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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Optical particle counter measurement of marine aerosol hygroscopic growth" *by* J. R. Snider and M. D. Petters

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We thank Professor Baumgardner for his review and his constructive criticism. Below we include his comments and our reply. In those instances where the text has been revised, we also attach the revised text.

Growth factors have been derived using a variety of methods in previous studies. The authors should put their results in the context of what has been previously published. For example, using two nephelometers, Hegg et al. (1997) measured the GF of aerosols in almost the same region off the coast of California, under and over marine stratocumulus and during the same season, but nine years earlier. They determined that the GF could vary between 1.2 and 2.4 (their Table I), but concluded that they were consistent with what being used to evaluate the impact of marine aerosols on radiative fluxes. Comparing their results using a technique different than those used in previous



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studies is not only a good sanity check that the technique is producing reasonable results but is also necessary if the intent of the submission is more than just an evaluation of another method for determining GF.

Two comments:

1 - We chose to compare our GF values to measurements from an HTDMA operated during ACE-I. The ACE-I comparator comes from ship-based measurements made in un-polluted southern Ocean air. We were interested in seeing how close our GF values were to those measurements. Since the latter are close to the expectation for a pure ammonium sulfate or pure sodium sulfate aerosol, and we expected to see some influence from non-hygroscopic material (Quinn et al. (2000), referenced in submitted manuscript), we were pleased to see that our expectations were met.

2- Hegg et al.’s Table 1 reports measurements from March, November and December 1994 (Hegg, D.A., D.S. Covert, M.J. Rood, and P.V. Hobbs, Measurements of aerosol optical properties in marine air, J. Geophys. Res., 101, 12,893-12,903, 1996). Measurements were made “..in the vicinity of the coast of the state of Washington or in the Puget Sound Basin of that state.” Because of the proximity of these measurements to the west coast and since the measurements were not made in summertime, it is our opinion this is not a good comparator.

The use of the FSSP300 for deriving GF is not an entirely new idea, although comparing it with the PCASP is. Perhaps it would still be relevant to the current submission to read the paper by Baumgardner and Clarke (1998) who discuss many of the same issues with the FSSP-300 but take a somewhat different approach to look at how humidity changes the particle volume and at one point in the paper show measurements that are consistent with the Tang et al. laboratory studies of common salts.

We appreciate that you brought this paper to our attention. We have included it in the list of techniques which are alternate to HTDMA (p. 12383 of the submitted manuscript). The relevant figure from Baumgardner and Clarke (1998) is Figure 8.



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On this same thread we have two further comments:

1 - In the revision we provide a more thorough explanation of the hygroscopic growth factor (GF) that we report. This clarification is detailed below.

2 - Changes in aerosol volume (observed by Baumgardner and Clarke) were compared with calculations based on Tang (1997) on the assumption that either NaCl or Na2SO4 is the hygroscopic material. The aerosol changes, observed and calculated, are expressed relative to the aerosol volume at 70% RH. This technique can judge if the rate of change of the aerosol volume, with respect to RH, is consistent with the dominance of either NaCl or Na2SO4 in the aerosol phase.

Page 12384, line 29: "Sampling conducted in dry air above the marine boundary layer (RH$<$40%) reveal GF values that are approximately equal to unity, as expected." Why would the growth factor above the boundary layer have an expected value of unity?

We thank Professor Baumgardner for motivating a clarification. The paragraph is revised as:

We analyze PCASP and F300 measurements and derive the GF of particles of dry diameter larger than that accessible with a conventional HTDMA. Results are presented for 31 constant-altitude circles flown within and above a summertime marine boundary layer. We report data from seven days during the time of peak stratocumulus cloud occurrence over the northeastern Pacific. Measurements conducted in dry air above the marine boundary layer (RH$<$=36%) were used to infer the sample flow rate through the sample area of the F300 and to also establish that hygroscopic growth factors in this regime are close to unity. The latter result is expected since the ambient RH is too low to sustain water amounts on the F300-detected particles significantly in excess of that on the PCASP-detected particles. For measurements made within the boundary layer, where the ambient RH ranged between 71 and 96%, we report GF values which are somewhat smaller than that of laboratory generated sodium sulfate particles.



