

Measurements of Some Aerosol Properties Relevant to Radiative Forcing on the East Coast of the United States

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ABSTRACT

Airborne measurements of aerosol light-scattering efficiencies are presented for a portion of the northeast Atlantic seaboard of the United States during July 1993. The measurements suggest a value for the sulfate light-scattering efficiency in the range $2.2\text{--}3.2\text{ m}^2\text{ g}^{-1}$, which is lower than the value used in recent modeling assessments of the climate impact of aerosols. In general, the sulfate light-scattering efficiency decreased with increasing altitude in a manner consistent with concurrent measurements of aerosol size distributions. Some limited measurements of cloud condensation nuclei and sea-salt particles are also presented.

1. Introduction

Anthropogenic aerosols may modulate global climate both directly through aerosol backscattering of solar radiation to space (e.g., Charlson et al. 1991) and indirectly through the modulation of cloud albedo (Twomey 1991). Although the overall uncertainty (or, in the case of the indirect effect, even the magnitude) of climate forcing by aerosols is not known (Penner et al. 1993), several recent studies have suggested that sulfate aerosols, which are relatively well characterized, can significantly modulate global climate (cf. Charlson et al. 1992; Kiehl and Briegleb 1993). However, the impacts of the direct and indirect effects of sulfate aerosols on global climate are dependent on several, as yet, poorly characterized parameters. In the case of the direct forcing, a key parameter is the light-scattering efficiency of sulfate (i.e., the amount of light scattered per unit mass of sulfate). For the indirect effect, the sulfate cloud condensation nuclei (CCN) nucleation efficiency (i.e., the number of CCN per unit mass of sulfate) is of crucial importance (Hegg et al. 1991, 1993a). The values currently used for these aerosol parameters, as well as others, are based on very limited data (Penner et al. 1993). The validity of the assessments of aerosol forcing depends on the assumption that these limited observations are representative of the global atmosphere. This assumption is questionable, not only because of the sparsity of measurements (particularly in remote areas of the globe) but also because most of the available measurements are from

surface observations, which are not always representative of values aloft.

In a recent study we presented the results of some airborne measurements of the light-scattering efficiency and cloud nucleation efficiency for sulfate aerosols over the mid-North Atlantic Ocean (Hegg et al. 1993a). These results suggested that the values of these parameters can be quite different in remote locations than they are in polluted airsheds. Measurements over the remote oceans are of particular importance in evaluating indirect radiative forcing by aerosols, since the sensitivity to such forcing reaches maximum values in clean locales (Twomey 1991). By contrast, the direct effects of aerosols on solar radiation are most important in highly polluted regions, where aerosol concentrations reach maximum values. In recognition of this situation, we recently obtained airborne measurements of aerosol light-scattering efficiencies and cloud nucleation efficiencies on the northeastern Atlantic seaboard of the United States, a locale that is within one of the major zones of radiative forcing by anthropogenic aerosol predicted by current climate models (e.g., Charlson et al. 1991). We report here on our analysis of these data.

2. Instrumentation and description of the field study

The measurements reported were obtained as part of the National Aeronautic and Space Administration's Smoke, Clouds and Radiation Experiment (SCAR-A), which was conducted in July 1993 and centered on Wallops Island, Virginia. All of the measurements discussed in this paper were obtained aboard the University of Washington's Convair C-131A research aircraft. Research flights were flown out of Wallops Island and extended from northern Virginia to New Jersey, both just inland and just off the Atlantic coast.

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The weather during the operational period was hot and humid with daytime temperatures typically in excess of 30°C and relative humidities of 80% or higher. Average values of the light-scattering coefficient due to particles were commonly well above 10^{-4} m^{-1} , which is indicative of the aerosol haze that is usually present under such conditions in this region. Scattered boundary layer cumulus clouds were occasionally present: they generally appeared in the late morning or early afternoon and reached their maximum vertical extent in the late afternoon. On one occasion, a dry cold front passed through the area, temporarily bringing relatively haze-free air.

