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The dependence of aerosol light-scattering on RH over the Pacific Ocean

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[1] Measurements of the relative humidity dependence of aerosol light scattering are reported from three experimental venues over the Pacific Ocean. The measurement platform utilized was the CIRPAS Twin Otter aircraft. Results are compared with previous measurements at other locales and with theoretical models. The relatively low values of hygroscopicity obtained in marine air are consistent with a substantial organic component to the aerosol. *INDEX TERMS*: 1610 Global Change: Atmosphere (0315, 0325); 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 3359 Meteorology and Atmospheric Dynamics: Radiative processes

1. Introduction

[2] Recent assessments of the global radiative forcing of climate by atmospheric aerosols suggest that even the direct forcing has a substantial component over the oceans [IPCC, 2001]. In part this is due to the relatively high hygroscopicity of marine aerosols coupled with the high relative humidities (RH) found in the marine boundary layer (MBL). The accurate assessment of this forcing certainly requires a substantial knowledge of the relative humidity dependence of marine aerosol light scattering. Indeed this dependence has long been identified as a key factor in aerosol direct forcing of climate [cf., Charlson *et al.*, 1992]. However, relatively little data bearing on this question has yet been generated for marine aerosols. This is particularly true of data above the surface layer, i.e., airborne data, despite the fact that the very few studies that have obtained such data have shown that vertical variations in aerosol hygroscopicity can be substantial, and have a significant impact on aerosol optical depths [e.g., Hegg *et al.*, 1997; Kotchenruther *et al.*, 1999; Gasso *et al.*, 2000].

[3] Much of the data available on the hygroscopicity of aerosols in marine air is, unsurprisingly, from the venue of the North Atlantic, obtained during the TARFOX and ACE-2 experiments [e.g., Carrico *et al.*, 2000; Swietlicki *et al.*, 2000; Gasso *et al.*, 2000; Kotchenruther *et al.*, 1999]. For the vast area of the Pacific, only a few measurements are available [cf., Hegg *et al.*, 1996; Berg *et al.*, 1998]. In this study we present data on aerosol hygroscopicity to augment this sparse Pacific data base, particularly with regard to measurements well above the sea surface.

2. Methodology

[4] Because the underlying motivation for this study is the relative humidity dependence of light scattering by marine aerosols, we have measured this dependence directly, i.e., utilize nephelometers rather than TDMA's, which measure size. Furthermore, because of the need for good temporal resolution of the

hygroscopicity, we present data from our continuous, wet/dry nephelometer humidograph system [Hegg *et al.*, 1996; Gasso *et al.*, 2000]. This system consists of three nephelometers (Radiance Research, Seattle, WA), one operating at above ambient RH (and above the deliquescence point of likely marine aerosols), one at close to ambient RH and one at a "dry" RH (i.e., at or below a nominal 40% RH). The nephelometers in the humidograph effectively measure scattering from particles in the size range from 0.1 to $\sim 5 \mu\text{m}$ diameter, the upper limit defined by the sample inlet passing efficiency and forward truncation of scattering in the nephelometers. The instrument has been flown aboard the CIRPAS Twin Otter aircraft on three recent field campaigns over the Pacific Ocean. The time resolution of the instrument is ~ 7 seconds, which yields a horizontal resolution of ~ 350 m at the normal sampling airspeed of the Twin Otter ($\sim 50 \text{ m s}^{-1}$). Similarly, at the normal rate of climb (or descent) of the Twin Otter, the vertical resolution is ~ 25 m.

[5] The three venues from which data will be presented are the DECS (Detrainment and Entrainment in Coastal Stratus), ACE-Asia (Aerosol Characterization Experiment) and RED (Reduced Evaporative Duct) field experiments. These campaigns took place in 1999, Eastern Pacific; 2001, Western Pacific; and 2001, Central Pacific, respectively. For the littoral experiments (DECS and ACE-Asia) in particular, non-marine scenarios were frequently encountered. However, we concentrate here on only those Twin Otter flights for which (on the basis of such factors as wind direction and the aerosol size distribution), the aerosol sampled could be considered predominantly marine.

