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Hegg, D. A.; Covert, D.S.; Jonsson, H.H.; Liu, Y.; Crahan, K.K.

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Measurements of aerosol size-resolved hygroscopicity at sub and supermicron sizes

D. A. Hegg,¹ D. S. Covert,¹ K. K. Crahan,¹ H. H. Jonsson,^{2,3} and Y. Liu⁴

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[1] Airborne measurements of size-resolved aerosol hygroscopicity are presented using an optical particle counting and sizing technique. The measurement range of 0.25 to 3.5 μm is significantly greater, and extends to larger sizes, than previous in situ techniques. Preliminary results reveal a peak in aerosol hygroscopicity in the 0.5–1.5 μm diameter size range in both marine and polluted aerosols. Geometric growth factors range from 1.3 to 1.5 and 1.1 to 1.3 for the sub and super-micron particles, respectively.

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1. Introduction

[2] Aerosol hygroscopicity is a key factor in the impact of aerosols on the direct aerosol radiative forcing of earth's climate [Charlson *et al.*, 1992]. Indeed, much of the short-wave light scattering by which aerosols impact the radiative balance is attributable to the water content of the aerosol [cf. Hegg *et al.*, 1997]. Similarly, hygroscopicity at very high RH essentially defines the ability of the aerosol to activate cloud droplets and thus contributes to the indirect aerosol forcing of climate [cf. Intergovernmental Panel on Climate Change, 2001]. Aerosol hygroscopicity is also an important factor in the chemical reactivity of aerosols, modulating the interaction of the aerosol surface with numerous important gas phase species and defining the nature of the aerosol bulk phase vis a vis chemical reactivity as well [Rossi, 2003; Rudich, 2003].

[3] An important aspect of the aerosol hygroscopicity is its size dependence, due largely to size-dependent chemistry. Additionally, the scattering efficiency of aerosols is strongly size dependent and thus additional scattering due to hydration is also a function of size [cf. Hegg *et al.*, 1993]. Hence, the size-dependent hygroscopicity of an aerosol will significantly impact its overall effect on the radiative balance. While there has long been evidence that aerosol hygroscopicity is size dependent [e.g., Winkler and Junge, 1972], the data are sparse, particularly for super-micron aerosol, where the effect of the hitherto necessary collection substrates on the results also clouds the picture. For submi-

cron aerosol, substantially more data are available, most gathered with Tandem Differential Mobility analyzers (TDMA's), which have the advantage of measuring in situ. However, TDMA's can typically measure the hygroscopic growth only up to around 0.5 μm dry diameter due to the upper size limit for most DMA measurements. Hence, there is a decided deficit in our knowledge of the hygroscopicity of ambient aerosols with dry diameters above a nominal 0.5 μm , a range that includes a substantial fraction of the efficient light scattering range of ambient aerosols. We address this issue here utilizing a new instrument, the Aerosol Hydration Spectrometer (AHS) that measures in situ aerosol hygroscopicity over a nominal range from 0.25 to 3.5 μm dry diameter.

2. Observational Plan

2.1. Experimental Venue

[4] The geographic location of our measurements is off of Monterey Bay on the central California coast, between 35 and 37 degrees North latitude and 121 and 125 degrees West longitude. They were thus centered in a marine venue, but one that commonly experiences periods of continental and even polluted air. Airborne sampling was done both in and above the marine boundary layer (MBL) throughout this region in the course of 12 flights conducted during the CARMA-III campaign (August, 2005). Both horizontal traverses of the MBL, typically at 30 m MSL and cloud base, and vertical profiles from 30 m MSL through the MBL inversion were carried out.

2.2. Measurement Methodology

[5] The in-situ data described here were obtained with the CIRPAS Twin Otter aircraft instrumentation package. Most components of this package have been described in previous publications [cf. Hegg *et al.*, 2002; Wang *et al.*, 2002]. However, the principal instrument utilized, the AHS, is new and, while a detailed description will be forthcoming, we present the key features of this instrument relevant to the current discussion here.

[6] The AHS consists of two optical particle counters (OPC's) running at two different relative humidities, one relatively low but well above the likely efflorescence point of the aerosol being sampled (inter-sample values ranged from 48–53% for the data presented here), and the other at $\sim 90\%$ (88–92% for the data presented here). It is important to note that the sample paths to both OPC's are nearly entirely vertical to avoid sedimentation losses and the normal operational residence time along each RH path is a nominal 2 s. However, some recent studies have suggested that a 2 s RH conditioning time may be insufficient for the sampled aerosol to reach thermodynamic equilibrium at the higher RH [cf. Chuang, 2003]. To address this, an alternate sample

¹Department of Atmospheric Sciences, University of Washington, Seattle, Washington, USA.