The complete suite of instruments aboard the C-131A aircraft has been described by Hobbs et al. (1991). Most of the measurement techniques central to the present study, namely, nephelometry for measuring particle light scattering, filter packs for particulate sulfate and SO_2 , a CCN spectrometer, and a suite of instruments to measure aerosol size distributions and mass concentrations, have been described by Hegg et al. (1993a,b). The only instruments used in the present study that have not been previously described are an extended-range differential mobility particle sizing system (DMPS) and a salt-particle counter. We discuss below both these instruments and the application of the aerosol sizing system aboard the Convair C-131A to the present analysis.

The DMPS has been used extensively to measure submicron aerosol size distributions in the atmosphere (e.g., Reischl 1991). However, by far the most commonly used DMPS, the commercial instrument manufactured by Thermo-Systems Inc. (TSI), has a lower aerosol size cutoff at approximately 0.02- μm diameter. To extend the lower size-detection limit, several extended-range DMPS instruments have been designed (Reischl 1991) and used (Winklmayer et al. 1991). The DMPS that we used was built by us following the design of Winklmayer et al. The size range of our DMPS was 0.01–0.56- μm diameter. To accommodate the lower range, a TSI model 3025 ultrafine condensation nucleus counter was used as the particle detector. The 0.56- μm upper size limit was imposed by the impactor that was used to eliminate large particles, which are subject to multiple charging and therefore missizing. The instrument was calibrated using various monodispersed sodium chloride aerosols produced with a Colison generator and sized with a TSI electrostatic classifier.

The batch sampler for aerosol sizing used in this study has been described by Radke (1983). However, its use in this study to estimate submicron aerosol mass requires some additional discussion. Determination of aerosol mass is most accurately done by gravimetric analysis using aerosol filters. However, for aircraft use, this methodology has the drawback of poor spatial resolution due to the need for long sampling intervals. Therefore, we used our particle sizing system to mea-

sure the aerosol volume and then converted this to aerosol mass with an assumption as to the particle density. Such a procedure has been used for many years to estimate aerosol mass and has been found satisfactory for the submicron size range (cf. Ouimette and Flagan 1982). We have compared aerosol masses determined in this way using our airborne particle sizing system with gravimetric mass measurements obtained by means of filters. For example, using data from biomass emissions, Radke et al. (1984) obtained a regression relationship between the aerosol mass derived from our particle sizing system (M_{ss}) and gravimetric mass (M_G) of

$$M_{ss} = (0.86 \pm 0.009)M_G - (0.07 \pm 0.04)$$

with a correlation coefficient r^2 of 0.997. Based on laboratory measurements of aerosols generated from biomass burning, the density of the aerosol was taken as 2 g cm^{-3} . An assumed density of 2.15 g cm^{-3} , which is well within the limits of uncertainty, would have yielded essentially exact correspondence between M_{ss} and M_G .

For the present study we used just one particle-sizing instrument to cover aerosols in the submicron size range that is of most importance to light scattering; this avoids intercalibration between instruments. The instrument selected, the ASASP-100X (manufactured by Particle Measuring Systems Inc.), has a long history and has been used in several calibration studies (cf. Liu et al. 1992). Two main issues arise when employing the ASASP-100X for aerosol mass determination: a correction for the relatively high index of refraction of the latex spheres (compared to aerosols) that are used to calibrate the ASASP-100X, and the mean density of the aerosol particles. Fortunately, aerosol indices of refraction in the atmosphere show little variance about a central value of 1.5 (cf. Sloane 1984; Sloane and Wolff 1985; Zhang et al. 1994), which is the value used in this study. This constancy permits application of a straightforward correction for index of refraction. The densities of inorganic salts (sulfates, nitrates, chlorides, etc.) range from about 1.7 to 2.0 g cm^{-3} , while the densities of organic compounds in the atmosphere range from slightly less than 1 to about 1.5 g cm^{-3} (cf. Sloane 1984). Since, on average, about 50% of the aerosol mass on the east coast of the United States is sulfate and 30%–50% organic (White 1986; Malm et al. 1994), we assumed a mean aerosol density of 1.5 g cm^{-3} in this study. Based on the range of chemical compositions reported for East Coast aerosols, we estimate the uncertainty in this mean density to be $\pm 15\%$. Uncertainties due to instrument sizing, flow rates, etc. are approximately 10%. Hence, the uncertainty in the assumed mean aerosol density dominates the overall uncertainty of about $\pm 25\%$ in the derived aerosol mass.

