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Aerosol number-to-volume relationship and relative humidity in the eastern Atlantic

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Abstract. Measurements acquired from the Office of Naval Research (ONR) Pelican research aircraft during the second Aerosol Characterization Experiment (ACE 2) are analyzed to derive values for the dry (RH = 40%) aerosol number-to-volume ratio in the submicron size range. This ratio is found to be relatively constant, with a mean value of 168 ± 21 μm^{-3}, in agreement with previous studies elsewhere. The impact of ambient relative humidity (RH) on the dry number-to-volume is also quantified and a procedure for estimating the dry from the ambient ratio established. Finally, the feasibility of a remote retrieval of the aerosol number concentration in the submicron size range, essentially the cloud condensation nucleus concentration active at a nominal 0.2% supersaturation, is partially assessed.

1. Introduction

A key linkage between global chemical transport models, used to relate anthropogenic emissions with atmospheric concentrations, and global climate models, used to estimate radiative forcing based on atmospheric concentrations, is the aerosol number to mass ratio. This arises because chemical models use aerosol mass as the key prognostic output, whereas climate models require, at least implicitly, aerosol number concentration as input. The number-to-volume ratio, in particular, largely defines the number of cloud condensation nuclei (CCN) available per unit mass of aerosol [cf. *Hegg and Kaufman,* 1998] and thus plays an important role in indirect aerosol radiative forcing within climate models. Much of the work to date on this relationship has centered on the ratio of CCN to sulfate mass, largely because of the widely shared belief that sulfate is the main anthropogenic species responsible for indirect radiative forcing by aerosols. Most such studies have found a sublinear relationship between aerosol number (or CCN number) and sulfate mass [e.g., *Boucher and Lohmann,* 1995]. However, those studies, which have examined the relationship between aerosol number and total mass (or volume), have suggested a surprisingly linear relationship in both continental [*Leaitch et al.,* 1986] and marine [*Hegg and Kaufman,* 1998] air. Within the marine scenario the aerosol number-to-volume relationship in roughly the submicron size range has been found to be not only linear but also relatively constant [*Hegg and Kaufman* 1998; *Raes and van Dingenen,* 1998]. It is potentially of great significance and readily testable.

Most indirect radiative forcing attributed to aerosols arises over the oceans, an area for which in situ aerosol data are notoriously sparse. On the other hand, satellite retrieval of aerosol optical depth and, under favorable circumstances, some aerosol sizing information is potentially feasible from both the operational AVHRR sensors [*Ignatov et al.,* 1998] and the projected sensors on the EOS satellites, including MODIS [*Tanre et al.,* 1997] and MISR [*Kahn et al.,* 1997]. For oceanic aerosols a derivation of the column aerosol mean mass or volume from the optical depth is relatively straightforward [*Fraser et al.,* 1984]. Hence the apparent constancy of the marine aerosol number-to-volume relationship supports the feasibility of large-scale remote retrieval of oceanic CCN concentrations, a potential database for assessment of indirect radiative forcing. However, it is clearly the dry aerosol number-to-volume ratio that is of significance. It is the mass of potential solute, not solute plus water of hydration, which determines CCN activity. Thus the dry aerosol volume must be retrieved, whereas what is actually retrieved is the ambient aerosol volume, a quantity strongly modulated by ambient, relative humidity (RH) [cf. *Covert et al.,* 1972; *Durkee et al.,* 1986]. A question thus naturally arises as to the feasibility of a satellite retrieval of the requisite columnar dry volume for refining estimates of aerosol indirect forcing.

Currently, look-up tables are commonly used to retrieve aerosol properties. While quite successful for some quantities, they do not produce single-valued inversions. Their success depends simply on how good a match can be found between observed radiances and those generated by the model aerosols contained in the table. Hence a very large model database may be necessary for retrieval of a multivariate function such as CCN activity, and even then success can be very uncertain.

In this study we explore a possible alternative approach to CCN retrieval which takes advantage of the apparent circumscribed variability in the dry number-to-volume relationship. To do this, we first utilize in situ data on the aerosol number-to-volume relationships acquired from the Office of Naval Research (ONR) Pelican aircraft during the Aerosol Characterization Experiment (ACE 2) centered on the Canary Islands to further test the constancy of the number-to-volume relationship for marine aerosols. We then

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assess the impact of ambient RH on several key links in two proposed alternative paradigms for retrieval of ambient CCN concentrations from satellite observations. The first and least challenging paradigm involves retrieval of the dry aerosol alone. The second, additionally, requires retrieval of the aerosol volume mean radius. While more demanding in terms of remote sensing data, it should yield a more constrained and accurate CCN retrieval.

2. Instruments and Database

2.1. Instruments

The measurements reported here were all acquired from the ONR Pelican aircraft. An overview of this aircraft has been presented by *Bluth et al.* [1996]. Essentially, two Pelican instruments were involved in the analysis presented here and are described below. A summary of their characteristics is given in Table 1.

