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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Organics in the Northeastern Pacific and their impacts on aerosol hygroscopicity in the subsaturated and supersaturated regimes" *by* K. K. Crahan et al.

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Response to referees' comments on "Organics in the Northeastern Pacific and their impacts on aerosol hygroscopicity in the subsaturated and supersaturated regimes"

Anonymous Referee #1

Clarifications were added to the abstract and introduction explicitly stating that closures between the aerosol chemical and physical properties were explored.

1) Svenningsson et al. (2005) did not achieve closure between the observed growth of the MIXSEA particles and the ZSR method of predicting solution activity. Potential explanations offered were a mis-sizing of the aerosol diameter by the TDMA caused

by evaporation of the aerosol or the marine aerosols drying to non-spherical particles, the formation of sodium sulfate and ammonium chloride in the solid state, an insoluble core, and the interactions of organics with sodium chloride in solution not accounted for in the ZSR method.

As this manuscript attempts to reproduce aerosol growth using the Köhler equation and not the ZSR method to predict solution activity, only the mis-sizing of the aerosol diameter by the TDMA, an insoluble core, or formation of less soluble salts in the dry aerosol are alternative reasons for the failure to achieve closure. To further investigate this, the following paragraphs were added to the results section:

Other physical explanations remain possible for the observed discrepancy between the Köhler model and observations. Case 1 was chosen for further study using the Köhler model assuming that the organics remain in the solid state and the proportional chemical composition remains the same unless otherwise stated.

A mis-sizing of the aerosol dry diameter by the TDMA may be caused by evaporation of aerosol components or the marine aerosols drying to non-spherical particles. However, to achieve agreement between observations and the Köhler model, the dry aerosol diameters would need to be reduced from 50 nm, 100 nm, 150 nm and 200 nm to 12 nm, 17 nm, 19 nm , and 17 nm.

Another potential explanation is that the van't Hoff factors are lower than the experimentally derived values of 2.0, 2.0, and 2.2 for ammonium nitrate, sodium chloride, and ammonium sulfate, due to the preferential formation of sodium sulfate and ammonium chloride in the solid state (Svenningsson et al., 2005). This seems to be more plausible as the Köhler model is highly sensitive to the chosen van't Hoff factors. Uniformly decreasing the van't Hoff factors to 1.5 reduces the growth of Case 1 to 1.49, 1.53, 1.54 and 1.54 for the 50 nm to 200 nm particles, in closer agreement to observations.

Finally, the possibility remains that the smallest particles may contain a higher ratio of organic to inorganic chemical constituents. While size-resolved data are not available from the CARMA II field campaign, other studies suggest that the formation of marine aerosols favors organic material in the smaller size range (O'Doud et al., 2004). Increasing the fulvic acid concentration within Case 1 by a factor of 8 at the expense of ammonium sulfate produces DGFs of 1.49, 1.53, 1.53 and 1.54 for the 50 nm to 200 nm particles.

While some combination of the above scenarios may explain the observed aerosol growth, it is difficult to assess in more detail without knowing the size-resolved chemistry of the dry particle. Another possible explanation is that the Köhler model does not adequately account for the non-linear non-additive interactions between the organic components and inorganic components in solution.

2) The authors agree that a film is only one possible explanation. This has been clarified in the results and conclusions, with a further investigation of the Köhler theory similar to above (exploration of the impact of differing van't Hoff factors and organic contents), as well as comments on how the internal and external mixing states may impact the results. The following sentences have been added:

As with the previous section, the Köhler model was modified within case one to provide alternate physical explanations for the observed critical supersaturation. It was found that the aerosol molecule would need to be composed of over 86% organic material in order for the critical supersaturation of the 100 nm particle to fall within the error bars of the observations. Assuming the same percent composition as stated in Table 4, the van't Hoff factors of the inorganic constituents would have to be significantly below one in order to achieve closure for the 100 nm particle in case one.

It is difficult to assess the impact of higher RHs on the monolayer coverage without knowing the size of the hydrated aerosol at those RHs, and reliable measurements of aerosol growth do not exist at those high RHs, to my knowledge. But to address the point to the best of our ability, a sentence has been added in Section 3.3 stating: "With a DGF of 1.6, five of the aerosol populations observed retain a complete monolayer, and at DGFs between 1.7 and 2.0, four of the aerosol populations retain complete coverage."

The Svenningsson model is dependent on solution molality and carbon molality, and thus aerosol chemical composition. While adequately reproducing the overall impact of the water activity experienced by a generic hydrated sea salt aerosol, its simplicity will fail to capture the more subtle variations in water activity caused by small changes in chemical composition. A paragraph explaining this has been added in Section 3.2.

A description of the CCN thermal cloud chamber as well as a clarification of how the critical supersaturation was determined using the cloud chamber were added in Section 2.1.

The correlations between the dicarboxylic acids and ammonium sulfate and sodium chloride are now noted.

Ships may be another source of anthropogenic aerosols over the ocean. However, strong ship stack plumes were avoided during the field campaign, and in a well mixed marine environment, ship stacks likely contribute little to the overall anthropogenic aerosol burden.

Referee P. Chuang

The Köhler model was expanded upon, and a section better explaining the CCN thermal cloud chamber was added, as explained above.

Section 3.1

1) The section examining correlations between aerosol chemical components has been expanded, using 0.5 as a lower bound.

2) IOM has been changed to InOM in order to minimize confusion with Insoluble Particulate Organic Matter. It is Insoluble Oxidized Material (primarily soil and dust) and is

defined in Equation 2.

3) Correlation coefficients are r by definition.

Section 3.2

1) Gamma values are included in Figure 4 and 6. k values are not calculated as they cancel in the ratio of two measured particle scatter at two RHs, as measured by the UWPH. UWPH is defined in Table 1.

2) (4221, Line ~20) We believe that 7% of organics can result in a large change in aerosol growth compared to an aerosol of purely inorganic material. Using the Kohler model, an aerosol of 50% ammonium sulfate and 50% sodium chloride and dry diameters 50 and 100 nm have DGFs(85%) of 1.74 and 1.78. Assuming 8% fulvic acid as an insoluble core at the expense of ammonium sulfate, the DGFs(85%) are reduced to 1.73 and 1.77. Using the Svenningsson model with the later chemical composition, the DGFs(85%) are further reduced to 1.53 and 1.56. Furthermore, we don't believe that the IPOM is a tracer for any other chemical constituent as chemical closure was achieved between the chemically resolved mass and the PCASP, as explained in the text. IPOM represents all insoluble particulate organic material from each sampled aerosol population, and as IPOM is not correlated with any other chemical constituent, it alone appears to be responsible for the high negative correlation with the gamma values. Both IPOM and ammonium sulfate are less hygroscopic than sodium chloride, the only chemical constituent strongly associated with positive aerosol hygroscopicity, and thus both are responsible for depressing the aerosol hygroscopicity relative to sodium chloride. This is clarified in the text. This is explained as ammonium sulfate has a higher molecular weight and lower density than sodium chloride translating to less ion molality per unit mass compared to an equivalent mass of sodium chloride, impacting the solute effect of the Köhler equation.

3) (4222, line5) The exact mission times of the filters have been added to the caption beneath the graph.

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4) (4222, line 11) The origin of the 12 points is four sizes (50 nm, 100 nm, 150 nm and 200 nm) for each of the three case studies. This is clarified in the text.

5) (4222, eq7) A sum has been added to equation 7.

6) (4224) Unfortunately, we do not have any size-resolved chemical speciation for the organic components. The impact of this is explored somewhat as described in the response to referee #1, response 1 when the amount of fulvic acid is varied in an attempt to achieve closure between the Köhler model and the observations.

7) (4225, line ˜10 AND 4225, line ˜15) To clarify our argument, we are not arguing that the Köhler model is wrong. The Svenningsson model is a form of the Köhler equation with more detailed parameterization for how organics behave in solution. We are arguing that the current limited treatment of organics in the traditional form of the Köhler model is insufficient to reproduce observed marine aerosol growth, and it is only when the impact of organics is more accurately modeled within the Köhler equation does the bulk model output match observations. This is clarified within the conclusions.

Section 3.3

1) (4225, line 19) Agreed. The water activity was increased relative to that calculated by the Köhler equation. This has been corrected.

2) (Line 24) More references have been included.

3)(4226, line 12) It has been changed to “instrumental noise and atmospheric variability.”

4) (Line 17) The suggested figure (Figure 9) has been added.

5) (Line 16-18) The predicted supersaturations for the 100 nm particles using the various models and chemical compositions ranged from 0.18-0.63 %. Thus for the 100 nm particle, the sensitivity of the observed supersaturation to model initializations and assumptions should be observable.

6) (Line 19) This has been clarified in section 2.1, as mentioned in the response to referee #1 (2., Paragraph 4).

FIGURES

1) (Figure 4). Mass closure was achieved through comparison of the chemically resolved mass and the mass using PCASP measurements and an aerosol density of 1.9 g cm-3. The figure establishing aerosol mass closure between the chemically resolved mass and the PCASP mass is now prior to the chemical fraction speciation results.

2) (Figure 7) The asterixes were actually ‘x’ with error bars. The ‘x’s have been changed to triangles. The variability of the DGF seen in the TDMA results but not in the Svenningsson model may be caused by a couple of things. As explained above and added to the paper, is explained in part due to the fact that the bulk chemical analysis is unable to capture the chemical variability within the aerosol size distribution. This is further limited by the Svenningsson model inability to correct for chemical variability within the idealized sea salt mixture. However, as stated in the paper, the bulk approach is adequate for capturing overall trends and simplifies modeling efforts.

3) (Figure 8) The data is represented now by asterixes, and the graph is now only three orders of magnitude.

Anonymous Referee #3

1A) It is true that some error is introduced using the assumed concentration of the idealized sea salt mixture from the Svenningsson model. However, this is not the reason for the improved agreement between the Köhler model and the Svenningsson model. Using the idealized sea salt mixture from the Svenningsson model, the Köhler equation predicts DGFs of 1.55, 1.59, 1.60, and 1.61 for diameters of 50 nm, 100 nm, 150 nm, and 200 nm, while the corresponding Svenningsson model DGFs are 1.44, 1.47, 1.48 and 1.48. As the only difference between the models is the inclusion in the Svenningsson model of the nonideal behavior of organics in solution, something that is not calculated in the Kohler mode, the depression of the DGF is primarily a factor of the nonideal behavior of the solution. Additionally, there is some correction allowed in the Svenningsson model for solutions of different compositions as the solution activity is measured as a function of solution molality. Thus, while the model is somewhat limited in its ability to calculate the DGFs of mixtures that deviate from the idealized laboratory mixture used by Svenningsson, this paper supports that the simplifications used within the Svenningsson model are not only adequate to predict aerosol behavior in the subsaturated regimes, it is superior to the simplifications using the Köhler model and the bulk analysis method as it is currently commonly used. This is now explained in more detail in the conclusions.

1B) This has been addressed in the response to Referee #1 Comment #1. The Köhler model was varied until there was closer agreement between the Köhler model and the observed DGF through variation of the van't Hoff factors, organic concentration, and dry aerosol diameter. However, it is difficult to make any conclusion about how well this represents reality without size-resolved dry chemical compositional data.

1C) The authors agree that surface tension should not play a significant role in particle growth for particles of this size. However, as the impacts of surface tension have been receiving a lot of attention recently, and we think it is important to include (eg: Svenningsson et at., 2005; Mircea et al., 2005; Ervens et al., 2005).

2) Closure between aerosol growth and the University of Washington Passive Humidigraph (UWPH) measurements have been attempted in a previous paper (Crahan et al., 2004). The conclusion was that in marine environment the scattering attributed to the fine mode aerosols measured by the PCASP is not sufficient to account for all particle scatter measured by the UWPH, especially in the dry mode. However, the uncertainties associated with the coarse mode measurements made by the FSSP were so large that a meaningful closure is not possible. To further support this point, below are some scattering closure measurements for the CARMA II campaign:

Case:	PCASP calc. Scatter (Mm-1)	UWPH scatter(Mm-1)	UWPH RH (%)
Case 1:	4.1	29	30
Case 2:	4.3	17	29
Case 3:	3.8	15	29

3) The authors feel that the uncertainties estimated by the reviewer are somewhat larger than actual uncertainties. The uncertainties within the HTDMA are small, with the largest uncertainty likely resulting from the internal RH measurements, as suggested by the reviewer. However, the Edgetech dewpoint sampler has an accuracy of +/- .2 C, translating to an uncertainty within the RH of only +/- 1%, resulting in an error of only 6% within the DGF. This is much smaller than the error observed within the Köhler model. This has been clarified within the text.

The loss of particles at the inlet of the Twin Otter aircraft has been studied in detail and published in Hegg et al., 2005. It was found that the transmission efficiency of particles of a diameter of 3.5 microns or less was about 100%. Thus we expect the number concentration measured by the PCASP to be representative of the concentration measured by the CCNC inside the aircraft. This is also supported by the closure achieved between the PCASP measurements and the chemical concentration measured on the filters (collected through the aircraft inlet) as seen in Figure 4.

The cloud chamber measure each point in three minute time steps over about 40 minutes. The data is now shown explicitly in Figure 9.

The error associated with the PCASP due to is also small, and was calculated. As stated in Section 3.3, the PCASP was calibrated using an refractive index of both 1.41 and 1.59. While the true refractive index likely lies closer to 1.41 because the aerosol mixture contains organics (palmitic acid (m=1.43) and oxalic acid (m=1.42)) and water (m=1.33) as well as sodium chloride and ammonium sulfate. However, the error caused by an unknown refractive index, using the two calibration refractive indices as upper

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and lower bounds, was propogated through and found only to cause an uncertainty of 22% on average of the total aerosol volume for the three case studies. The largest uncertainty remains supersaturation within the cloud chamber.

Minor Points:

1) The OMC/OC ratio for oxalic acid is 3.75, and the OMC/OC ratio for palmitic acid is 1.33, as pointed out by the reviewer. The mass-weighted average OMC/OC ratio is 2.3. This is consistent with previous studies of non-urban organic aerosols (Turpin et al., 2000). This is now stated in the text.

2) The equation used was the same used by Quinn and Bates, 2005, who in turn cited Malm et al., 1994 and Perry et al., 1997. The reference has been changed to Quinn and Bates.

3) While neutralization with ammonium is an extreme assumption, it allows for the estimation of the smallest possible percentage of mass occupied by the organics, in order not to overstate the prevalence of organics in the marine atmosphere. Using this assumption, aerosol mass closure was achieved between the PCASP volume measurements and the chemical mass measurements. These calculations have been moved to section 2.2. Chloride, sodium, sulfate and nitrate were all measured explicitly. The percent loss of chloride due to chloride depletion is only 31%.

4) The suggested changes to the figures were made. The filters where sodium and chloride were below the detection limits were associated with days with low winds. Thus it is feasible that sea salt composed a minor fraction of the total aerosol population at that point.

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