The above discussion implicitly assumes that the aerosols measured are not heavily hydrated. This assumption is certainly valid for our measurements. Prior

TABLE 1. Aerosol light-scattering coefficients b_{sp} at a wavelength of 550 nm, sulfate and aerosol mass concentrations for particles with diameters between 0.18 and 1.9 μm , and CCN concentrations at 1% supersaturation.

Date (1993)	Altitude (km)	b_{sp} (m^{-1})	$[\text{SO}_4^-]$ ($\mu\text{g m}^{-3}$)	Aerosol mass ($\mu\text{g m}^{-3}$)	Aerosol mass - sulfate mass ($\mu\text{g m}^{-3}$)	CCN (cm^{-3})
12 July	0.31	3.4×10^{-5}	4.6	13.6	9.0	—
	1.56	2.2×10^{-5}	4.2	9.7	5.5	—
14 July	0.63	3.5×10^{-5}	2.7	13.4	10.7	—
	3.13	BDL*	1.9	—	—	—
16 July	0.31	BDL	1.4	3.8	2.4	—
	1.25	7.1×10^{-6}	3.8	8.3	4.5	—
19 July	0.16	BDL	0.9	—	—	—
	0.63	BDL	2.6	4.8	2.2	—
	1.56	3.1×10^{-5}	12.6	13.6	1.0	—
20 July	0.63	6.2×10^{-5}	16.2	18.9	2.7	335
	1.56	2.1×10^{-5}	9.1	8.8	-0.3	344
25 July	0.78	3.2×10^{-5}	12.3	18.7	6.4	—
	1.56	6.4×10^{-6}	4.7	9.8	5.1	314
	2.19**	3.0×10^{-5}	14.4	15.9	1.5	303
28 July (1st flight)	0.31-1.25	3.2×10^{-5}	9.7	16.3	6.6	—
	0.56	1.6×10^{-5}	9.0	13.3	4.3	—
28 July (2d flight)	0.78	1.6×10^{-5}	9.2	12.1	2.9	—
	1.56	3.4×10^{-6}	3.4	6.0	2.6	—

* BDL—below the detection limit of the nephelometer ($5 \times 10^{-7} \text{ m}^{-1}$).

** Haze present at this altitude.

to entering the bag sampler used to obtain the sulfate mass and light-scattering measurements, and the bag sampler that fed the ASASP-100X, the aerosol were dried either by modest heating or by diffusion dryers. The relative humidity in both samplers was about 40% or less (measured by a Vaisala "humi-cap" sensor). At such humidities, atmospheric aerosols contain only a few percent of water by mass (Hanel 1976). Both bag samplers have similar ambient sampling efficiencies (determined by impaction) and were filled simultaneously for the cases analyzed in this paper.

An important unresolved issue in assessment of the indirect forcing of climate by aerosols is the number of CCN that do not derive from sulfur gases. Over, and adjacent to, oceans, sea-salt particles may contribute to the CCN, but few measurements are available on the size distributions of sea-salt particles—a necessary precursor to such an assessment. During several of our flights the size distributions of sea salt between 0.1 and 5 μm in diameter were measured using a flame photometric detector (FPD) coupled with a pulse-height analyzer. The FPD used a reducing hydrogen-air flame. The sea-salt particles were measured through detection of the sodium-D line during the combustion process. The instrument was calibrated using NaCl particles generated by a Colison atomizer and sized by a TSI electrostatic classifier for the smaller sizes and a Bergland-Liu aerosol calibrator for the larger particles. This same salt counter was used by Slinn et al. (1983) to

measure the size distributions of salt particles over the Pacific Ocean.

Eight research flights were undertaken during SCAR-A. Altitude-dependent data on sulfate number and mass concentrations and the particle light-scattering coefficient were obtained on all flights. Additionally, on most flights, submicron particle size distributions were measured with the DMPS. CCN concentrations and sea-salt particle size distributions were measured on a few of the flights.