[6] Several different parameters have been utilized in past studies to characterize the RH dependence of aerosol light scattering, for example the hygroscopic growth factor constituting the ratio of light scattering for a particular aerosol at some designated high and low humidities (e.g., 80 and 30%). We have chosen, however, to present our results in terms of the γ exponent of the well-known relationships due to Kasten [1969]:

$$\frac{b_{\text{sp}}(\text{RH})}{b_{\text{sp}}(\text{RH}_0)} = \left\{ \frac{1 - \frac{\text{RH}}{100}}{1 - \frac{\text{RH}_0}{100}} \right\}^{-\gamma} \quad (1)$$

The γ exponent defined by (1) has the advantage of offering easy explicit interpolation over a wide range of RH's, i.e., it in principle defines the entire functional form of the dependence of light scattering on RH. On the other hand, particularly for aerosols with marked deliquescence, it may fit the actual data rather poorly [cf., Covert *et al.*, 1980; Kotchenruther *et al.*, 1999]. However, a number of studies have suggested that such deliquescence is not commonplace in marine aerosols unless they have been dried to $< 20\%$ RH, a very rare occurrence. Baring this, Equation (1) does a reasonable job of representing the light-scattering dependence on RH [e.g., Swietlicki *et al.*, 2000; Gasso *et al.*, 2000]. It should nevertheless be understood that both our measured and calculated γ 's are for the upper or "wet" portion of any potential aerosol

Table 1. Values of the γ Exponent Measured in Three Recent Field Studies

Date	Project	γ_{sfc}^a	$\gamma_{500\text{ m}}$	$\gamma_{1000\text{ m}}$	Marine Air
6/28/99	DECS	0.10	0.20	—	N
6/29/99	DECS	0.30	0.60	—	Y
7/02/99	DECS	0.25	0.35	0.90	N
7/06/99	DECS	0.65	0.85	—	Y
7/07/99	DECS	0.63	0.70	0.65	Y
7/09/99	DECS	0.55	0.45	—	N
7/10/99	DECS	0.34	0.39	—	Y
7/14/99	DECS	0.55	0.55	—	N
7/15/99	DECS	0.60	0.60	0.4	N
7/17/99	DECS	0.50	0.45	—	N
7/19/99	DECS	0.43	0.75	—	Y
7/20/99	DECS	0.50	0.50	—	N
04/03/01	ACE-ASIA	0.39	0.34	0.35	Y
04/06/01	ACE-ASIA	0.35	0.40	0.45	Y
04/08/01	ACE-ASIA	0.30	0.35	0.40	N
04/12/01	ACE-ASIA	0.25	0.20	0.20	N
04/16/01	ACE-ASIA	0.42	0.42	0.40	Y
04/17/01	ACE-ASIA	0.35	0.35	0.30	N
04/19/01	ACE-ASIA	0.35	0.30	0.25	N
04/20/01	ACE-ASIA	0.33	0.25	0.25	Y
04/23/01	ACE-ASIA	0.27	0.27	0.35	Y
04/25/01	ACE-ASIA	0.36	0.46	0.65	Y
04/26/01	ACE-ASIA	0.20	0.20	0.17	Y
8/22/01	RED	0.70	0.20	0.25	Y
8/23/01	RED	0.42	0.42	0.40	Y
8/27/01	RED	0.63	0.56	0.51	Y
8/28/01	RED	0.50	0.60	0.55	Y
8/29/01	RED	0.47	0.45	0.43	Y
8/30/01	RED	0.42	0.42	0.42	Y
8/31/01	RED	0.45	0.45	0.45	Y
9/04/01	RED	0.15	0.15	0.25	N
9/05/01	RED	0.15	0.15	0.05	N
9/06/01	RED	0.13	0.13	0.25	N
9/10/01	RED	0.21	0.21	0.37	Y
9/14/01	RED	0.20	0.20	0.18	Y

^a Variable but typically 30 m above the sea surface.