²Department of Meteorology, Naval Postgraduate School, Monterey, California, USA.

³Center for Interdisciplinary Remotely Piloted Aircraft Studies, Naval Postgraduate School, Monterey, California, USA.

⁴Pacific Northwest National Laboratory, Richland, Washington, USA.

flow path has been built into the AHS with a conditioning time of ~ 45 s. This path can be activated by a flow valve to permit assessment of kinetic limitations to particle growth on each research flight.

[7] The 90° ($\pm 45^\circ$) scattering OPC's (Welas Model 1200 manufactured by Palas, GmbH., Karlsruhe, Germany) do not have the severe Mie resonances of laser spectrometers, displaying single-valued correspondence between particle size and pulse height [cf. *Schumann*, 1990; *Liu et al.*, 1985]. The OPC's have a nominal measurement range from 0.2 to 20 μm diameter but were calibrated only up to a size of ~ 9 μm , the upper size limit of our aircraft inlet [*Hegg et al.*, 2005]. The calibration was done with silica spheres (Duke Scientific) and hydrated NaCl and NH_4NO_3 aerosol size selected with a DMA (TSI model 3071, St. Paul, MN). The resolution of the OPC's varied over size, as expected, but was on the order of 50 nm from 0.2 to 3.0 μm . A lower size limit of ~ 0.25 μm was indicated for these aerosols, whose indices of refraction lie in the range of 1.4–1.45, quite similar to those we expect for the sampling venue. Nevertheless, because we are comparing optical size distributions at different hydrations and the hydration not only increases size but decreases the mean index of refraction of the particles due to water's relatively low index of refraction, a slight correction for the index of refraction effect was made using formulae from *Hanel* [1976] for the dilution factor of index of refraction and *van de Hulst* [1957] for the impact on the Mie scattering efficiency.

[8] These correction factors were used to convert from the measured optical diameter to physical diameter. After such correction, the “wet” and “dry” size distributions were compared to derive the diameter growth factors as a function of size. The analysis procedure utilized was the “Descriptive Hygroscopic Growth Factor” (DHGF) methodology developed by *Nowak* [2006], in which the number size distributions of both the “wet” and “dry” spectra are integrated downward in size. For any particular dry size, the wet size at which the cumulative wet number concentration is equivalent to the cumulative dry number concentration defines the size to which the dry particles have grown. The DHGF is simply the ratio of the wet and dry sizes. This approach assumes that, above a certain large size, there are no particles sampled (an excellent assumption in our case) and has several advantages. It avoids ambiguities concerning possible multiple dry sizes contributing to a given wet size due to different hygroscopicities and the integration procedure itself acts as a smoothing filter, enhancing the signal to noise ratio. On the other hand, it does not permit differentiation of particles with differing hygroscopicity that have the same size. AHS samples were typically 20 minutes in length (maximum of 40 minutes) and the spectra should be regarded as spatial and temporal averages. Uncertainties in the DHGF's are calculated based on the variance derived from the laboratory calibrations.

[9] Two final aspects of the AHS calibration and measurement procedure should be noted. First, to test the accuracy of the hygroscopicity measurements, pure, submicron salt particles were generated by Collison atomizer followed by size selection with a TSI electrostatic classifier. DHGF values measured for such particles were in good agreement with theoretical predictions. Second, on each flight, the equivalency of the two AHS flow paths was verified by

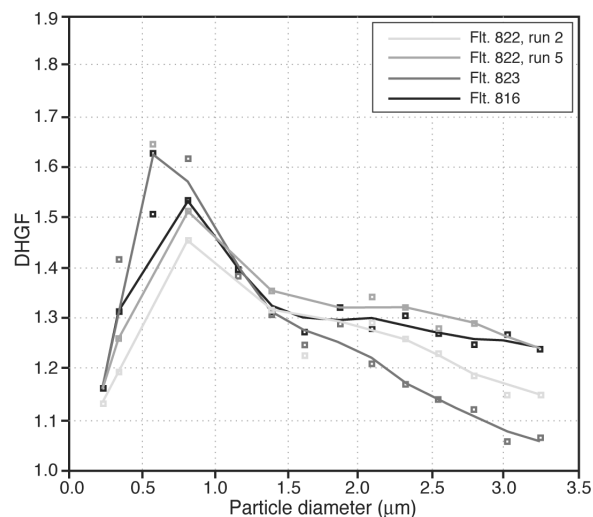


Figure 1. Marine DHGF spectra measured during CARMA-III. Points shown are measurements and the curves are LOWESS fits. Note that the mean measurement uncertainty in the submicron range is 0.14 while that in the supermicron range is 0.08.