3. Results and discussion

a. Aerosol and sulfate light-scattering efficiencies

Values of the light-scattering coefficient due to aerosols (b_{sp}), concurrent measurements of sulfate mass and estimates of aerosol mass concentration, for particles with diameters between 0.18 and 1.9 μm , and CCN concentrations at 1% supersaturation are shown in Table 1. The sulfate mass was measured directly by filter pack (Ferek et al. 1991) and sea-salt sulfate was subtracted using sodium as a tracer. The total aerosol mass was derived from measured aerosol size distributions, as described in section 2. The sulfate masses are known to within $\pm 5\%$, and the total aerosol mass to $\pm 25\%$.

A linear regression of b_{sp} onto the total submicrometer (measured from 0.18- to 1.9- μm diameter) aerosol mass M_{sa} yields

$$b_{sp} = (3.2 \pm 0.6)M_{sa} - (1.6 \pm 0.86) \times 10^{-5}, \quad (1)$$

where b_{sp} is in inverse meters (measured at a wavelength of 550 nm) and M_{sa} in grams per cubic meter (Fig. 1). The regression coefficient r^2 for the empirical relationship (1) was 0.67. While the regression fit is somewhat poorer than values commonly reported (typically around $r^2 = 0.9$) (e.g., Waggoner and Weiss 1980), the regression slope of $3.2 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$ (viz., the aerosol light-scattering efficiency) is similar to other measurements in polluted airsheds (e.g., Waggoner and Weiss 1980; White 1986).

Because of its potential role in climate forcing by aerosols, the light-scattering efficiency of sulfate is a key parameter. The regression of our data for b_{sp} onto non-sea-salt sulfate mass yields

$$b_{sp} = (2.1 \pm 0.8)[\text{SO}_4^-] + (7.3 \pm 7.3) \times 10^{-6}, \quad (2)$$

where b_{sp} is in inverse meters and the sulfate mass $[\text{SO}_4^-]$ is in grams per cubic meter (Fig. 2). The ostensible sulfate light-scattering efficiency suggested by the regression slope is thus $2.1 \pm 0.8 \text{ m}^2 \text{ g}^{-1}$, which is not significantly different from the value just derived for the scattering efficiency of the aerosol mass as a whole. However, the value of r^2 for (2) is only 0.38. This poor correlation is not unexpected. We have previously noted (Hegg et al. 1993a) that b_{sp} is an integral property of the total aerosol submicron mass, of which sulfate contributes only a part, often a rather small part. As can be seen from Table 1, low sulfate mass concentrations were sometimes measured concurrently with relatively high values of the measured aerosol mass

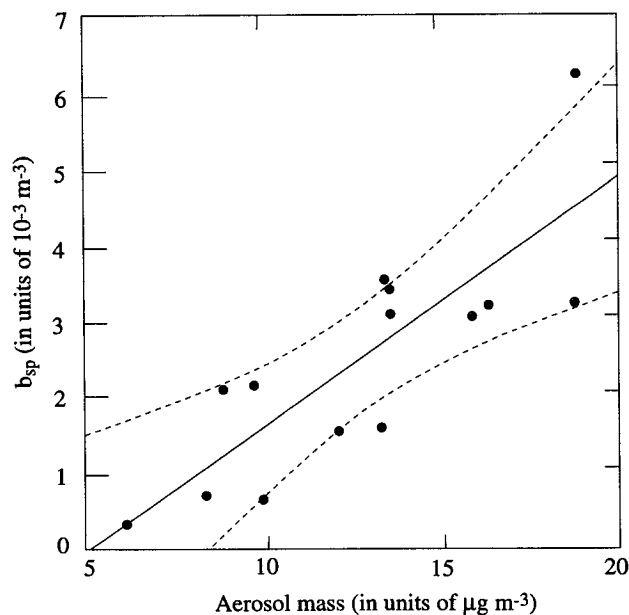


FIG. 1. Particle light-scattering coefficient b_{sp} at a wavelength of 550 nm vs aerosol mass. The best-fit linear regression (solid line) and 95% confidence limits (dashed lines) are also shown.

