be expanded upon somewhat.

9. The AMS misses refractory material. It is argued that sea salt particles should not contribute substantially to the submicron number concentrations, but I would suspect the nitrate is in the form of sodium nitrate and not ammonium nitrate in this environment. Can the authors comment?

10. equation (3): although kappa can be identified with the indicated terms if Raoult’s Law and the assumption of ideal behavior are assumed to apply, the kappa values in Petters and Kreidenweis for inorganic species do not use this assumption. They are computed using water activity relationships in the literature that account for nonidealities.

11. p. 9792 line 13: "For organic species, the derivation of kappa from experimental data is based on the assumption that sigma_w=0.072 J m-2;" In fact this assumption is applied to the fitting for ALL species, not only the organics.

12. p. 9793, line 12: "Sea salt is present mainly in large particles": What is meant by large?

13. After all the assumptions have been applied, what kappas are arrived at for use in

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the calculations? It might be interesting to report these values.

14. Section 4.3.2: the sensitivity is really the sensitivity of the overall kappa (assuming internal mixing) to the assumed kappa for one constituent. Because kappas for inorganics are larger than those for organics, the exact assumed kappa_org does not matter if the volume fraction of organics is not too large, because the volume-weighted average is dominated by the larger inorganic numbers. Some slight rewording could make this more clear here.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9783, 2008.

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