The first instrument central to the current analysis is the passive cavity aerosol spectrometer (PCASP)-100X manufactured by PMS Inc. It measured particle sizes between 0.06 and 1.8 μm radius (based on calibration standards; see below) in 15 discrete size bins utilizing laser light scattering. It thus is roughly coincident with the submicron size range, or accumulation mode, of ambient aerosols ($0.1 \lesssim r \lesssim 1.0$). Total aerosol number concentration from this instrument is a reasonable surrogate for the number of CCN active at ~0.2% supersaturation in marine air [cf. *Hegg and Kaufman,* 1998; *van Dingenen et al.,* 1995]. Aerosol volume is obtained by integration of the PCASP size distribution. Airborne use and calibration of the PCASP-100X has been discussed by *Liu et al.* [1992]. We employed similar procedures utilizing polystyrene-latex spheres and NaCl particles generated with an atomizer and sized with an electrostatic classifier as calibration standards. Because the PCASP-100X was run throughout the study reported here with its heaters off, the sampled aerosol was measured at a temperature only ~1.5°K above ambient (due to dynamic heating) and was thus hydrated (the PCASP relative humidity (RH) was calculated indirectly from the measured nephelometer temperature and RH assuming water vapor conservation). It was therefore also necessary to correct the measured sizes and derived quantities, such as aerosol volume, to a prescribed, low RH (40%). This permitted deconvolution of the effect of water from that of other aerosol constituents (and to correct for the impact of water of hydration on the aerosol index of refraction vis à vis the calibration standards). This leads us to consideration of the second central instrument in the analysis.

Because of the restricted space and payload weight available in the Pelican the elaborate instruments usually utilized to measure the impact of RH on aerosol properties (e.g., Tandem Differential Mobility Analyses, scanning humidigraphs) could not be utilized. Instead, a simplified version of a light-scattering humidigraph was developed on the basis of earlier designs [e.g., *Vanderpol,* 1975]. This device consisted of two nephelometers, one operating at below ambient RH (obtained by heating the sample a nominal 5°C above ambient) and one at above ambient RH (obtained by passing the sample through a passive humidifier). We assume a functional form for the RH dependence of the particle light scattering coefficient (σ_{sp}), based on pervious work, of

$$\sigma_{sp}(RH) = \sigma_{sp}(RH_0)\,(1 - RH)^{-\gamma}. \quad (1)$$

RH_0 is some reference RH and γ is a quasi-empirical fitting parameter [cf. *Kasten,* 1969; *Hänel,* 1976; *Hegg et al.,* 1996]. With γ, one can either interpolate to obtain ambient scattering or extrapolate to obtain "dry" scattering by aerosols. For aerosols with marked deliquescence points, such as certain pure salts, this formula does not yield particularly good data fits. However, for typical mixed aerosols in modestly to heavily polluted marine air, it works well. This issue is discussed extensively by *Kotchenruther et al.* [1999]. Both the instrument and a discussion of the procedures to obtain the γ parameter are more fully discussed by *Gassó et al.* [1999].

For the present study it is also necessary to relate the dependence of light scattering on RH to the dependence of aerosol size on RH. This can be dealt with in a straightforward though approximate manner. The scattering from individual aerosol particles is a function of their geometric cross section and the Mie scattering efficiency. For most of the size range of particles, which commonly dominates light scattering ($0.1 \lesssim r \lesssim 1$ μm), the Mie scattering efficiency is approximately proportional to r. Hence one would expect the scattering to be proportional to $\sim r^3$. Data reported by *Tang* [1996], in fact, support this proportionality for sulfate and sodium chloride particles. This, in turn, suggests that the dependence of aerosol volume on relative humidity would be the same as that for light scattering, and that values of γ derived from the light-scattering measurements could be used for aerosol volume corrections using an expression analogous to equation (1). This, in fact, is what has been done in this study with the quantities $V(RH)$ and $V(RH_0)$ substituted into equation (1) for $\sigma_{sp}(RH)$ and $\sigma_{sp}(RH_0)$, respectively. Again, for intercomparison with other studies and to eliminate most of the water of hydration, a reference RH (RH_0) of 40% has been

Table 1. Characteristics of Two Main Instruments Aboard the Pelican Aircraft Used in This Study

Instrument	Manufacturer	Time Response	Principle of Operation	Measurement Size Range (Uncertainty)
PCASP-100X	PMS	1 Hz	laser light scattering to measure aerosol size distribution	$0.06 \lesssim r \lesssim 1.8$ μm (±6%[a])
UW Passive humidigraph	in house	6 Hz	two integrating nephelometers, one operated below ambient RH and one above (RHs measured internally and externally)	$0.1 < r < 2.5$ μm (±10%[b])

[a]Based on counting statistics for the first 10 channels (see text).
[b]Based on a 6 s average; larger averaging times yield lower uncertainties.