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Also, we have revised the first paragraph of Section 3.2 as:

Values of GF for the seven above-cloud segments (one for each flight) are plotted in the left panel of Fig. 3. We expect these GFs to be close to unity because the ambient RH is too low (<=36%) for chemically-bound water to make a substantial contribution to the size of the particles detected by the F300. This is indeed the case with all of the above-cloud GF values plotting within +-17% of GF=1. Averaged GF value is 1.06+-0.09 (7 above-cloud segments).

Page 12387, lines 9-27: The discussion of how the sample area of the FSSP-300 is derived by comparing the counting statistics of PCAS and FSSP300 is very difficult to follow. Why are counting frequency statistics being used as opposed to comparing the absolute number of particles counted in the overlapping size range? The methodology here is very difficult to follow and too brief to understand how the final value of sample area is obtained, a value that turns out to be within area reported by the manufacturer, within the uncertainty of technique used in the derivation. The independent derivation I think is a critical aspect of this paper as it shows that the concentrations measured by the PCASP and FSSP-300 are consistent and hence there is no major instrument issues to resolve before the derivations of GF. What is missing is a more succinct explanation. It should also be noted in this section of the paper that obtaining the overlapping size intervals is very sensitive to the assumed refractive indices for both the PCASP and FSSP-300. The fact that the derived sample area is so close to that measured by the manufacturer in the laboratory and derived from optical considerations, is further proof that differences in refractive indices from those that are assumed and actuality will probably have a very small impact on the derived GF.

We apologize for the confusion. In the revised text we provide more detail on the calculation, including an explicit statement of the Poisson distribution function and a definition of all terms. Also, we conclude the discussion of the F300 sample area calculation with information directed toward the related critique of reviewer #2. Specifically, reviewer #2 asked if the AF we calculate is better than what is obtained by forcing



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the averaged F300 concentration to agree with the averaged PCASP concentration. In the revision we make the point that these two approaches yield nearly the same project-averaged AF. One final comment: The AF we derive is average=0.034+-0.006 mmˆ2. What we wrote in the original manuscript was average=0.034+-0.060 mmˆ2. We apologize for the typographic error in our representation of the standard deviation of the sample area.

The particle count rate distribution, corresponding to the above-cloud segment of RF01, is shown for both OPCs in Figure 1 (red and blue). We emphasize that these two distributions are constructed by pooling particle count rate measurements archived in the NetCDF file (Sect. 2.2). In contrast to such empirically-based count rate distributions, a theory-based distribution was formulated on the assumption that particle counting by F300 can be described by the Poisson distribution function (Young, 1962). A parameter used in the theory is the segment-averaged F300 count rate (CF) which we derived as

CF=CP*U*AF/VP (1)

Here CP is the segment-averaged PCASP count rate (0.4$<$D$<$0.8 um), U is the segment-averaged airspeed of the C-130, VP is the segment-averaged PCASP sample flow rate (Sect. 2.3) and AF is the largest of two F300 sample areas reported by Baumgardner et al. (1992) (0.05 mmˆ2). The fraction of seconds with a specified number of counted particles (N) was formulated according to Poisson theory as

f(N)=((CF)ˆN)*exp(-CF)/N! (2)

We show the prediction of Eqs. 1 and 2, assuming AF =0.05 mmˆ2, as a black histogram in Figure 1. It is apparent that the theory-based distribution peaks at 1 particle per second while the empirical F300 distribution peaks at zero particles per second. A corrected F300 sample area was derived by adjusting AF in Eqs. 1 and 2 until the theory-based distribution agreed with the empirical F300 distribution at a count rate of zero particles per second. The result is shown (gray) and corresponds to AF =0.033



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mmˆ2. While the agreement at zero count rate is forced, the predicted particle count rates at one, two and three per second are also in reasonable agreement with the empirical F300 distribution. This calculation was repeated for the other six above-cloud segments. We use the average of this set, average=0.034+-0.006 mmˆ2 in our analysis. Assuming AF =0.034 mmˆ2 and a representative airspeed for the C-130 (U=110 m/s), the F300 sample flow rate is 3.7 cm3/s, about a factor of four larger than that of the PCASP. Finally, we note that our result for the project-averaged F300 sample area differs only slightly from that obtained by forcing the above-cloud segment-averaged F300 concentration to be equal to the above-cloud segment-averaged PCASP concentration. For the latter technique we obtain average=0.043+-0.010 mmˆ2.