running each path at the same RH and ensuring that the DHGF's calculated from the identical paths were unity.

[10] In addition to the physical measurements, limited data on the aerosol chemical composition are available in the form of bulk filter samples, analyzed as described by *Gao et al.* [2003], and individual particle analysis from SEM substrates, analyzed as described by *Laskin et al.* [2003].

3. Results and Discussion

[11] Figure 1 displays four DHGF size spectra representative of the range found for marine conditions, by which we mean relatively low levels of SO_2 (< 0.5 ppbv) and HYSPLIT back trajectories over water for at least 96 hours prior to sampling. However, it should be noted that such conditions do not correspond to pristine marine air. For example, SEM/EDAX samples obtained during the study commonly show substantial sulfur, oxygen and nitrogen present in the particles that are predominantly NaCl, i.e., sea salt. Hence, in this coastal venue, aerosol is commonly aged or processed marine. All of the marine spectra shown were obtained at 30 m MSL. Several interesting general features are apparent. Up to a diameter of ~ 0.6 – 0.8 μm , the hygroscopicity increases with increasing size, peaks and then, at around 1.5 μm , has a more gentle, monotonic decline with increasing size. There is substantially more variance between the spectra at the super 1.5 μm sizes. While the Poisson counting error does increase at these larger sizes, leading to higher variance, the overall uncertainty in the DHGF's decreases since the relatively coarse size discrimination of the OPC's is actually the main source of uncertainty in the measurements (for most of our size range) and decreases rapidly with particle size. Hence, the increase in variance at larger sizes is likely a real phenomenon. For example, the spectrum for flight 823 appears somewhat anomalous and for this flight a comparison of SEM/EDAX results with the more typical flight 822 shows that there are

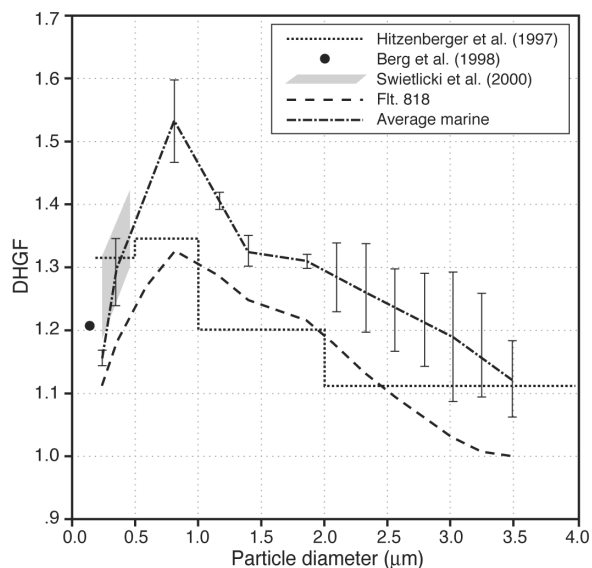


Figure 2. Polluted aerosol DHGF spectrum measured August 18th (flt 818) compared to the average marine spectrum and selected previous measurements. The previous measurements have been adjusted to the AHS measurement RH range using the hygroscopicity determined in these studies.

more soil dust super $1.5 \mu\text{m}$ particles (i.e., particles which are 90% or more Ca, Mg, Si, O, K and Fe) present in the sample taken concurrently with the 823 spectrum than that for 822 spectrum. Conversely, for the three marine spectra with higher hygroscopicities in the super $1.5 \mu\text{m}$ range, the winds speed was $\sim 10 \text{ m s}^{-1}$ whereas it was a modest 3 m s^{-1} for flt 823, suggesting less sea salt, with its high hygroscopicity, was present.

