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Atmospheric Chemistry and Physics 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 #1 Review

The study by Wang et al. addresses the analysis of cloud condensation nuclei (CCN) data acquired during the MASE campaign. The authors have identified three different air masses (boundary layer (BL), free troposphere (FT), and above clouds (AC)) that differ in their origin, and, thus, in aerosol chemical composition and size distributions. They show that for BL and FT aerosols the assumption of an internal mixture of inorganic and insoluble organics is sufficient to obtain good closure between mea-

sured and predicted CCN number whereas they suggest that for AC aerosols more information on organics' hygroscopicity have to be available. Based on the variation in organic properties they discuss in the CCN closure study the authors have performed an estimate of the extent to which uncertainty in organic aerosol properties translate into uncertainties in radiative forcing. They show that composition effects are greatly reduced in clouds and they conclude that the error is only significant if particles are composed of $>$ 90% organics; in all other cases the properties of the inorganic fraction dominates the hygroscopic properties of the population and the influence of the organics on cloud drop number concentration over a wide range of hygroscopicity is minor. This study represents a nice combination of a detailed analysis of CCN data and a discussion of the significance of measurement and/or model uncertainties for the broader picture of radiative forcing. The topic is certainly well suited for Atmospheric Chemistry and Physics and I recommend its publication after my comments below have been addressed.

Thank you for your encouraging review.

General comments

1) The authors conclude that because of the different shape of the AC aerosols size distributions as compared to BL and FT aerosols, the organics in the AC aerosols are externally mixed. Since this assumption has a significant impact on their following results, more detail should be given to their linear combination approach to fit separate modes to the measured size distributions (p. 9794, l. 4 ff.). The large underestimate of CCN in Figure 6 is due to the fact that about 90% of all particles are excluded as CCN, and, thus, it is not so much the organic properties but the mixing state of the organic (insoluble) particles that leads to the significant deviation in Figure 6. The assumption certainly represents an extreme case and the authors should emphasize this fact more clearly in their discussion: How likely is it that 'above cloud' particles are externally mixed with all other aerosol compounds? Can any information be given about the origin, and, thus, age of these particles? In Figure 4, it seems that the smaller

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particles (<˜ 200 nm) have even higher organic fractions that the larger ones. Is it possible that different organic compounds are present and only newly formed small organic particles are externally mixed whereas other organics are internally mixed in the larger mode?

*** Response ***

We thank the referee for raising this important point. We agree that it is very unlikely that organics were externally mixed with all other species for the AC aerosol. In our calculation, the AC aerosol was assumed as an external mixture of internally mixed modes, not a complete external mixture. For the example shown in Fig 5, the aerosol was assumed an external mixture of two lognormal modes, and within each mode, all species (i.e., sulfate, nitrate, and organics) were internally mixed and the composition of the mode was constant, independent of particle size. We have clarified this in the manuscript. We also agree with the referee that the assumption of aerosol mixing state can strongly impact the predicted NCCN, and we have carried out additional calculations using other aerosol mixing state assumptions. 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). Regardless of the assumed mixing state, assuming insoluble organics significantly underestimates NCCN for the AC aerosol. The assumption of a complete external mixture severely underestimates NCCN (as suggested by the referee). The ratio of predicted to measured NCCN is the lowest, 0.22, when assuming a complete external mixture with constant composition, and is the highest, 0.71, based on the assumption of a complete internal mixture. The ratios

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are almost identical, 0.46 and 0.48, when the AC aerosol is assumed as an external mixture of internally mixed modes and an internal mixture with size-dependent composition, respectively. We expect that the AC aerosol was most likely external mixtures of internally mixed modes or internal mixtures with size-dependent composition. A complete internal mixture is inconsistent with the size-dependent composition observed by the AMS, and a complete external mixture is also deemed unlikely for the aged AC aerosol. The extreme scenarios of a complete internal mixture and a complete external mixture serve as the limiting cases in our analysis. The additional calculations and discussion are now included in the manuscript.