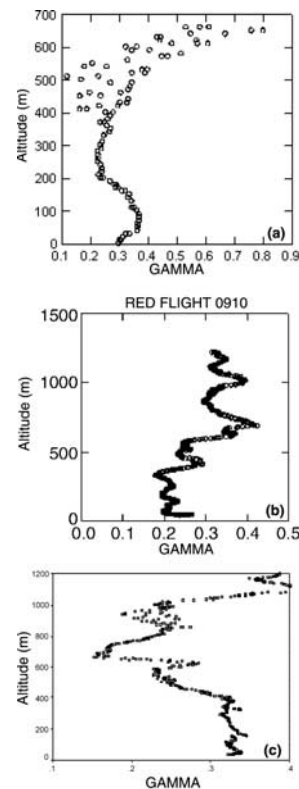
hysteresis loop where deliquescence is not manifested. We assume this is reasonable for the MBL.

3. Results and Discussion

[7] Measurements of γ from 35 research flights over the Pacific Ocean are shown in Table 1. Of these, 21 were judged to be in marine air, the remaining flights displaying evidence of the presence of either pollution or dust (in ACE-Asia) or volcanic emissions (RED). The grand mean for the marine near surface (a nominal 30 m above the sea surface) data shown is 0.41 ± 0.03 , compared with a mean for the nonmarine cases of 0.34 ± 0.05 . This relative decrease in hygroscopicity with departure from marine conditions is similar to that observed in ACE-2 [e.g., Gasso, 2000], although in this instance the marine and nonmarine means do not significantly differ. This marine average is also in accord with a mean value for six near surface (≤ 100 m altitude) samples of 0.47 ± 0.03 reported by Hegg *et al.* [1996] from flights conducted off of the California coast during MAST. Comparison with the surface data of Berg *et al.* [1998], taken

Table 2. Mean Values of γ as a Function of Altitude and Study (Marine Values Alone are Shown)

Project	Locale	γ_{sfc}	$\gamma_{500\text{ m}}$	$\gamma_{1000\text{ m}}$
DECS	East N. Pacific	0.47 ± 0.07	0.66 ± 0.08	—
ACE-Asia	West N. Pacific	0.33 ± 0.03	0.33 ± 0.04	0.37 ± 0.06
RED	Central N. Pacific	0.44 ± 0.06	0.41 ± 0.05	0.40 ± 0.04

**Figure 1.** Vertical profiles of γ from (a) DECS (Eastern Pacific), flight of 6/29/99; (b) RED (Central Pacific), flight of 9/10/01; and (c) ACE-Asia (Western Pacific), flight of 4/20/01.

aboard the *R.V. Discoverer* in the North East Pacific, is much less straightforward since this data is from a humidified TDMA and consists of growth factors to 90% RH in a particle size range which only partially overlaps the effective light-scattering size range for Mie scattering. Nevertheless, we estimate a mean value for the North Pacific of ~ 0.4 , again in reasonable agreement with the mean values for our data.

[8] It is also of interest to look at variability in γ with altitude and over the three regions of the Pacific for which data are presented. Variability as a function of these parameters is summarized in Table 2. It is interesting that, despite the screening for at least obvious nonmarine cases, the ACE-Asia mean γ values are systematically lower than those for the other two study venues. Dust was ubiquitous during the ACE-Asia study period and it is possible some dust was always present, even when discernible dust layers were not apparent, and that this contributed to the lower γ values.

[9] On the other hand, little evidence of significant vertical variability can be seen in the mean values with the exception of the significant increase between the surface and 500 m means seen in DECS. [Note that the scattering signal was too low at 1000 m during DECS to permit calculation of a meaningful average value at 1000 m. This was no doubt due to the strong MBL inversion present during DECS which much inhibited vertical transport of aerosol.] However, examination of individual cases suggests this may be misleading. Examples of vertical profiles from each of the experimental venues are given in Figure 1 and show marked variability in the vertical. The relatively stationary mean values appear to be the result of the canceling of individual cases of either increasing or decreasing γ with altitude.