[12] Comparison of the marine spectra with previous measurements provides an interesting context. Shown in Figure 2 is the mean of the four marine spectra shown in Figure 1 together with examples from the few previous TDMA measurements in a marine venue that fall into our measurement range. Both the measurements of *Berg et al.* [1998] and those of *Swietlicki et al.* [2000] are consistent with our measurements but their relatively narrow measurement range does not capture the complexity of the size-dependent hygroscopicity.

[13] Also shown in Figure 2 is an example of a DHGF spectrum taken in polluted air, the only one we obtained with sufficiently high particle counts to permit DHGF's to be calculated out to $3 \mu\text{m}$ diameter. On August 18th (flight 818), a surge of air propagated up the California coast from just off shore of the Los Angeles Basin in a relatively narrow band – a “Southern Surge.” The shape of the DHGF spectrum for the pollution aerosol is very similar to that for the marine examples but the DHGF's are systematically lower. The bars associated with the mean marine spectrum are standard deviations rather than standard errors and it is likely that the polluted DHGF's are significantly as well as systematically lower than those of the marine aerosol. For polluted aerosols, there are limited data on the size dependent hygroscopicity available and it is interesting to compare examples with our data. In Figure 2, data from *Hitzenberger et al.* [1997] are plotted against our

spectrum of polluted air. The *Hitzenberger et al.* line is the mean of two spectra obtained in Mainz during the summer season. The spectra were obtained by sampling with a Berner multi-stage impactor, placing each size stage in a controlled environmental chamber and measuring the weight gain as the chamber humidity was ramped to 90%. The DHGF's are for a spread of $\sim 45\%$ to 90% RH, virtually the same as for our data. Given the much cruder size resolution of the *Hitzenberger* data, we consider the agreement with our polluted spectrum to be quite good.

[14] Another aspect of the polluted aerosol hygroscopicity that is quite important is the transformation to a more marine character. In Figure 3 we show examples of two polluted spectra, the first is once again that for flt 818 just discussed and the second that for flt 819. While taken in the same Southern Surge of polluted air, the transit time to the sampling point for the 818 spectrum was ~ 20 hrs whereas that for the 819 spectrum was ~ 30 hrs (based on HYSPLIT back trajectories). A lack of counts at higher particle sizes did not permit measurement of the 819 DHGF's above $\sim 1.8 \mu\text{m}$ and the 818 spectrum has been truncated to correspond. The more aged spectrum of flt 819 is virtually identical with the marine air mean and decidedly higher than that for the “fresher” pollution of flt 818, suggesting that the transition from fresh to aged pollution can be quite rapid.

[15] A more extreme contrast with the DHGF's of the marine aerosol is provided by the aerosol in a biomass fire plume transported to the operations area from southern Oregon. The identification of the fire plume is unequivocal, based on both HYSPLIT back trajectory and aerosol levoglucosin concentrations an order of magnitude higher than any others encountered during the study [cf. *Gao et al.*, 2003]. A DHGF spectrum obtained in this plume on August 13th (flight 813) is shown in Figure 4, together with that from the polluted plume of flight 818 and the average marine spectrum.

[16] The most striking feature of the fire aerosol spectrum is the much lower hygroscopicity of the aerosol between 0.5 and $1.5 \mu\text{m}$ diameter as compared to either the marine or

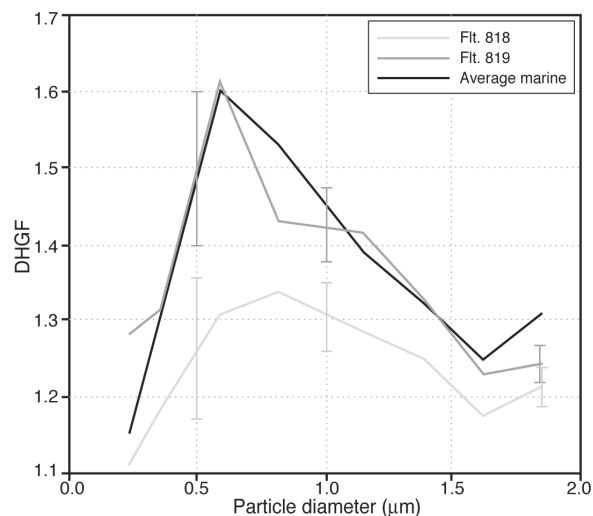


Figure 3. Comparison of two polluted DHGF spectra with different aging times to the average marine spectrum. Error bars are 95% confidence intervals.