Table 2. Research Flights of the Office of Naval Research Pelican Used in the Present Analysis

Flight Number	Date	Mission Type	Maximum Altitude, km	Average σ_{sp}, m^{-1}
3	6/21/97	clear column	3.6	7×10^{-6}
5	6/23/97	clear column	3.5	4.5×10^{-6}
8	6/30/97	clear column	3.6	7.7×10^{-6}
11	7/4/97	cloudy column	2.0	5.5×10^{-6}
14	7/7/97	cloudy column	1.25	3.8×10^{-5}
15	7/8/97	clear column	3.9	2.3×10^{-5}
17	7/10/97	clear column	4.0	2.1×10^{-5}
20	7/17/97	clear column	4.0	1.5×10^{-5}
22	7/19/97	cloudy column	2.2	1.8×10^{-5}
23	7/20/97	cloudy column	3.9	1.5×10^{-5}

used. Thus values of the aerosol volume calculated from the size distribution at the measurement RH were converted to aerosol values at 40% RH using the modified form of equation (1).

2.2. Database

Of the 17 research flights conducted during the ACE 2 experiment on and around the Canary Islands from June 16 to July 25, 1997, six were devoted to vertical profile measurements in clear air. This is the scenario most favorable for the sort of analysis presented here, and all six such flights are examined. Additionally, however, it was found feasible to retrieve clear air data from four flights devoted primarily to column measurements in cloudy air and thus expand the database. Furthermore, these additional flights permit a more representative picture of conditions in the study area to be obtained. Table 2 summarizes the flights used in this study. From the flight average values of the aerosol light-scattering coefficient shown in Table 2, it can be seen that a considerable range in aerosol loading is present in the data but that no systematic difference between clear and cloudy days is evident. There is, however, a clear temporal trend in the data. On and before July 4, the scattering is indicative of marine background air, whereas after this date, more polluted air appears to be present. Total aerosol concentrations measured by CN counter also suggest this, as do back trajectories calculated using the ECMWF model (D. Collins, personal communication, 1999).

3. Analysis

3.1. Number-to-Volume Ratios

To derive flight average number-to-volume ratios, we perform a linear regression of the PCASP number concentration onto the PCASP volume concentration for each respective flight, the slope of the regression yielding the number-to-volume ratio. All of the flights in Table 2 contained at least one vertical profile from approximately the surface to the maximum altitude shown in Table 1 and commonly 2 or more such profiles. Hence the values of the number-to-volume ratio are essentially columnar averages of the lowest few kilometers of the troposphere, encompassing much of the aerosol optical depth. However, before presentation of these columnar values, an explanation of the data filtering which proved necessary to obtain them is in order.

Because of the relatively clean nature of the airshed sampled, particle counts in the upper channels (11-15) of the PCASP were low and erratic, resulting in much enhanced noise in the number-to-volume ratio. The most straightforward way of addressing this problem is time averaging. However, to permit easy collation of the PCASP data with the humidigraph data and provide some spatial resolution for other analyses, a somewhat more elaborate procedure was implemented. First, only the first 10 of the 15 PCASP channels (~0.05-0.5 μm radius), for which the counting statistics yielded an uncertainty of ±6%, where used in the regression analysis. Then, to compensate for the overestimate in the number-to-volume ratio attendant to disproportionately removing number and volume from the regression analysis, the flight average ratio of the PCASP volume for the first 10 channels to that for the entire PCASP range was used to correct the ratio to a value representative of the entire PCASP range. While this will, of course, add variance back into the number-to-volume ratios, it renders them comparable to values measured in more polluted locations where the entire PCASP size range has been utilized [e.g., *Hegg and Kaufman*, 1998]. The added variance will be much less than that which would result from inclusion of the value outliers in the regression á priori because the regression is a least squares fitting, i.e., a second-order minimization very sensitive to outliers, whereas averaging is a linear process. The various steps in this process are shown in Table 3. The fitted slopes for the 10 channel fit are shown (note that the R^2 values are for a regression with constant to facilitate interpretation, whereas the slopes given are forced through zero) together with the mean 10 channel volume fractions.

Values of the corrected number-to-volume ratio are given both for the entire altitude range of each flight and, where sufficient data were available, only for that portion of the flight below the boundary layer inversion. These last calculations were undertaken to test for the possibility of a significant difference in the number-to-volume ratio between the boundary layer and the entire vertical column, i.e., the domain actually retrieved in remote sensing. It can be seen that there is no difference between the boundary layer and the columnar values. This suggests, at least for this data set, that the columnar values implicitly retrieved by remote sensing will be representative of boundary layer values most relevant to low-cloud properties. (It is important to note, however, that the similarity between the columnar and the boundary layer values does not mean that the free tropospheric values are the same as the boundary layer values of the number-to-volume ratio, and in fact, they commonly are not.) An example of the regression analysis leading to the values given in Table 3 is shown in Figure 1.

