

Interactive comment on “Measurements of size-resolved hygroscopicity in the California coastal zone” by D. A. Hegg et al.

D. A. Hegg et al.

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RESPONSE TO REVIEWERS' COMMENTS ON ACPD 2008-0097

1. Reviewer No. 2

1.1 Summary comment The reviewer has called for a number of justifications or clarifications, particularly with regard to the water mass derived from the DHGF measurements and the linkage between the UNMIX analysis and the derived DHGF's. We try to clarify these points below, detailing our proposed changes, or justifications, in our responses to the specific comments.

1.2 Specific comment (SC) on decreasing DHGF with size and the linkage to the size-resolved chemistry. The amount of MOI data is rather limited (six samples) but shows a fairly consistent picture. While the NaCl concentration certainly increases with size, in

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absolute terms monotonically and in relative terms commonly, the mass concentration above 1 micron is still mostly sulfate. For example, in the 0.77 to 1.4 micron range the sulfate to chloride ratio is about 3, from 1.4 to 2.5 it is 1.4 and from 2.5 to 8 it is about 1.3. Hence, we would not expect to see a hygroscopicity like that of NaCl in the larger size ranges. Nevertheless, we would agree that the reviewer has raised an interesting issue here and were ourselves mildly surprised to see the decrease in hygroscopicity with increasing size shown in our data. We feel that it is important to remember that we are not dealing with pure NaCl here or, indeed, even pure sea salt, as is illustrated by our Figure 2. (It is also why we choose to refer to our more background aerosol as marine rather than sea salt.) What is present is a mix of sea salt, sulfates, nitrates and organics, with the sea salt becoming only relatively more important with size. We note that Andreae has argued that such is to be expected even in background air in the Northern Hemisphere (Science, 315, 50-51, 2007) and is also consistent with the relatively complex composition suggested by the study of Snider and Petters for roughly the same locale, as cited by the reviewer. Additionally, from our previous measurements in this area, which included some information on individual particle composition, the composition mix is commonly internal and also can include soil dust (Hegg et al, Geophys. Res. Lett., doi:10.1029/2006GL026747, 2006). As Tang has pointed out (cf., J. Geophys. Res., 102, 1883-1893, 1997), such salt mixtures (even disregarding the organics) have hygroscopicities considerably less than that of NaCl, or pure sea salt. While it is beyond the scope of this study to try to model the aerosol hygroscopicity based on its detailed composition, using, perhaps, some variant of the UNIFAC model, we find it quite conceivable that the variation with size of the salt mix would decrease the hygroscopicity in the manner observed, though we prefer not to speculate on this issue in the manuscript. What we ARE sure of, based on our calibration of our apparatus and our ability to recover the proper hygroscopicity of test salts, including NaCl (cf. Hegg et al, Aerosol Sci. Technol., 41, 873-883, 2007), is that the hygroscopicity does indeed decrease with size to the extent observed. To meet the reviewer's concern, we propose to now include an abbreviated version of the

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above discussion in the text near the start of section 4.1, where the observed DHGF spectra are first introduced. In this discussion, we will specifically note the decrease with size, offer some rationalization as per above, and cite appropriate references.

1.3 SC on the AHS measurement RH's. The same RH's were always used in the measurements of DHGF's, nominally 45 and 85%. The oblique reference to abnormality refers to tests in which each channel of the AHS is run at the same RH to test channel equivalence. We propose to slightly re-write the text to clarify this.

1.4 SC on problems with optical detection Most of the issues associated with using OPC's are discussed in the cited references (Hegg et al, 2006, 2007). Briefly, the particles are always on the upper branch of the hysteresis loop in both channels and so are solution drops, i.e., spherical. Changes in index of refraction upon increased hydration are corrected for using formulae from Hazel and van de Hulst. (Note that the effects are much smaller than those in Snider and Petters because we are using white light, 90 degree scattering OPC's.) The only issue raised by the reviewer not discussed is that of enhanced lensing of black carbon and thus absorption upon increasing hydration. (We note that the effect of black carbon absorption in and of itself cannot be a factor since it is the same in each channel.) We agree that in principle this effect should be calculated but consider it unlikely this is a significant effect. Liu et al (JQSRT, 74, 195-204, 2002) assessed possible differences between the radiative impact of black carbon included within and interstitial to cloud drops (i.e., for a truly impressive growth factor) and found no appreciable difference. Lensing effects in cloud drops (~10 mm diameter) will far exceed that in aerosol particles due to the much longer ray paths and we thus discount this as a significant factor in our analysis. Nevertheless, we propose to now state this assumption in the text.