2) As a consequence of the mixing state assumption for AC particles, the authors show that AC particles have to be hygroscopic (kappa = 0.12) whereas best closure for BL and FT masses is obtained for the assumption of insoluble organics. If the extreme mixing state is indeed reality, how can the difference in organic properties be explained for the different scenarios? It has been shown that the kappa of organics can span several orders of magnitude (Petters and Kreidenweis, 2006). For the sensitivity analysis of N(CCN), N(drops) and radiative forcing, it might be more useful to investigate a wider range of kappa covering a wider range (on a logarithmic scale).

*** Response ***

Based on the additional analyses described above, assuming insoluble organics substantially underestimates NCCN regardless of assumed aerosol mixing state. For the AC aerosol, the kappa_org derived from closure study is ~0.1 (based on mostly probable mixing state scenarios, either an external mixture of internally mixed modes or an internal mixture with size-dependent composition). Whereas closure agreements were achieved with the assumption of insoluble organics (i.e. kappa_org=0) for the FT and BL aerosols, a value of 0.1 for kappa_org actually leads to better closure agreements (Fig. 7, the ratio of the predicted to measured NCCN is 1.04 and 1.01 for the FT and BL aerosols, respectively.). However, it is worth pointing out that because the predicted NCCN is insensitive to kappa_org for the FT and BL aerosols, good agreements can

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be obtained for a wide range of kappa_org values for the two types of aerosols. The hygroscopic properties of the organics in the three types of aerosols could be the same (or similar). If that was the case, it is consistent with the results from the closure analyses presented. Petters and Kreidenweis (2007) show that kappa_org can span several order of magnitudes from 0.002 to 0.25 for typical ambient organics. The calculations were carried out for kappa_org ranging from 0 to 0.25, which should represent the typical kappa_org range.

Specific comments

p. 9786, l. 10: What 'chemical processes during cloud nucleation' are you referring to?

*** Response ***

The activation of CCN is mainly a physical process. "chemical processes" is now removed from the sentence.

p. 9788, l. 20: Replace 'as possible' by 'if possible'

*** Response ***

Done

p. 9788, l. 22: What is meant by 'state parameters'? 'Mixing state'?

*** Response ***

The "state parameters" refers to ambient temperature, pressure, and relative humidity, not 'mixing state'. It is now clarified in the text.

p. 9789, l. 19 ff.: Was the supersaturation corrected for gradients in the CCN counter?

*** Response ***

The details about the CCN counter calibration and correction of supersaturation are now included in the manuscript. Please refer to the response to comments by Rose et al.

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p. 9792, l. 12: The van't Hoff factor is the product of the number of ions and the osmotic coefficient. Was the factor for the inorganic salts corrected for non-idealities or was the maximum number of ions assumed?

*** Response ***

The van't Hoff factor is corrected for non-idealities of water activity. The van't Hoff factors used in this study are 2.5, 2.5, and 1.9 for (NH4)2SO4, NH4HSO4, and NH4NO3 respectively.

p. 9796, l. 10/11: It has been shown in CCN studies that water-soluble organics do not necessarily exhibit a kappa value greater than 0 (cf. e.g., Ervens et al., 2007). The reason for this apparent contradiction is that the analytical method that is used t extract water-soluble organics from particulates (Particle-Into-Liquid-Sampler) operates at very high dilution whereas the water/solute mass ratio at particle activation (S ˜ 1) might not be sufficient to dissolve the organics.

*** Response ***

We agree with the referee on this. This point is now clarified in the text: It is worth pointing out that some water-soluble organics may exhibit a kappa value of zero. The reason for this apparent contradiction is that the analytical methods used to extract water-soluble organics from particulates (e.g. Particle-Into-Liquid-Sampler) operates at very high dilution, whereas the water to solute mass ratio at particle activation may not be sufficient high to substantially dissolve the organics (Ervens et al., 2007)

p. 9796, l. 22: Rephrase and use something like 'the number of solute moles was determined by the inorganics' since - according to Koehler theory - it is the number of moles not the ion concentration (note: most organic do not form ions) that determines hygroscopicity

*** Response ***

The sentence is rephrased as:

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'the solute concentrations were dominated by the inorganics'

p. 9798, l. 1ff: Clarify that the drop-CCN relationship is valid for internally mixed aerosols that have bulk composition (i.e. no change in composition with size). Was the study by Sotiropulou also performed for stratus/stratocumulus clouds?