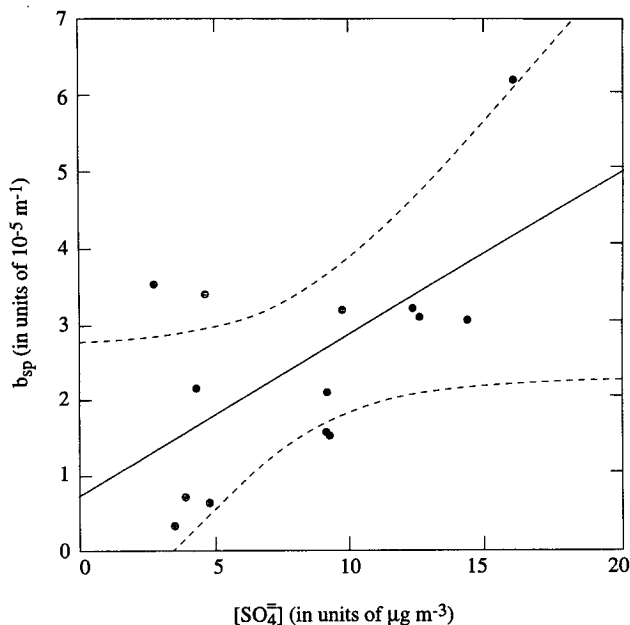


FIG. 2. Particle light-scattering coefficient b_{sp} at a wavelength of 550 nm vs sulfate mass. The best-fit linear regression (solid line) and 95% confidence limits (dashed lines) are shown.

(essentially the total submicron aerosol mass) and high light-scattering coefficients. Thus, is general, for this dataset most of the light scattering was not associated with sulfate. To assess scattering by sulfate alone, the value of b_{sp} should be reduced by the ratio of the sulfate mass to the total submicron aerosol mass. This is essentially equivalent to equating the submicron scattering efficiency for the aerosol in general with the scattering efficiency for sulfate. As we have pointed out previously (Hegg et al. 1993a), there are firm grounds for such an assumption. Given this fundamental assumption, the simplest approach to estimating the sulfate light-scattering efficiency is to equate it with that of the submicron aerosol mass derived above. However, it is also useful to perform the regression of reduced b_{sp} onto sulfate mass since the reduction of b_{sp} by the sulfate mass fraction influences the slope of the regression line, giving more statistical weight to samples that are mostly sulfate. Performing the above indicated reduction in b_{sp} prior to regressing onto sulfate mass results in the regression equation:

$$b_{sp}(\text{SO}_4^-) = (2.7 \pm 0.4)[\text{SO}_4^-] - (6.2 \pm 3.8) \times 10^{-6}. \quad (3)$$

Since the covariance between dependent and independent variables introduced by using sulfate as a cofactor in the dependent variable will automatically enhance r^2 , this covariance must be removed from the assessment of r^2 . Doing this, the r^2 value for the regression improves only modestly from that for uncorrected b_{sp} and sulfate, namely, $r^2 = 0.48$. More significantly, the

sulfate light-scattering efficiency calculated in this manner is much less uncertain than the unreduced sulfate efficiency and closer to the light-scattering efficiency of the total submicron aerosol mass (viz., $3.2 \pm 0.6 \text{ m}^2 \text{ g}^{-1}$), as expected. Nevertheless, it should be noted that (1) and (3) do not represent physically distinct estimates of the sulfate scattering efficiency. They are derived from identical assumptions and merely represent the same fundamental analysis with different sample weighting.

Another approach to estimation of the sulfate scattering efficiency is that of multiple linear regression of the particle scattering onto the various mass components of the aerosol (e.g., White 1986, 1990). In this case, the two available mass components are sulfate mass and the difference between the total aerosol mass and that of sulfate (see Table 1). Such a procedure has its own pitfalls, as discussed by White (1986) and Sloane (1986), but it can provide useful insight into the issue at hand, particularly when the two aerosol components used in the regression analysis (in this case sulfate and nonsulfate aerosol mass) are not correlated. Indeed, for our data, these components are negatively correlated ($r = -0.51$). This in itself is interesting in that it illustrates the lack of general applicability of the aerosol model advocated by Anderson et al. (1994), as discussed by Hegg et al. (1994).