Page 12389: How was the Poisson sampling error derived in equation 3? The usual way to calculate the sampling error is via the binomial probability distribution and is typically stated as N1/2/N.

We see this is an issue of semantics. The binomial probability distribution becomes the Poisson distribution in the limit of large number (See Young, 1962). Since hundreds to thousands of particles are detected in the overlapping size range during a 30 minute flight segment (Figure 1, original manuscript), our number is large. Hence we applied Poisson statistics. For Poisson statistics the standard deviation is the square root of the average number (See Young, 1962). So it appears that Professor Baumgardner is referring to the _relative_ standard deviation of the spectral density in his comment (also see page 8038 of Baumgardner et al., 1992). In contrast, we formulated the standard deviation of the spectral density on page 12389.

Page 12388: The discussion about the differences between the wing=mounted instruments and the internally operated LAS has no relevance to the objectives of this paper and should be removed as it only confuses the issue.

This discussion is removed from the revised manuscript.

Page 12390: Line 28. What is "Vida Infra";?



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We have corrected this. Here is the revision:

The effect of the anticipated refractive index shift, from n=1.59 to n=1.41 (Table 2), is quantified using an optical-to-actual diameter ratio which we estimate to be 0.75 based on measurements reported by Stolzenburg et al. (1998).

Page 12392, line 5: The assumption that there is no BC is probably not warranted for two reasons: 1) OC abd BC are usually very highly correlated and the conclusion of this manuscript is that between 40 and 80% of the aerosol mass is non-hygroscopic material, i.e. OC, hence there must most likely be significant BC in the particles and 2) recent studies, i.e. Ace Asia and PacDex have shown that there is a significant amount of OC and EC that is transported from Asia. It could well be that the BC in the core of some of the aerosol particles is quite small and the subsequent effect on the size threshold definitions also negligible. It would be much more convincing if the authors ean a few refractive indices through the Mie code for the scattering angles of the FSSP-300 and varying amounts of BC, using the volume mixing rule, to show the potential effect.

Professor Baumgardner’s suggestion is a good one. Calculations based on a graphitic carbon (soot) core surrounded by a liquid water shell are available for the FSSP-100 (See Gayet et al., JOAT, 13, 1300-1310, 1996). We note that the FSSP-100 detects light scattered into the same angles as the F300. From Figure 3 of Gayet et al., and assuming a soot-to-water volume fraction of 10ˆ-3, the calculation reveals that the undersizing is about 15%. If the soot-to- water volume fraction is 10ˆ-6 then the undersizing is 4%. This means that the particles detected by the F300 could be 4 to 15% larger, depending on the amount of soot. Given that we don’t know how much light absorbing material was associated with the particles and because the trajectories show no compelling evidence for the air coming off of North America, we feel that our statement on p. 12392 (original manuscript) adequately summarizes the uncertainty. Consequently, we did not change this section of the text. For the convenience of the editor, and the reviewers, we include the relevant sentence here:



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Hence, if the insoluble portions of the sampled particles are composed of light absorbing materials (e.g., hematite or light-absorbing carbonaceous materials) consideration of an additional bias is needed. We cannot rule out the possibility that a significant amount of water-insoluble and light-absorbing material was present in the studied particles, but this possibility is attenuated by carbon monoxide measurements made on board the C-130 and by an analysis of airmass trajectories.

Page 12393: The derivation of the growth factor uses a comparison of the coefficients from curve fits of a power law to the regions of the size distributions from the PCASP and FSSP300 that overlap and are monotonically decreasing in concentration with size. This definition assumes that the slopes of the two distributions are identical and only a scaling factor separates the two, a scaling factor that used to define the GF. This section has to be expanded with a more clear explanation for the basis of this way of defining the GF. Previous studies have used diameter, volume or scattering coefficient defined at two RH values to determine the GF. There has to be some explanation between these previous definitions and the one used in this paper. It is not at all clear how this definition of the GF is truly a measure of the change in particle diameter or volume as a function of RH. This definition obviously is what brings about the assumption that the GF should be equal to unity above the boundary layer when the RH is low, but is very deceiving to the reader who is accustomed to a growth factor that is not related to the RH but is related to the properties of the aerosol particle itself. It was not until reaching section 3 that I finally realized that all the references to a growth factor in previous sections had to do with the unique way of defining hygroscopic growth but can not be directly related to what others have used as a definition. This has to be clarified and in fact I recommend that the term "growth factor" not be used but that some other term is defined that is relevant to how the value is derived in equation 6. Secondly, the theoretical underpinning of this new definition is not clear. Why should one expect that the slopes of the two distributions be the same when the RH of the PCASP is low and that in the FSSP 300 at the ambient? The particles that are falling in the size range of the FSSP300 are smaller particles measured by the PCASP that have grown