*** Response ***

The CCN concentrations were calculated using both bulk (size-independent) composition and size-resolved composition measured by an AMS in the study of Sotiropoulou et al. (2006). In addition, that study examines the ratio between the relative uncertainty in Nd to the relative uncertainty in NCCN (i.e., Dln(Nd)/Dln(NCCN)) , and it is expected that the ratio depends on the shape of the CCN spectrum, which is often more influenced by the shape of aerosol size distribution. The ratio was examined over a wide range of updraft velocities, including those typically observed in status/stratocumulus clouds, and it was found that the ratio was less than 50% in majority of the cases.

p. 9798, l. 25: Repeat here that the large variation in radiative forcing for the AC aerosols is due to the assumption of a different mixing state.

*** Response ***

Based on the additional calculations carried out (described above in response to general comment #1), regardless of the assumed aerosol mixing state, the ratio of predicted to measured NCCN and therefore the radiative forcing are very sensitive to kappa_org, a result of high organics volume fraction in the AC aerosol. The additional calculations and discussion are included in the revised manuscript.

p. 9804, l. 27: This statement of the accurate prediction using an average kappa seems very strong. Since one would predict probably similarly good results if kappa is different within a factor of 2, I suggest to rephrase: 'can be predicted sufficiently accurate'.

*** Response ***

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Interactive Comment

The sentence is rephrased as:

'can be predicted with sufficient accuracy'

p. 9805, l. 12: The statement that 'an average kappa(org) may be sufficient for many aerosol types' seems to be a contradiction to your CCN analyses where you showed that for two out of three cases kappa can be assumed to be zero. Here again, you should clarify that successful CCN closure could be only obtained under the assumption of external mixing of hygroscopic organics.

*** Response ***

We thank the referee for raising this important point. For the Free Troposphere and Boundary Layer aerosols, CCN closure agreements were achieved when assuming kappa_org as zero. As pointed out in the manuscript, the predicted NCCN is insensitive to the value of kappa_org,. Figure 7 shows that assuming a constant kappa_org of 0.12 leads to better agreements between predicted and measured NCCN (At kappa_org =0.12, the ratio of predicted to measured NCCN is 1.06 and 1.02 for the FT and BL aerosols, respectively). For the comment on the mixing state assumption, please refer to the response to general comment #1. The additional analyses with other aerosol mixing state assumptions show that the predicted NCCN when assuming an internal mixture with size-dependent composition is essentially identical to that based on an external mixture of internally mixed modes. At kappa_org =0.12, closure agreement is obtained for the both most probable mixing scenarios.

Figure 2c: Can you comment on the size distributions of the organics? Are the peaks around 90 nm and 200 nm different modes or artifacts due to the resolution of the measurements?

*** Response ***

In Fig. 2c, the peaks around 90 and 200 nm were due to poor counting statistics of the AMS pTOF mode data at very low aerosol loading.

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Fig. 8: (i) The figure caption should refer to Eq.-17 in order to make it easier to understand the connection between the two y-axes. (ii) Add to the figure caption that this estimate refers to an internal mixture without any size-dependent composition and a reference value of kappa = 0.12.

*** Response ***

Reference to Eq. (17) is added in the caption of Fig.8. The reference value of kappa_org is also added in the caption. The estimate refers to an internal mixture, but not limited to aerosol with size-independent (constant) composition. For internal mixture with size-dependent composition, xorg is simply the organics volume fraction at Dpc (as described in page 9800 line 12-13).

Technical comments

p. 9789, l. 21; p. 9790, l. 5: quadrupole

Corrected.

p. 9789, l. 25: 'particle time of flight' (not fight)

Corrected.

p. 9792, l. 22/23: Reword: Either 'the concentration [...] is small' or 'the solution is [...]

The sentence is reworded.

p. 9795, l. 26: add 'with' (associated with)

Done.

p. 9796, l. 10: Replace organics by organic

Done.

p. 9804, l. 23: Replace 'archived' by 'achieved'

Done.

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p. 9806, l. 25: Worsnop

Done.

p. 9806, l. 23: physical

Done.

Figure 5: Choose different colors. The cyan and blue lines are hard to distinguish.

Done.

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