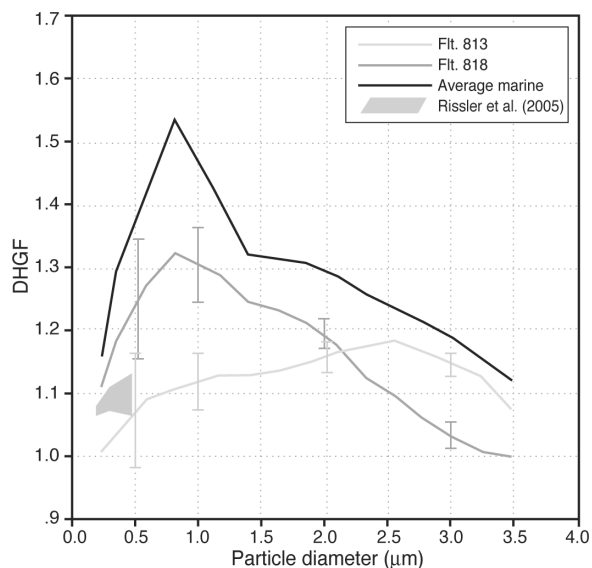


Figure 4. Comparison of the DHGF spectrum from a biomass fire (flt 813) with the polluted spectrum from flt 818 and the average marine spectrum. Error bars are 95% confidence intervals.

polluted cases. Tests with the longer conditioning time of the AHS (45 s vice the normal 2 s) suggest that a small but significant portion of this depression, $\sim 15\%$, is kinetic (this is the only CARMA DHGF spectrum that exhibited such an effect). Whether kinetic or thermodynamic (i.e., truly different water equilibrium), an explanation is necessary.

[17] The trajectory-based travel time for the aerosol from its source is ~ 24 hrs, slightly longer than that for the polluted aerosol of flight 818. Similarly, ozone levels (a reasonable proxy for overall organic oxidant levels) on the 13th both above and below the inversion were higher than on the 18th (30 vs 20 ppbv in the MBL, > 50 vs 25 ppbv above the inversion). SO_2 concentrations (again, a proxy but now for precursors of inorganic soluble mass) were higher on the 13th than on the 18th (~ 1 ppbv vs ≤ 0.5 ppbv as measured by a TECO 43S). Hence, more rapid in situ aging for the 18th aerosol seems implausible. On the other hand, the composition of the fire aerosol itself suggests a reduced hygroscopicity, being $\sim 80\%$ organic by mass, much higher than that typical for Los Angeles pollution [cf. Gray *et al.*, 1986], though we have no chemical measurements on the 18th to confirm this for our specific case. Interestingly, our fire spectrum is consistent with recent measurements by Rissler *et al.* [2004] on fire plume aerosols in Amazonia (shown in Figure 4), suggesting that such low hygroscopicity for fire aerosols may be common.

4. Conclusions

[18] The measurements of aerosol hygroscopicity presented here span a much larger range of the aerosol spectrum than has commonly been previously explored, certainly than has previously been explored with in situ, real-time measurement. The results provide a broader context for these limited previous measurements. While our measurements confirm the general increase in hygroscopicity with increasing particle size up to $\sim 0.5 \mu\text{m}$ diameter

previously found with TDMA's for marine venues, they also show that this increase corresponds to the small-size side of a prominent peak or maximum in the aerosol hygroscopicity curve centered at $\sim 0.8 \mu\text{m}$. This peak then tails into a more gentle, monotonically decreasing hygroscopicity from ~ 1.5 to $3 \mu\text{m}$ diameter.

[19] Measurements on industrial polluted and biomass burning aerosols show much reduced hygroscopicity compared to the marine cases, with the contrast most extreme in the sub-micron size range. Indeed, in the case of the fire aerosol, the reduction is sufficiently large to alter the functional form of the hygroscopicity-size relationship. The exploratory results shown here suggest the AHS used to obtain them will be a valuable tool in expanding our limited data base on the hygroscopicity of super-micron aerosols.

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- D. S. Covert, K. K. Crahan, and D. A. Hegg, Department of Atmospheric Sciences, University of Washington, MC 351640, Seattle, WA 98195, USA. (deanhegg@atmos.washington.edu)
- H. H. Jonsson, Department of Meteorology, Naval Postgraduate School, Monterey, CA 93943, USA.
- Y. Liu, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA.