Atmos. Chem. Phys. Discuss., 6, S1628–S1632, 2006
www.atmos-chem-phys-discuss.net/6/S1628/2006/

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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.

Anonymous Referee #3

Received and published: 8 July 2006

Review of ACPD 6, 4213-4249, 2006 Crahan et al.

Overview:

This paper reports observations of marine aerosol properties made from an aircraft in the NE Pacific. Measurements include chemical composition, hygroscopicity (DGF at 85% RH), humidity-dependent scattering coefficients (f(RH) up to RH=80%), and CCN activity. The authors attempt closure between the various observations, with limited success, not surprising due to the difficulty in making these observations from aircraft and the approximations that are necessary in the data interpretation and calculations. The authors discuss the relatively large fraction of total mass represented by organic

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species, point out the important role of organic species in modifying aerosol water uptake properties, and propose that lack of closure might be attributable to the nonideal behaviors of these constituents.

The attempts at composition-DGF closure showed that each considered model yielded fairly similar DGFs, that is, apparent composition differences had rather minor influences across the various cases (1.65-1.75; 1.5-1.65), with larger differences between models. In contrast, measured DGFs had a bigger range, 1.35-1.7. The measured GFs are difficult to reconcile with the critical supersaturation values required for activation, which are more consistent with aerosols having DGFs significantly lower than observed.

Major comments:

I appreciate the considerable effort that went into collection of this data set, and agree it is a worthy addition to the body of literature on marine aerosol properties. However, I feel that some of the proposed explanations of the observations should be reformulated before this paper is published in ACP and offer the following points for consideration.

1. The authors compare the “Köhler” model to the Svenningsson et al. (2005) model containing sodium chloride (not sea salt, as is incorrectly indicated in Table 4). The Svenningsson model does better at reproducing the GF and activation data. Crahan et al. conclude this is because it is not valid to treat the solution as ideal. There are two problems with this conclusion, which also appears in the Abstract.

(a) The fractional composition of assumed species in the Svenningsson model does not in fact match the observations very well. In particular, the observations have more sodium chloride and ammonium nitrate, which are very hygroscopic species, and considerably less fulvic acid, which has limited hygroscopic growth. Therefore it is not surprising that the “Köhler” model predicts higher DGFs. It would be more valid to adjust the composition in the Köhler model to be equivalent to the Svenningsson mass fractions and then make a conclusion about deviation from ideality.

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(b) Svenningsson et al. essentially did the calculation suggested in (a) and did find that the experiments showed less hygroscopic growth than expected by mixing individual components. However, in Section 3.2.1 of the Svenningsson paper, they note “we can not make conclusions on the reason for the deviation from the ZSR method”. They point out that as the original solution is dried, it is possible to form complex salts from this mixture, some of which may be hydrated crystals. If this happens, then the mass of ionic material in the dry particle is actually quite a bit less than would be computed from the dry diameter and an assumed density, and the growth in the HTDMA would be lower than expected for the computed mass. This is an equally or more plausible explanation for unexpectedly-low observed DGFs as the assertion of highly nonideal solution behavior.

It is not surprising that the surface tension plays very little role in calculation of DGFs. The Kelvin term is relatively small for 100 nm particles.

2. There is a missed opportunity to see if the measured DGFs are consistent with the f(RH) from the scattering measurements. While the RHs that these observations were made at do not match, a model can be fit to the DGF observations at 85% RH and then extrapolated down to the nephelometer RH. By checking the level of agreement it could at least be noted whether the measured DGFs appear to be approximately consistent with the change in scattering due to RH, or too low in some cases as is suggested from the comparisons with models based on composition.

3. My final major point concerns how the DGFs and critical supersaturations might be reconciled. Assuming the RH inside the HTDMA was larger than the setpoint, even as high as 92%, adjusts the DGF(85%) downward (I estimate to about 1.16-1.42, based on typical growth curves and the extreme assumption that RH=92% for the measurements). However, for DGF(85%) $>$ 1.2, we generally still expect lower Sc’s than those measured. However, as discussed above, the comparisons in Figure 7 suggest that if anything, the measured DGFs are too low compared with those expected based on composition. Therefore, it is difficult conceptually to reconcile the high water contents

of the aerosol below 100% RH with the relatively high critical supersaturations required for activation to cloud droplets.

The authors suggest the high measured Sc's were due to "activation delay" in the instrument, caused by film forming compounds - that is, the measured Sc's are an artifact and are not indicative of the expected equilibrium values. While this explanation cannot be ruled out, I suggest that a more plausible explanation for the discrepancy may lie with the methodology used to deduce the critical diameter at each selected Sc.

The activated number of particles was compared with the PCASP size distribution to deduce when 50% activation was reached. However, the PCASP is an external probe, while the CCNC was operated inside the aircraft and sampled through an inlet subject to aerosol losses, and there are likely further losses through the instrument fittings. If particle losses were not quantified and corrected for, then it is plausible that it was necessary to push the Sc toward higher values (and smaller diameters) in order to activate enough particles to reach 50% of the PCASP number concentration values. This would bias all of the measurements toward higher Sc, as is seen in the observations in Figure 9. Were the CCNC measurements pushed to 100% activation? If so, then the total number concentrations from the CCNC and PCASP can be compared to support or rule out this possibility.

Also, (a) I believe that this CCNC has a quite small sample volume. How long did the CCNC measurements take? The role of heterogeneity in particle type during the flights was pointed out in the paper. (b) Finding the 50% activation diameter in the way described assumes that neither the size distribution nor composition changes with time or location. Finally, (c) there are considerable uncertainties in the sizing by the PCASP: having to correct for both refractive index and residual water at an unknown low RH. These size changes can significantly affect the activation properties, as has been discussed extensively in the literature (e.g., Snider, Tellus, 2000). I feel that the uncertainty in the CCN measurements must be considerably larger than that estimated here.

Minor points:

p. 4218: the choice of compound for estimating compound mass from the carbon mass affects not only the estimated mass fraction, but also the hygroscopic nature. The choice of oxalic acid yields OMC/OC $>$ 3, larger than generally assumed in mass closure studies. The choice of palmitic yields OMC/C˜1.3, a reasonable choice. A low molecular weight yields more moles per gram, leading to higher hygroscopicity in the Kohler model. The choice of oxalic is not consistent with the composition in Table 4.

p. 4218: Equation (2): it is not clear to me this equation is from the referenced text. I believe it is that used in the IMPROVE formula, except the contributions of titanium have been dropped. The assumptions going into the coefficients are not as direct as indicated. The correct reference needs to be inserted here.

p. 4218, last sentences: Were gravimetric mass measurements made? It is not correct to assume neutralization by ammonia, and ammonium was not measured. More like there was chloride depletion and thus the relevant salts are sodium sulfate and sodium nitrate. This also relates to the issues regarding interpretation of the DGFs and whether the particles form hydrates, and to the discussion on p. 4221.

On Figures, indicate the DGFs are at 85%.

Figure 4 is impossible to read in black and white. Also, it seems some samples have no sea salt. Is this reasonable?

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