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Atmospheric
Chemistry
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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.

J. Wang et al.

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We thank this referee for thoughtful suggestions and comments. Point-to-point responses are listed below.

Anonymous Referee #3

Received and published: 14 August 2008

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

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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 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.

Response

The details about the CCN counter calibration is now included in the manuscript. Please refer to the response to comments by Rose et al.

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

Response

Thank you for your encouraging comment.

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.

Response

We thank the referee for the comment and constructive suggestions. We agree that aerosol mixing state can strongly impact the predicted NCCN, and we have carried out additional calculations with other assumptions regarding the aerosol mixing state. The NCCN of the AC aerosol was also predicted assuming an internal mixture with size-dependent composition (i.e., at each size, particles have the same composition, and the composition varies with size as shown from the AMS pTOF data), a complete internal mixture with constant composition (i.e., all particles have the same average composition across the entire sub-micrometer size range, same as the FT and BL aerosols), and a complete external mixture with constant composition (i.e., all species are externally mixed at all sizes. The composition is constant across the entire sub-micrometer size range, and is derived from the AMS MS mode data). The extreme scenarios of a complete internal mixture and a complete external mixture, which are not realistic for the observed AC aerosol, serve as the limiting cases in our analysis. The predicted NCCN show large differences among different mixing state assumptions, suggesting that aerosol mixing state strongly impacts the predicted NCCN. However, regardless of the assumed aerosol mixing state, the ratio of predicted to measured NCCN is highly sensitive to kappa_org, a result of high organics volume fraction in the AC aerosol. This is also consistent with later analyses and results shown in Fig. 8. The effect

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of aerosol mixing state on predicted NCCN is most significant at low kappa_org and gradually decreases with increasing kappa_org. As expected, at kappa_org similar to kappa value of sulfate, the predicted NCCN becomes independent of the aerosol mixing state. At kappa_org of 0.1, based on the two limiting cases, the predicted NCCN of the AC aerosol has a uncertainty range of -11% to 17% due to the uncertainty in aerosol mixing state, which is substantially smaller than that at kappa_org =0 (insoluble organics). The additional calculation and discussion are included in the revised manuscript.

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 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.

Response

The AC aerosol is assumed as external mixtures of internally mixed lognormal modes, and within each mode, all species are assumed as internally mixed and the composition of the mode is constant (i.e. independent of particle size). This is now clarified in the text.

5. In Figures 2-4 the number distributions are shown along with AMS-observed component mass 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?

Response

For FT and BL aerosols, the pTOF data were often very noisy due to low aerosol loading, which prevent meaningful comparison. For the AC aerosol, the mass distribution derived from SMSP number distribution using an average density agrees fairly well with total mass distribution measured by the AMS. In our closure study, the vacuum aerodynamic and mobility diameters are related as follows. For the FT and BL aerosols, the aerosol is assumed as complete internal mixtures with constant (i.e. size-independent) composition. Vacuum aerodynamic diameter is the product of mobility diameter (assuming spherical particles) and the average density calculated from AMS MS mode data (bulk composition). For the AC aerosol, the aerosol was assumed as an external mixture of internally mixed lognormal modes. In each of the (lognormal) modes, the species were assumed as internally mixed, and the composition of mode is independent of particle size. For each of the modes, vacuum aerodynamic diameter is related to mobility diameter in the same way described above for the BL and FT aerosols. The average density for each mode is computed based on the composition of the mode derived through fitting the size-resolved AMS data described in Section 4.2.

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.

Response

We agree with the referee. The accurate knowledge of overall kappa_org is required to accurately predict NCCN and the first indirect aerosol effect. The detailed knowledge of individual properties of all organic components is not necessary. This is now clarified in the manuscript. Following the referee's suggestion, we have conducted additional sensitivity calculations (see reply to comment #3), it was found that regardless of the assumed aerosol mixing state, the ratio of predicted to measured NCCN is highly sensitive to kappa_org, a result of high organics volume fraction in the AC aerosol. The effect of aerosol mixing state on predicted NCCN is most significant at low kappa_org and gradually decreases with increasing kappa_org. At kappa_org of 0.1, based on the two limiting cases, the predicted NCCN of the AC aerosol (with high organics volume fraction) has a uncertainty range of -11% to 17% due to the uncertainty in aerosol mixing state, which is substantially smaller than that at kappa_org =0 (insoluble organics).

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 class.

Response

We agree with the reviewer that size-resolved composition and mixing states of particles are also very important in predicting NCCN. The sentence simply points out that complete speciation of the aerosol organic components remains almost impossible with current techniques, and one of the focuses of this paper is to examine the uncertainty in predicted NCCN and first indirect aerosol effect due to the uncertainty in the organics hygroscopicity. We have added following sentences to stress the importance of size-resolved composition and mixing in the text:

"Accurate prediction of NCCN requires the knowledge of size-resolved composition and mixing state of aerosol , which are often not available for ambient aerosols. Furthermore, ambient aerosols often consist of..."

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.

Response

We thank the referee for raising this important point. The following discussion is added to the text:

The value of n(lnDp)/N_CCN depends on the shape of particle size distribution and Dpc, and is generally high near the peak diameter of the number size distribution n(lnDp). In addition, n(lnDp)/N_CCN also varies with supersaturation, which determines Dpc. The value of n(lnDp)/N_CCN is often lower at higher supersaturation, which corresponds to a higher denominator NCCN. This might be one of the reasons that better closure agreements were often achieved at higher supersaturations.

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?

Response

We agree in this environment the nitrate might be in the form of sodium nitrate instead of ammonium nitrate. If that was the case, as sodium nitrate is formed through heterogeneous replacement of chloride by nitrate in individual sea-salt particles, it is expected that the contribution from sodium nitrate should also be small because of the typical low number concentration of sea salt particles. In addition, at the vaporizer temperature of 600 C (during MASE), a fraction of sodium nitrate would be detected by the AMS, In our calculations, the detected nitrate was assumed as ammonium nitrate. It is worth pointing out that the kappa value of ammonium nitrate is similar to that of sodium nitrate. The mass fraction of nitrate was generally quite very during MASE.

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.

Response

The calculation of van't hoff factor takes into consideration the non-idealities of water activity. It is now clarified in the manuscript.

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.

Response

We agree with the referee on this point. The sentence is rephrased to:

"The derivation of kappa from experimental data is based on the assumption that sigma_w =0.072 J m-2..."

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

Response

The typical mode diameter of sea salt particle size distribution is greater than 300 nm, and the typical concentration of sea salt over ocean is often less than 10-20 cm3. This is clarified in the manuscript.

13. After all the assumptions have been applied, what kappas are arrived at for use in the calculations? It might be interesting to report these values.

Response

The kappa values used in this study are 0.61, 0.70, and 0.74 for $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3, respectively. For the AC aerosol, kappa_org derived from closure study is ˜0.1. As pointed out by the referee, whereas a value of 0.1 for kappa_org also leads to closure agreements for the FT and BL aerosols, the predicted NCCN is insensitive to kappa_org, and good agreement can be achieved for a wide range of kappa_org values for the two types of aerosols.

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.

Response

The sentence is rephrased as:

"the solute concentrations were dominated by the inorganics due to the high solubility of sulfate and nitrate (i.e. high kappa values). The additional contribution from soluble organics, which has relatively low kappa_org, was only secondary. Therefore, the overall kappa, a volume-weighted average for all species, is insensitive to kappa_org. As a result, for a wide range of kappa_org, the variations in the predicted NCCN and the ratio of predicted to measured NCCN are small for the FT and BL aerosols."

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