The values of the dry number-to-volume ratio shown in Table 3, with a mean value of 168 ± 21 (SE) μm^{-3}, are quite similar to values obtained during the Tropospheric Aerosol Radiative Forcing Observational Experiment (TARFOX) experiment of 206 ± 2 μm^{-3} (for $0.06 < r < 1.5$ μm) and of other marine values concurrently cited by *Hegg and Kaufman* [1998] of 184 ± 25 μm^{-3} (for $0.06 r < 1.5$ μm). Such values are also quite similar to ship-based measurements in the same general area recently reported by *van Dingenen et al.* [1998] (166 ± 31 for $0.04 < r < 0.40$ μm). Finally, it is worth pointing out that the number-to-volume ratio is simply related to the volume mean radius of the aerosol particles and that a

Table 3. Calculated Values for the Slopes of the Aerosol Number-to-Volume Regressions

Flight	Date	Altitudes	Regression Slope Through (0), μm^{-3}	Submicron to Total Volume Ratio	Corrected Regression Slope, μm^{-3}
3	6/21/97	all	453 (0.52)	0.55	249
		Z<1 km	447 (0.23)	0.55	246
5	6/23/97	all	532 (0.54)	0.54	287
		Z<1.5 km	531 (0.42)	0.54	287
8	6/30/97	all	95 (0.37)	0.90	86
		Z<1.2 km	99 (0.26)	0.90	89
11	7/4/97	all	420 (0.51)	0.34	143
14	7/7/97	all	306 (0.80)	0.68	208
15	7/8/97	all	297 (0.91)	0.67	199
		Z<1 km	295 (0.80)	0.67	198
17	7/10/97	all	153 (0.95)	0.78	119
20	7/17/97	all	282 (0.14)	0.47	133
		Z<0.75 km	312 (0.001)	0.47	147
22	7/19/97	all	162 (0.91)	0.55	89
		Z<1 km	161 (0.91)	0.55	89
23	7/20/97	all	244 (0.97)	0.69	168
		Z<1 km	260 (0.94)	0.69	179
				mean (all Z)	168 ± 67 (standard deviation of mean) ±21 (standard error of mean)

The slopes are for an RH of 40%. Values for the regression R^2 are shown in parentheses. Uncertainties in the individual regression slopes are 2% or less of the slope magnitudes.

value of ~170 μm^{-3} corresponds to a volume mean radius of ~0.11 μm. This value is in reasonable agreement with accumulation mode volume mean radii reported in the literature for marine aerosol [cf. *Fitzgerald,* 1991]. Thus the available data suggest a relatively constant value for the number-to-volume ratio under commonly occurring conditions, at least when averaged over the timescale of ~5-10 days. However, day-to-day variation can be better than a factor of 2 and these maritime values do differ from values of the number-to-volume ratio reported for continental aerosols. For example, *Leaitch et al.* [1986] reported a number-to-volume ratio of roughly 100 ($0.06 \leq r < 1.5$ μm) for aerosols in eastern North America. In this regard it is important to note that the incursion of continental aerosols into the marine environment will also impact the aerosol number-to-volume ratio.

In several instances during the ACE 2 study, Saharan dust was advected over the study area, usually at altitudes higher than 2 km. Within the dust layers the relationship between the aerosol number and the volume concentrations is poorly defined with linear regression coefficients generally well below 0.5. Furthermore, though difficult to quantify, the number-to-volume ratios in these dust layers appear to be systematically lower than those in either polluted or clean marine air. Relatively low ratios for such dust, more similar to those for continental aerosols, have been reported previously [*van Dingenen et al.,* 1998].

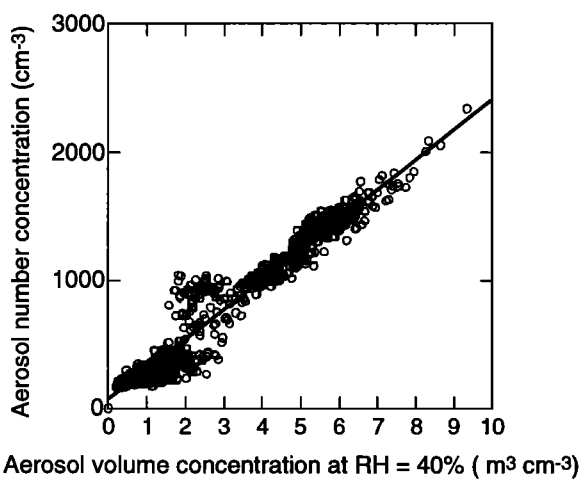

Figure 1. Plot of the aerosol number versus volume concentration at RH = 40% from the PCASP-100X for the entire flight of July 20, 1997 (Pelican flight 23). This example does not have the regression line forced through zero in order to illustrate the commonly small values for the unforced intercept.

3.2. Effect of Relative Humidity

Because the PCASP-100X was operated at near ambient RH, it was necessary to go through a rather elaborate data processing exercise to retrieve the number-to-volume ratios of the dry aerosol, the parameter actually of interest in assessment of aerosol indirect radiative forcing. This naturally leads to the question of correcting for relative humidity effects in general, particularly when engaged in remote retrievals of aerosol volume. For example, Figure 2 shows regressions of aerosol number and volume in the marine boundary layer (MBL) at several RHs, the ambient RH, the RH in the PCASP itself (the measurement RH), and the "dry" RH used as a comparison standard (40% RH). Clearly, the RH will have a marked impact on the ambient number-to-volume ratio. The impact of this effect can be assessed most directly by a multiple linear regression of the ambient number-to-volume ratio onto both the dry ratio and the ambient RH of each flight. The standardized regression coefficients for the dry ratio and RH then give the relative impact of the two independent variables. Results of this analysis are presented in Table 4. A comparison of the standard regression coefficients is also shown graphically in Figure 3. The results

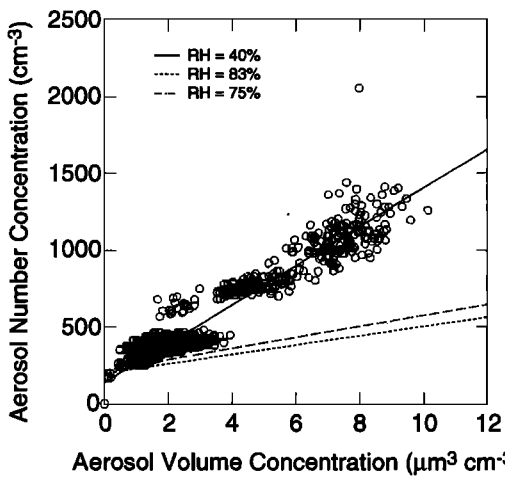

Figure 2. Plots of the regression lines of aerosol number versus volume concentration from a portion of the MBL for three different RHs for the flight of July 19, 1997 (Pelican flight 22): the measurement RH (75%), ambient RH (83%), and a dry reference RH (40%). Data points are shown for the dry RH.

shown in Figure 3 demonstrate that the ambient RH commonly plays a significant and sometimes a dominant role in the magnitude of the ambient number-to-volume ratio.

One striking aspect of the calculations presented in Figure 3 is the variability in the impact of RH. Some portion of this, of course, is simply due to the variability in ambient RH itself. However, this is certainly not the whole story. The correlation between the relative impact of RH (as quantified by the ratio of standardized regression coefficients for RH and the dry number-to-volume ratio) and RH itself is a modest 0.75, indicating that only 57% of the variance can be explained by RH. The residual variance must be due to other factors, such as differing chemical compositions and thus hygroscopicity, variations of the size distribution with altitude, or simply noise.

One interesting physical explanation for the complex RH dependence is suggested by the recent study of *Baumgardner and Clarke* [1998]. Analyzing data from the ACE 1 field study centered near Cape Grim, Tasmania, these authors find that at higher RHs the apparent number of particles in the accumulation mode increased and attributed this to the growth of particles into the measurement size range of their instruments via increased hydration at higher RHs. Such an effect, coupled with the partially independent effect of growth in particle volumes with higher RH for particles in the accumulation mode ab initio, might well result in a complex nonlinear relationship between number and volume as a function of RH. To test for significant particle growth into the measured size range, aerosol number concentration was regressed onto the measurement RH for each of the flights examined. To eliminate an incidental correlation between aerosol number concentration and RH due to the ubiquitous correlation of both RH and number concentration with altitude, the regressions were restricted to altitudes below 1000 m. Values of R^2 for the regressions varied between 0.0004 and 0.33 with a mean of 0.11 ± 0.01 (SE). Hence while there is indeed some evidence for a significant effect such as that found by Baumgardner and Clarke on at least a few of the flights examined here, for the ACE 2 data set as a whole, this phenomenon appears to be a second-order effect.

Another aspect of the multiple linear regression results of interest concerns the linearity of the dependence of the ambient number-to-volume ratio on RH and the dry number-to-volume ratio. Using the multiple-regression R^2 as a measure of linearity, analysis reveals that R^2 is negatively correlated (linear correlation coefficient $r = -0.59$, probability of observed correlation being due to chance $p = 0.075$) with the ratio of RH to dry number-to-volume standard regression coefficients, i.e., as the relative impact of RH increases, the linearity of the relationship decreases. Given the nonlinear nature of the RH dependence of particle size and thus volume, this is scarcely surprising. It does, however, point to the need to consider this nonlinearity in any scheme to retrieve either the dry aerosol number-to-volume ratio or the dry aerosol volume from remote retrievals.

Table 4. Results of the Multiple Linear Regression of the Ambient Number-to-Volume Ratio $(N/V)_{amb}$ onto the Dry Ratio $(N/V)_{dry}$ and the Ambient RH

Flight	Date	$\overline{RH}$[a]	Standard Coefficient $(N/V)_{dry}$	Standard Coefficient RH	R^2
3	6/21/97	60	0.54	-0.78	0.80
5	6/23/97	57	0.53	-0.88	0.78
8	6/30/97	60	0.87	-0.37	0.91
11	7/4/97	73	0.35	-0.84	0.90
14	7/7/97	88	0.19	-0.96	0.81
15	7/8/97	36	0.82	-0.26	0.97
17	7/10/97	50	0.97	-0.04	1.0
20	7/17/97	52	0.89	-0.36	0.94
22	7/19/97	71	0.72	-0.28	0.84
23	7/20/97	31	0.78	-0.28	0.96

[a]Flight average RH.

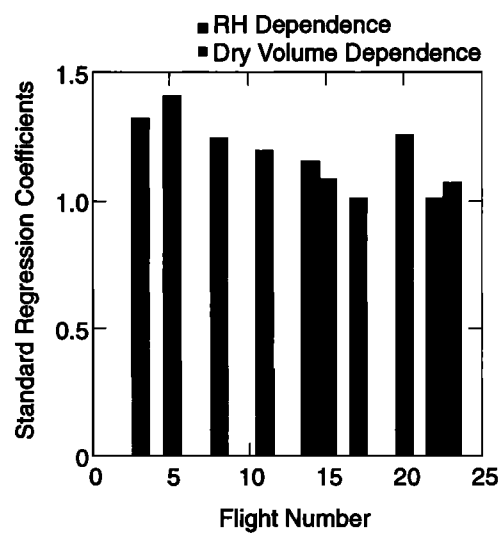

Figure 3. Standard (normalized) regression coefficients for the multiple linear regression of ambient aerosol number-to-volume ratio onto the ambient RH and dry number-to-volume ratio for each of the ACE 2 flights analyzed.

3.3. Recovering Dry Aerosol Properties

The ultimate objective of the recovery of dry aerosol properties is the prediction of the ambient aerosol number concentration in the accumulation size range (~0.1-1.0 μm radius), essentially the number of CCN active at a nominal 0.2% supersaturation (for marine air). In principle, with a universal number-to-volume ratio for marine air, one can get this by retrieval of the dry aerosol volume. While the ambient aerosol volume, with various assumptions, is retrievable from the aerosol optical depth [e.g., *Fraser et al.*, 1984; *King et al.*, 1992], conversion to the dry volume involves knowledge of the ambient RH, the hygroscopicity of the aerosol, and application of a transformation from ambient to dry size. Utilizing the data presented above, we explore here the impact on the accuracy of the CCN retrieval of several of the assumptions which must be made in any operational retrieval.

The first step in the process is the selection of an appropriate transformation to convert the ambient aerosol volume to the required dry volume. The simplest approach would be a linear conversion. However, the regression data shown in Table 4 suggest that such an approach is not viable. The mean value for the standard regression coefficient for RH is 0.51 ± 0.33; that is, the dispersion is 64% of the mean value. This is simply indicative of the variability in aerosol hygroscopicity even in the marine atmosphere, as well as the nonlinear dependence of aerosol hydration on RH suggested by equation (1).

A somewhat more sophisticated approach to dry aerosol volume recovery would, in fact, be to use a function of the form of equation (1) to recover the dry aerosol volume, an approach obviously consistent with the approach used to correct individual data points to a 40% RH. Now, however, for practicality the feasibility of using a single value of gamma (γ) for marine aerosols must be examined. To address this issue, flight average values of γ are calculated and reported in Table 5. The functional relationship between the dry aerosol volume V_{dry} and the ambient volume V_{amb} is the hypothesized to be of the form

$$V_{dry} = V_{amb}\left(\frac{1-RH}{0.6}\right)^{\bar{\gamma}}, \quad (2)$$

where $\bar{\gamma}$ is the flight average of γ. Values of V_{dry} calculated for each intraflight data point are then linearly regressed against the right side of equation (2). Values for the regression coefficients and the R^2 value for each flight are also shown in Table 5. It can be seen that the regression slopes are generally close to unity, the intercepts small compared to flight mean values for the dry volume (5%, on average), and the R^2 values reasonably high. The one important exception to this is the case of flight 22 (July 19, 1997) for which an R^2 value of only 0.25 was obtained. Clearly, the hypothesized relationship is not applicable to these data. Cloud was widespread on this flight and cloud-impacted samples proved difficult to screen. We speculate that evaporating cloud drops, which would not be expected to follow the proposed form of equation (2), may have contaminated a significant number of the data points. We shall not include this flight in the further analyses.

At least as significant as the goodness of the fits shown in Table 5 is the fact that the flight average value of γ show only modest interflight variability. The mean values for γ is 0.60 ± 0.09. Furthermore, an interesting dichotomy is apparent in the data, which permits even more variance reduction. On flights 14, 15, 20, and 22 a number of ACE 2 investigators reported evidence of Saharan dust at significant levels in the study area [cf. *Smirnov et al.*, 1998; *Schmid et al.*, 1999]. From Table 5 it can be seen that these flights had significantly lower values of γ than those flights for which no evidence of dust was reported. Stratifying γ by the presence of dust, the nondusty cases had a mean value of 0.66 ± 0.03 and the dusty cases 0.51 ± 0.05. Because there are some grounds for believing that dusty cases are separable from nondusty cases in remote retrievals (e.g., anomalously low values of the Angstrom coefficient when dust is present), the differentiation between dust-free marine values of γ and "dusty" values of γ seems useful and practical.

Given the potential utility of equation (2) as a methodology for recovery of aerosol dry volume and hence of CCN number concentration, a further step in the recovery process can be tested with the data in hand. With the flight (or columnar) average values of γ and RH, can we utilize the measured values of the ambient columnar aerosol volume, the parameter recoverable from satellite observations, to obtain a credible estimate of in situ CCN concentrations? This is first done by using the product of the dry aerosol volume and the mean value for the aerosol number-to-volume ratio derived above, namely 168 ± 21. The estimates of CCN concentration so derived are displayed in Table 6 and compared with the observed values by

Table 5. Analysis of the Nonlinear Dependence of Aerosol Dry Volume on RH Using a Form of Equation (1) (See Text), $V_{dry} = V_{amb}(1 - RH_{amb}/0.6)^{\gamma}$

Flight	Dust	Mean RH_{amb}, %	$\bar{\gamma}$	k	B	R^2
3	no	60	0.65 ± 0.004	0.96 ± 0.01	0.08 ± 0.02	0.77
5	no	57	0.69 ± 0.01	1.02 ± 0.01	–0.02 ± 0.01	0.88
8	no	60	0.69 ± 0.005	1.06 ± 0.07	0.75 ± 0.01	0.71
11	no	73	0.68 ± 0.004	1.06 ± 0.01	–0.04 ± 0.01	0.89
14	yes	88	0.53 ± 0.002	0.93 ± 0.01	0.45 ± 0.04	0.86
15	yes	36	0.43 ± 0.01	0.92 ± 0.003	0.11 ± 0.02	0.99
17	no	50	0.63 ± 0.01	1.49 ± 0.01	–0.35 ± 0.04	0.98
20	yes	52	0.51 ± 0.01	0.91 ± 0.01	0.05 ± 0.01	0.94
22	yes	71	0.55 ± 0.01	1.12 ± 0.04	0.16 ± 0.01	0.25
23	no	31	0.62 ± 0.01	1.0 ± 0.003	–0.02 ± 0.01	0.99

The left hand of this equation is regressed onto the right side with slope k and intercept B.

Table 6. Predictions of the Number of CCN Active at a Nominal 0.2% Supersaturation (N_{CCN})

Flight	Predicted Dry Aerosol Volume, $\mu m^3/cm^3$	Predicted N_{CCN} (From N/V=168), cm^{-3}	Retrieved Dry N/V Ratio, μm^{-3}	Predicted NCCN (From Columns 2 and 4), cm^{-3}	Observed N_{CCN}, cm^{-3}
3	3.35	563	213	714	712
5	2.07	348	252	512	524
8	7.28	1223	75	546	546
11	4.21	707	122	514	418
14	6.97	1171	255	1777	1780
15	6.90	1159	144	994	994
17	5.27	885	135	711	715
20	4.34	729	54	234	446
22	—	—	—	—	—
23	3.41	573	154	525	447

means of linear regression (graphical comparison in Figure 4a). However, the regression equation so derived has an R^2 value of only 0.30. It is clear that the variance in the mean value of the number-to-volume ratio, while modest, renders a truly successful recovery of CCN concentrations for the cases reported here difficult.

A possible methodology to increase the accuracy of the CCN retrieval is suggested by the fact that in principle, the ambient number-to-volume ratio for individual retrievals can be derived from the aerosol effective radius, a parameter retrieval by a number of satellite algorithms. Specifically,

$$\frac{N}{V} = \frac{0.75}{\pi}(1.09)^{-3} r_{\text{eff}}^{-3}, \tag{3}$$

where the factor of 1.09 enters through the relationship between volume mean radius and effective radius found by *Martin et al.* [1994]. While the data are not available to us to test this refinement in its entirety, we can test one key aspect of it. The ambient number-to-value ratio in equation (3) must be converted to a dry ratio before multiplying by the retrieval dry volume to obtain the CCN number concentration. Utilizing essentially the same relative humidity dependence for the number-to-volume ratio previously employed for volume alone, the relationship between ambient and dry number-to-volume ratio is given by

$$\left(\frac{N}{V}\right)_{\text{dry}} = \left(\frac{N}{V}\right)_{\text{amb}} \left(\frac{0.6}{1-\text{RH}_{\text{amb}}}\right)^{\gamma}. \tag{4}$$

Values for the dry number-to-volume ratio calculated from equation (4) can be used to refine the retrieval of CCN number concentrations using the relationship

$$\text{CCN} = \bar{\gamma}_{\text{dry}} \left(\frac{N}{V}\right)_{\text{dry}}. \tag{5}$$

The values of $(N/V)_{\text{dry}}$ predicted for equation (4) are shown in Table 5 together with the CCN concentrations predicted from equation (5), as well as observed CCN concentrations. A linear regression of the observed values onto the predicted CCN values yields a regression equation

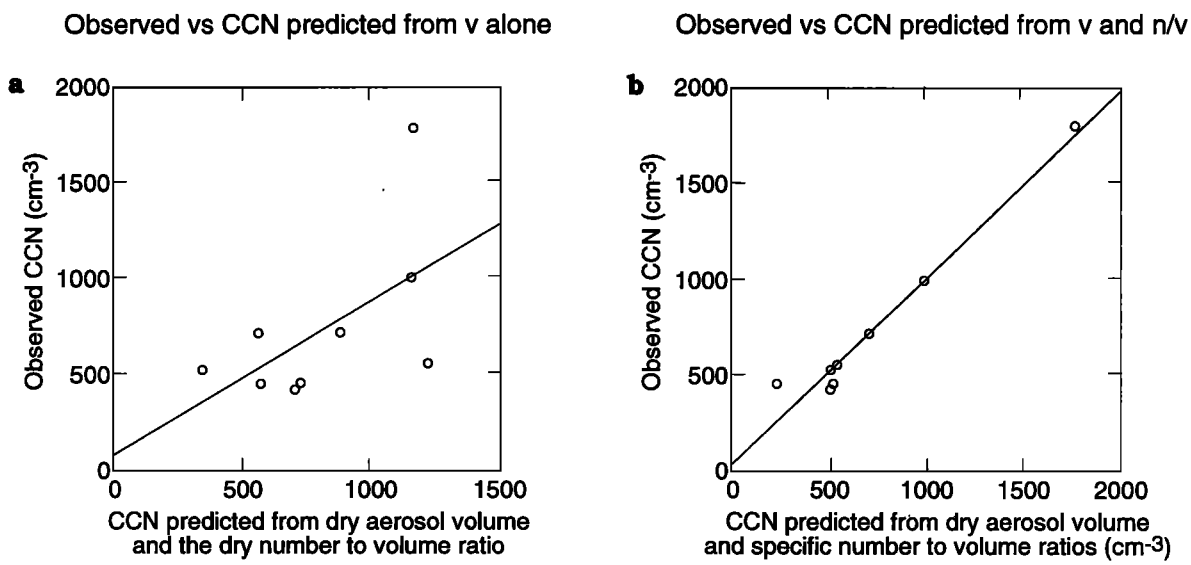

Figure 4. Plots of the observed CCN number concentration against the CCN number concentration predicted from (a) dry aerosol volume alone, (b) the produce of dry aerosol volume, and the dry number-to-volume ratio.

$$N_{obs} = 0.94\left\{\gamma_{dry}\left(\frac{N}{V}\right)_{dry}\right\} + 61, \quad (6)$$

with an R^2 of 0.97. This relationship is shown in Figure 4b. Clearly, the utilization of case-specific retrievals of number-to-volume ratios decidedly improves the accuracy of the retrieval of CCN number concentration. Indeed, the retrieval appears to be quite accurate in an absolute sense. However, a note of caution is in order. Neither the dry volume nor the dry number-to-volume ratio used to predict the CCN number concentration have been actual satellite retrievals. Rather, they have been derived from in situ measurements. What has been shown is that one can employ a relatively simple treatment of aerosol hygroscopicity (equations (2) and (4)) together with a simple hygroscopicity parameter characteristic of general aerosol types to recover the column dry aerosol volume concentration and number-to-volume ratio in marine air. These are necessary but certainly not sufficient steps in the formulation of a viable CCN retrieval. What remains to be tested is the application of the proposed formula to actual satellite-retrieved, ambient column aerosol volume and effective radius. Furthermore, the column mean values of RH used in the analysis done here are derived from in situ measurements rather than satellite retrieval. Radiometers such as the MODIS and MISR instruments to be flown on the EOS satellite can retrieve column water vapor and, with plausible assumptions as to the mean marine temperature profile for various synoptic situations (or even temperature profile retrievals from other satellites), provide estimates of column mean RH. Indeed, this can even be done, though with much less accuracy, by the AVHRR radiometers currently available. Nevertheless, an appraisal of the impact of the necessarily less accurate satellite estimates of RH on the retrieval of dry aerosol volume or number-to-volume ratio remains to be done.

4. Conclusions

Data on the number-to-volume ratio of marine aerosols over the size range from 0.06 to 1.8 μm radius have been obtained during the ACE 2 experiment and analyzed for constancy of the ratio at a nominal 40% RH. Although the ratio was not found to be as constant as in several recent studies, the ratio was found to be more restricted in range than either the number or the volume alone, with a central value of 168 ± 21 μm^{-3}, a value quantitatively in accord with these recent studies. Because the measured size range in marine air coincides reasonably well with the size of particles active at cloud supersaturations of ~0.2% and below, this relatively constant linear relationship suggests the possibility of a remote retrieval of CCN number concentrations. Furthermore, analysis of the RH dependence of the column mean aerosol volume suggests that a universal correction factor may be utilized to recover the requisite dry aerosol volume from the ambient volume which is the immediate product of any remote retrieval. However, application of the proposed retrieval procedure to measured column ambient aerosol volumes was able to recover the observed CCN number concentration with only modest success. To address this problem, a refinement in the retrieval procedure was then applied.

Essentially, while the measured variance in the marine aerosol number-to-volume ratio appears relatively small (<13%), it is still sufficiently large, particularly when the added variance of an RH correction is considered, to preclude an adequate retrieval. Hence the feasibility of retrieving not only the column dry aerosol volume but also the dry number-to-volume ratio (derivable, in principle, from the retrievable effective radius) was explored. It was found that the product of the predicted dry column aerosol volume and column number-to-volume ratio did in fact predict the CCN number concentration very well.

While encouraging, the above results are far from decisive as to the viability of a remote retrieval of marine CCN utilizing this technique. It is not clear that the aerosol effective radius can be retrieved with sufficient precision to produce meaningful number-to-volume ratios for specific scenes. Furthermore, only a limited number of cases have been examined here. Finally, and most importantly, not all links in the retrieval procedure have actually been tested. The application of the procedure to actual remote sensing data and comparison with concurrent in situ measurements of CCN remains to be done. Nevertheless, the approach explored here appears promising and offers an alternative to approaches based on look-up tables [e.g., *Tanre et al.*, 1997].

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