The multiple regression equation for b_{sp} , $[\text{SO}_4^-]$ and the nonsulfate mass [nonsulfate] is given by

$$b_{sp} = (2.2 \pm 0.4) [\text{SO}_4^-] + (1.8 \pm 0.6) [\text{nonsulfate}], \quad (4)$$

with a multiple regression coefficient r^2 [as defined by Eq. (7) of Kvalseth (1985)] of 0.89. The two regression coefficients in (4), interpretable as the aerosol light-scattering efficiencies for sulfate and nonsulfate mass, respectively, do not differ significantly. The value for the sulfate scattering efficiency is appreciably, though not significantly, lower than that suggested by Eqs. (1) and (3).

The value of the sulfate light-scattering efficiency given by the slope of (3), or interchangeably by the slope of (1), or the regression coefficient of (4), is of considerable interest. The location of our measurements was within one of the major areas of maximum radiative forcing by sulfate aerosols indicated by modeling assessments. Because the radiative forcing in these models varies linearly with the sulfate light-scattering efficiency, a comparison of the value suggested by our data with values used in these recent modeling assessments allows an assessment of the radiative forcing implied by our measured value of sulfate light-scattering efficiency. For such a comparison, we may choose the values based on (1), (3), or (4). Because we see no reason to give preference to any of these analyses, we have selected the intermediate value of $2.7 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$ from (3). In contrast to our results, Charlson

et al. (1991) used a value of $5 \text{ m}^2 \text{ g}^{-1}$ at a wavelength of 550 nm for the sulfate light-scattering efficiency. This relatively high value is due in part to a different set of assumptions concerning the nature of the sulfate light-scattering efficiency. Charlson et al. (1991, 1992) assume that the scattering due to aerosol mass other than sulfate (e.g., ammonium) can be subsumed in the sulfate light-scattering efficiency without simultaneously adding the additional mass to the sulfate mass (i.e., they assume that sulfate acts as a tracer for such mass). We think this is a poor assumption. (For a discussion of this issue see Anderson et al. 1994 and Hegg et al. 1994.) Indeed, for our dataset, both the negative correlation between sulfate and nonsulfate mass, and the regression coefficient of (4), argue against this assumption. Nevertheless, if calculated as we calculate ours (i.e., including only scattering due to the sulfate ion in the scattering efficiency), the sulfate light-scattering efficiency used by Charlson et al. (1991, 1992) would be $4.1 \text{ m}^2 \text{ g}^{-1}$ (assuming NH_4HSO_4 as the sulfate species present), which is still higher than our value. Hence, our value for the sulfate light-scattering efficiency suggests a global-averaged anthropogenic radiative forcing due to sulfate that is approximately 50%–65% (depending on whether 5.0 or 4.1 is used as the sulfate light-scattering efficiency in the Charlson et al. calculations) of that estimated by Charlson et al. (1991) ($\sim 0.6 \text{ W m}^{-2}$), that is, about $0.3\text{--}0.4 \text{ W m}^{-2}$ at 550 nm. Kiehl and Briegleb (1993) used a more relevant wavelength-dependent sulfate light-scattering efficiency derived from an assumed aerosol size distribution and a composition of 75% H_2SO_4 , 25% H_2O . If, following Kiehl and Briegleb, the sulfate-scattering efficiency is calculated including the scattering due to the water, the scattering efficiency is $5 \text{ m}^2 \text{ g}^{-1}$ at 550 nm. On the other hand, if it is calculated without including the scattering due to water (as we define our sulfate efficiency), the value at 550 nm would be $3.8 \text{ m}^2 \text{ g}^{-1}$. Assuming that the sulfate scattering efficiency values at other wavelengths can be scaled to that at 550 nm, our value of the sulfate light-scattering efficiency would suggest a value for the wavelength-integrated global radiative forcing due to anthropogenic sulfate that is 70% of that predicted by Kiehl and Briegleb ($\sim 0.3 \text{ W m}^{-2}$), that is, approximately 0.2 W m^{-2} .