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into the size range of the 300. In the paper by Strapp et al., I believe they actually try to look at the shift in the size distributions between the PCASP and FSSP-300 as a function of RH. It would seem to me that plotting the volume as a function of size from the two OPCs and then calculating the necessary shift in diameters between PCASP and FSSP-300 to match the two spectra would be a more relevant measure of the GF. Regardless, the explanation of how this technique produces a relevant measure of hygroscopic growth requires more detail that given at the moment.

These are all good points and we thank Professor Baumgardner for raising them. In response we make three comments.

1 - We have expanded the discussion of why our GF should be unity in the dry air above the boundary layer. These changes are discussed above.

2 - Our second comment has to do with which representation of the aerosol size spectrum to fit. We chose to fit the aerosol number spectrum, as opposed to the surface area or volume spectrum. For the diameter range of interest our choice is guided by the observation that number spectral density (dN/dlogD) is sharply decreasing with particle diameter, while dA/dlogD and dV/dlogD can be only weakly decreasing, invariant or increasing with particle diameter.

3 - We expanded the description of how we derive the GF and its relation to measurements made by other techniques. Yet, we did not define our measure of the hygroscopic response as something different from GF. Here is the revised text:

The averaged PCASP spectral densities, restricted to the constant-slope section, were fitted to a power function of the form

(dN/dlogDd)P=(alpha)P*(Dd)ˆbeta, (4)

Here (alpha)P and beta are fit parameters and Dd symbolizes the dry particle diameter. For the F300 data a single parameter, (alpha)F, was fitted with the slope parameter (beta) prescribed by the PCASP fit



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(dN/dlogDw)F=(alpha)F*(Dw)ˆbeta. (5)

Here Dw is the wet particle diameter and the constancy of beta in Eqs. 4 and 5 implies that the wet diameter is a multiple of the dry diameter. As we will see, the multiple can be interpreted as the hygroscopic growth factor. Our derivation of the growth factor relies on the equivalence of single point values of the fitted PCASP and F300 spectral densities, both evaluated within their respective constant-stop diameter ranges (Table 1). This equivalence is stated mathematically as

(alpha)P*(Dd)ˆbeta = (alpha)F*(Dw)ˆbeta (6)

The derivation of the GF also requires the replacement of the wet diameter in Eq. 6 with GF*Dd, on the assumption that the GF is a constant. With this assumption, which we discuss below, the hygroscopic growth factor is

GF=((alpha)F/(alpha)P)ˆ(-1/beta) (7)

Derived in this way, the GF represents the particle diameter shift needed to reconcile the dried PCASP spectrum with the humidified F300 spectrum.

The curve fitting discussed in the previous two paragraphs was conducted using a procedure known as curvefit (IDL, Research Systems Incorporated). Statistical weights passed to the procedure were evaluated as (1/(sigma)i)ˆ2 (Eq. 3). The derived GF values correspond to a range of dry particle diameter extending from 0.4 to 0.8 um and from 0.3 to 0.6 um in analyses of the above- and below-cloud flight segments, respectively (Table 1). As we already discussed, these dry sizes are larger than that typically monitored by an HTDMA. Eqn. 7 requires the substitution Dw=GF*Dd, which for constant GF implies that the same beta can be used to fit the PCASP and F300 spectra. Our approach is therefore contingent on GF being constant over the diameter range that specifies the constant-slope section. This assumption would be violated if either the Kelvin effect or chemical composition varied strongly with particle diameter. Using our base case model (Section 2.5) we evaluated the partial derivative dGF/dDd



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and concluded from its very small magnitude that the size-dependent Kelvin effect is of no consequence for the range of particle diameters of interest to this work. We also note the relatively narrow range of dry diameter used in the GF derivation, and in recognition of this, we discount the possibility of bias stemming from the constant composition assumption. Finally, we note that our hygroscopic growth factors should be comparable to that derived from instruments which report the GF as the ratio of a humidified and dried particle diameter, e.g., an HTDMA.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 12381, 2007.