1.5 SC on derivation of water of hydration from the humidigraph measurements. While it is not an important aspect of our analysis, we agree with the reviewer that we have been too cavalier on this point. Before discussing the derivation, however, we feel it important to note that the water values presented in the ANOVA analysis were derived

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to render the units for the matrix inversion homogeneous (DHGF values would not, of course, have mass concentration units), thus avoiding scaling problems. So long as the relative amounts of water are preserved, the absolute values of the water mass are not critical. The humidigraph data (scattering at set RH's which are fairly similar to though not identical to those used in the AHS) are first fit to a hyperbolic section as per Gasso et al to derive the "gamma" exponent to the RH dependence of the scattering. This is then used to interpolate the scattering ratio (scattering at 85% over that at 45%) to the same RH's used in the AHS. This is then converted to a diameter ratio as per Gasso et al. The additional volume and thus mass of the water is then calculated in a straightforward manner under the assumption of volume additivity as per Hanel (Adv. Geophys., 19, 73-188, 1976). We propose to discuss this procedure briefly in the text. As for consistency of the derived "scattering water" with those measured by the AHS, we agree that it should be done if it could be done but do not see how to do it in a definitive manner with the data we have in hand. The two instruments simply cover different (though overlapping) size ranges and, though the water contents derived are quite reasonable and not obviously inconsistent, a detailed comparison would require the aerosol size distribution over the nephelometer measurement range, i.e., down to roughly 0.1 μm diameter and we do not have this for the current data set.

1.6 SC Discussion of the source DHGF's in terms of literature values. Once again we agree with the reviewer that more should be done here. We propose to explicitly present in the text the DHGF values we used for marine, biomass burning and pollution aerosols (e.g., for submicron DHGF's, 1.13 for biomass fires, 1.62 for marine and 1.34 for polluted aerosol types). Further, for the submicron values and the Scattering DHGF's, we will compare them with literature values for the same aerosol types (e.g., Rissler et al, Atmos. Chem. Phys., 4, 2119-2143, 2004; Swietlicki et al, Tellus, 52B, 201-227, 2000). For the supermicron values, very little information is available (hence our study) but we will do what we can.

1.7 SC on comparison of variance reduction in UNMIX(?) compared to the Figure 9

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regression. We are a bit puzzled by this comment and thus not quite sure how to address it. Firstly, the results presented are for the UNMIX model, not the PMF model. Secondly, no measure of variance reduction is explicitly given. Typically, ~ 80% or more of the overall variance in the variable set is reduced by the first 3-4 factors (sources) and possibly it is this to which the reviewer is referring. If so, we must disagree that this is comparable to the variance reduction implied by the Figure 9 regression (~64%). The variance reduction associated with the eigenvectors is for all of the variables in the model input taken together (all of those listed in Table 2), essentially a mean, while that in the regression is for variance in the submicron DHGF values alone. The UMIX variance reduction associated with this single variable (assuming it and not a surrogate were actually input), could be appreciably less than the overall mean variance reduction. Nevertheless, to pursue the discussion, let us assume that the mean reduction is indicative of that for DHGF's. The relatively low variance reduction associated with the model prediction would then suggest that either the ZSR mixing rule is not entirely appropriate, or that internal variance in the characteristic DHGF values for the aerosol types is large, or both. We prefer the former and will allude to this in an expanded discussion of the uncertainty in the submicron values. We have already discussed the much more significant supermicron discrepancy.

1.8 SC on Table 1 The error in labeling will be corrected.

1.9 SC on Table 1 and 2 units The units will now be indicated more clearly (mg m⁻³ unless other wise indicated, e.g., mass fractions). The water contents are incremental going from 45 to 85% RH, as indicated in the text (we will add it to the caption as well).

1.10 SC on magnitudes of water contents in Table 1. We must disagree with the reviewer a bit here. He states that the water associated with the dry aerosol as per Table 2 is much too low, stating that sea salt at 80% RH would have a water mass 8 times the initial dry mass and also implying (presumably from Figure 8?) that our aerosol is ~ 75% sea salt. Firstly, as per our earlier response, one must be careful to note that the aerosol is not sea salt but rather "marine" and in fact has a good deal of sulfate

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and so forth in it. Furthermore, even assuming it is sea salt, the mass of water at 80 (or 85)% RH would not be 8 times the dry mass; the volume might be something like 8 times the dry volume, but the mass ratio is much less and in any case it is the DIFFERENCE between the wet and dry masses that is relevant, not their ratio. From Tang's EDB measurements (cf., Tang et al, J. Geophys. Res., 102, 23269-23275, 1997), one would expect the ratio of drop mass at 80% to the dry mass to be ~ 4.1 . As a rough check, if we apply this to the mean dry total mass in Table 1 (the only direct dry mass measurements we have) of 16.32 mg m⁻³, this would suggest a "wet" mass of 66.9 and a difference between the wet and dry masses of 51. If we add up the total water associated with the sub and super AHS measurements, and the scattering, we get a mean value of 36. While certainly low, given that we are not dealing with pure salt, and that the water is not the total water of hydration but rather that added going from 45 to 85% RH, this comparison does not look so bad to us even if we assume some redundancy in the scattering and submicron water of hydration - which is likely. Hence, we see no inconsistency in the table.