[10] The source of the variability in γ , either vertical or between venues is likely attributable to differences in the aerosol size distribution [cf., Hegg *et al.*, 1993; Tang, 1996], or differ-

Table 3. Values of γ Based on the Model of *Ming and Russell* [2001]

Aerosol Type	γ^a (fine)	γ^b (coarse)
NaCl	0.90	0.63
Inorganic sea salt	0.83	0.58
Sea salt (10% organic)	0.77	0.52
Sea salt (30% organic)	0.67	0.47
Sea salt (50% organic)	0.57	0.40
Sea salt (100% organic) ^c	0.13	0.09

^aCalculated for conditions where submicron aerosol dominate scattering, $D_{gn} = 0.1 \mu\text{m}$, $\sigma_g = 1.8$.

^bCalculated for conditions where supermicron aerosol strongly influence scattering, $D_{gn} = 0.4 \mu\text{m}$, $\sigma_g = 1.8$.

^cOrganic components of sea salt alone.

ences in chemical composition. Given that no systematic differences in the aerosol size distribution appears to be present between the venues examined (based on measurements by PMS/DMT FSSP 100-X, and DMT CAPS laser aerosol spectrometers) or even in the vertical over the ~ 30 m–500 m altitude range, compositional changes would seem the likeliest source of variability. While no chemical data are yet available, some interesting inferences can be drawn on the basis of observed γ values and recent modeling work.

[11] A good deal of the variability in aerosol hygroscopicity has been attributed, particularly recently, to the presence and properties of organics in the aerosol. Certainly an organic component has been found to be ubiquitous in marine aerosols [cf., *Novakov et al.*, 1997; *Middlebrook et al.*, 1998; *Putaud et al.*, 2000] and numerous studies, both theoretical and experimental, have demonstrated the impact of organics on aerosol hygroscopicity [e.g., *Gill et al.*, 1983; *Schulmann et al.*, 1997; *Zhidong et al.*, 1998; *Hansson et al.*, 1998; *Ellison et al.*, 1999; *Ansari and Pandis*, 2000]. Recently, *Ming and Russell* [2001] have modeled marine aerosol hygroscopicity in terms of electrolyte droplets containing organic as well as inorganic species. Even without recourse to hydrophobic coatings such as the suggested model of *Ellison et al.* [1999], the calculations suggest an aerosol hygroscopicity significantly less than that expected from inorganic sea salts alone. Values for the γ parameter based on the Ming/Russell model for various assumed organic mass fractions (with straightforward application of Mie theory to relate aerosol size and composition to light scattering) and typical marine size distributions are given in Table 3. Values are given for scattering either dominated by fine aerosols or for scenarios where the coarse mode makes a large contribution to total scattering. However, for the sampling scenarios encountered here, involving the ubiquitous presence of numerous sea salt particles, and thus substantial scattering from a significant coarse mode [cf., *Quinn et al.*, 2001], the coarse-modulated γ 's are most appropriate.

[12] Comparing the values of γ from Table 3 with those from Tables 1 and 2 suggest that consistency would require a bulk organic component on the order of 30% or greater. This is certainly in accord with values for the organic mass fraction of marine aerosols found in the Atlantic [*Novakov et al.*, 1997; *Putaud et al.*, 2000] but mass fractions in the Pacific appear to be substantially lower [e.g., *Kawamura and Sakaguchi*, 1999; *Matsumoto et al.*, 1998; *Okita et al.*, 1986]. With organic mass fractions on the order of 10% or less, the observed γ 's cannot be explained by a well-mixed organic component. However, hydrophobic organic coatings as suggested by *Ellison et al.* [1999] could reconcile the relatively low γ 's and low organic mass fractions. Recent work by *Chen and Lee* [1999] has suggested substantial reductions in aerosol hygroscopicity by organic surfactants that constitute as little as 5% of the aerosol mass. Nevertheless, until simultaneous measurements of aerosol hygroscopicity and composition, including organics, are in hand, this issue will be unresolved. Certainly more detailed

measurements of organic species, such as those recently carried out in the Atlantic [*Neususs et al.*, 2000] are in order for Pacific venues.

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