2. Reviewer No. 3. 2.1 General comments The reviewer raises two main points here in the general discussion, no doubt for emphasis; 1) we do not provide sufficient evidence for our organic film hypothesis and, 2) the essential meaning of the DHGF closure is not sufficiently clear. Because he raises these same issues in more detail in his specific comments, as with reviewer No. 2 we address these concerns in our detailed responses to these comments.

2.2 SC Pages 10536-10538, sec. 4.1, Figs 2, 4 and 6. The possibility that one has had differential advection for two different heights in the MBL - and thus two different source areas - cannot be dismissed out of hand but it is unlikely. Firstly, there is no evidence from Hysplit back trajectories of differential flow within the MBL during our study. Of course, model resolution is not particularly good within the MBL and this is therefore not decisive. However, there is also a more fundamental constraint at work here. It is really simply an issue of time scales. The back trajectories are over water for

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at least 20 hr prior to sampling (i.e., different sources are likely at least 20 hrs away) and vertical mixing over such an extended period will indeed wipe out vertical gradients due to different sources. On the other hand, in situ chemical reaction time scales for OH or even O₃ attack are on the order of minutes, short compared to vertical mixing time scales in the MBL. Hence vertical gradients due to in situ chemistry are perfectly feasible. We propose to include this brief discussion in the revised text.

2.3 SC Page 10536, lines 17-28 We certainly agree that mass fractions are the appropriate units to link with hygroscopicity - rather than absolute mass concentrations. In fact we do point out in the text that the soluble mass fraction for the data shown in Figure 2 does not increase with altitude (page 10536, lines 25-28). Furthermore, the total mass concentrations for the low and high altitude data shown in Figure 2 do not significantly differ (8.8 ± 1.7 mg m⁻³ for the low altitude samples and 7.3 ± 1.4 for the high altitude samples). Hence, the mass fractions are essentially the same as the mass concentrations shown in the figure. To help clarify matters, we will add this information to the figure caption and also allude to it in the text. As for Figures 4 and 6, as discussed in the text, the point of these figures is the presence of enhanced oxalate in the higher altitude samples, and at sizes corresponding to the enhancements in hygroscopicity. The oxalate is a marker for organic surfactant oxidation, our hypothesis being that it is the presence of such films that have restricted the hygroscopicity of the low altitude aerosol. This mechanism is definitely not associated with the mass fraction but rather with the total amount of oxalate - actually its precursor - compared to the aerosol surface area. We discuss this point further in response to a following comment by the reviewer (see response 2.5) but note here as well that we propose to add additional text to clarify the nature of the thin film mechanism.

2.4 SC page 10538, lines 9-17. We are not quite sure how to take this comment. We have cited already a number of studies that have measured such films on marine aerosol and, while we could cite more, we presume that the reviewer is well aware of these already. We would certainly concede that it is not clear that marine aerosols,

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or more specifically sea salt particles, are ALWAYS coated by such films and perhaps this is the point the reviewer is trying to make. To accommodate this quite reasonable viewpoint, we will add a caveat to our discussion to make it more clear that, while such coatings have been found, their frequency and distribution are not certain. Remember too, that we have already stated explicitly that our film oxidation mechanism is a HYPOTHESIS (e.g., page 10537, lines 3-4).

2.5 SC page 10538, lines 9-17. There appears to be a fundamental misunderstanding of what we are hypothesizing. The oxalate (and formate) we detect is a MARKER for fatty acids that coat the surface of the sea salt particles emitted from the ocean surface. We would agree with the reviewer that the oxalate mass itself is inconsequential as an additional solute. It is the action of the organic film that is key here, acting as a barrier to water uptake by the salt particles. Hence, as the film oxidizes and the soluble products absorbed into the drop, the aerosol hygroscopicity increases. There need only be enough surfactant to cover the initial surface, though likely the surfactant must be in the condensed state. A rough calculation well illustrates the small magnitude of the surfactant (or its reaction product) necessary. For the condensed state, alkanolic acids (or alcohols) typically have a coverage of $\sim 25 \text{ \AA}^2$ molecule⁻¹ or 4×10^{14} molecules cm^{-2} in a monolayer. From the AHS measurements there are roughly 10^2 particles cm^{-3} in the measurement size range of interest. Assuming 0.5 μm diameter particles, this yields a total surface area of $7.8 \times 10^{-7} \text{ cm}^2/\text{cm}^3$. This, in turn, suggests a need for $\sim 3 \times 10^8$ molecules cm^{-3} or 5×10^{-16} moles cm^{-3} of surfactant necessary for complete surface coating. From complete oxidation of this surfactant (and it is by no means necessary that the film be completely oxidized to break the film barrier), we would then expect to see $\sim 0.02 \text{ mg m}^{-3}$ of excess oxalate at the higher altitude - which is about what we see (Figures 4 and 6). To clarify the small amount of oxalate necessary for our hypothesis, we propose to put an abbreviated version of this discussion in the text.

2.6 Technical correct (TC) page 10534 We will add the reference.

2.7 TC Tables 1 and 2 We will make the labels consistent

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2.8 TC Fig 2 The program used to draft the figures does not accept capitals. The figures would have to be redrafted by hand to accommodate this suggestion. Since this can be quite expensive and there is no issue of clarity involved, we will do it only if we can get a good price on it.

2.9 TC Figs 3,5,7 The reviewer is quite right. We will correct the typos - units should be nm.

2.10 TC Figs 4and 6 Same as for response 2.8

3. Reviewer No. 4. 3.1 General comments No response seems necessary here.

3.2 SC page 10532, line 6 We agree that we have been too general here. We propose to change the wording on line 6 to, "...both to examine the mechanism for the increase in aerosol hygroscopicity with altitude...."

3.3 SC page 10532, line 8. We disagree. The UNMIX model is quite sensitive to the number of factors selected. If the source number is not compatible with the optimum variance reduction, the matrix will simply not invert (as stated in the text on page 10540, lines 27-28). We tried anywhere from 2-6 sources and achieved inversion only with 3. Possibly the reviewer is thinking of the PMF model where in fact the number of factors is simply specified ab initio - one of several reasons we chose to discuss the UNMIX results instead.

3.4 SC page 10532, line 11. We propose an additional statement that the regression analysis showed that the model had substantial prognostic power for submicron hygroscopicity but essentially none for the supermicron.

3.5 SC page 10534, lines 6-12. The filter sampling time varied from 12-40 minutes at a flow rate ranging from ~90 to 150 lpm, depending on altitude. The AHS measurements are essentially continuous and we averaged them over the filter sampling times for comparability. At the very high face velocity of our sampling, the collection efficiency of the Teflo filters is in excess of 99.99% for 0.2 mm diameter particles and larger. After

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collection, samples were stored at a nominal 4 ° C prior to analysis. The samples were analyzed over a week's time. We note that we have never observed significant artifacts using the above procedure, which we have tested extensively over the past 30 years. We will include this information in the revised text.

3.6 SC page 10535, lines 24-26. There were 15 flights, as stated. The number 24 refers, as stated in the text, to the number of horizontal traverses (page 10535, line 25). We thought it clear that there was more than one horizontal traverse per flight but will now state this explicitly. We will also define the meaning of MBL and MSL (marine boundary layer and mean sea level, respectively).

3.7 SC page 10536, line 2. DHGF was defined on page 10533, lines 23-25. We will clarify further.

3.8 SC page 10536, lines 6-7. Not significantly. The single 500 m sample did have a higher hygroscopicity but large uncertainty precluded significance. One reason for comparing means was to reduce uncertainty. The mean "higher level" from CARMA III was ~ 250 m. We will now specify this, as suggested.

3.9 SC page 10537, line 7. The oxalate and formate are important because they are markers for surfactants, which need be present only at quite low levels (see our response 2.5). The other species, lower still in concentration, are NOT markers and would only act as additional solutes, in which role their mass is trifling compared to those already noted. The proposed additional text, in response to comment 2.5 should clarify this somewhat but we will also add text at this point to make sure it is understood.

3.10 SC page 10541, line 3. Bootstrapping refers to a numerical technique to assess errors by multiple resampling of the input data set. We will now provide a reference for this technique, which is an integral component of UNMIX (or PMF).

3.11 TC page 10532, line 1. Change will be made.

3.12 TC page 10538, line 27. The mean altitude of the "higher" marine samples is

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about 250 m. The pollution and biomass samples were taken at altitudes ranging from 100 to 700 m. We will note the actual mean altitude of the "higher" samples.

3.13 TC 10540, line 15. Change will be made.

3.14 TC 10544, line 16. Change will be made.

3.15 TC Tables 1 and 2. The figures in Table 1 will be truncated as appropriate. For Table 2, what is shown is direct model output and it is not clear where to truncate. The figures are only important in a relative sense but we will figure out some consistent method of abbreviation. We will also change the text to make sure the discussion corresponds to the source labels.

3.16 TC General figures. Unit errors will be corrected (e.g., nm vice um) but capitalization may be an issue as per our response 2.8. We will try.

3.17 TC error bars. We will state errors in the caption since we do not wish to redraft the figures.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 10531, 2008.

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