Care must be taken not to overemphasize the significance of the sulfate light-scattering efficiency derived from our regression analyses. Certainly, we do not advocate using a single value for this quantity. Several earlier, ground-based studies suggest considerable variability in the sulfate light-scattering efficiency, even for polluted airsheds alone (e.g., White 1986, 1990). Certainly higher values of the sulfate light-scattering efficiency are to be expected in polluted airsheds since, in general, more of the sulfate mass is in the efficient Mie scattering size range than it is in nonpolluted air. As we have noted previously (Hegg et al. 1993a), such variability probably precludes the adoption of a single

global value for the sulfate light-scattering efficiency. Furthermore, while global values of sulfate radiative forcing of about 0.2 W m^{-2} would render such forcing of secondary significance when compared, for example, to CO_2 -induced warming ($\sim 2 \text{ W m}^{-2}$), on local and regional scales radiative forcing by sulfate is clearly important.

One hitherto largely neglected aspect of the aerosol light-scattering efficiency is its vertical variability. Previous measurements of aerosol light-scattering efficiencies in the eastern United States have been ground based and have, in general, produced somewhat higher values of the sulfate light-scattering efficiency than the airborne measurements presented here. For example, ground-based data for seven sites in the eastern United States reported by White (1990) suggest a value for the sulfate light-scattering efficiency of $5 \text{ m}^2 \text{ g}^{-1}$. It is important to evaluate whether such surface values are applicable to the entire atmospheric vertical column.

Because of temporal and horizontal spatial inhomogeneities, examination of the altitude dependence of the sulfate light-scattering efficiency can only be done for individual flights. Table 1 shows five cases of measured changes in the sulfate light-scattering efficiency with altitude. These data are summarized in Table 2. In four out of the five cases, the sulfate light-scattering efficiency decreased with increasing altitude. The one case in which it increased with altitude was associated with a haze layer aloft (we shall return to this case later). Discarding the case with increasing scattering efficiency with height, the mean value of the decrease in the sulfate light-scattering efficiency with height was $47\% \pm 32\% \text{ km}^{-1}$. This result is quite different from the only previous data reported on the altitude dependence of the sulfate light-scattering efficiency of which we are aware, that of Trägårdh (1982) in southern Sweden, who found essentially no vertical variability in the sulfate light-scattering efficiency. However, the b_{sp} values used by Trägårdh were not reduced to account for the fact that only about 30% of the measured aerosol mass was sulfate. Variability in the sulfate mass fraction with altitude may well have obscured an altitude dependence in the sulfate light-scattering efficiency. Interestingly, if we use $47\% \text{ km}^{-1}$ for the vertical gradient in the sulfate light-scattering efficiency to extrapolate our regression-derived value of the sulfate light-scattering efficiency ($2.7 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$) from our mean measurement altitude of about 1.1 km to the surface, a sulfate light-scattering efficiency of $5.6 \text{ m}^2 \text{ g}^{-1}$ is obtained, which is somewhat higher than, but close to, White's (1990) measured surface values for the eastern United States ($5 \text{ m}^2 \text{ g}^{-1}$). This possible explanation for the difference between our measurements of the sulfate light-scattering efficiency and previous surface measurements has important ramifications. If the sulfate (or aerosol in general) light-scattering efficiency is a function of altitude, then the surface-derived values of sulfate scattering efficiency are not appropriate

TABLE 2. Variation with altitude of the sulfate light-scattering efficiency at a wavelength of 550 nm.

Date (1993)	Altitude (km)	$b_{sp}(\text{SO}_4^{2-})/[\text{SO}_4^{2-}]^*$ ($\text{m}^2 \text{ g}^{-1}$)	$-\frac{\Delta}{\Delta z} [b_{sp}(\text{SO}_4^{2-})/[\text{SO}_4^{2-}]]$ ($\% \text{ km}^{-1}$)
12 July	0.31	2.5	—
	1.56	2.2	10
20 July	0.63	3.3	—
	1.56	2.4	30
25 July	0.78	1.7	—
	1.56	0.66	79
	2.19**	1.9	-298
28 July (2d flight)	0.78	1.2	—
	1.56	0.57	67

* Equivalent to b_{sp} per aerosol mass.

** Haze present at this altitude.

for use in calculations of aerosol optical depth and consequent radiative forcing. If a constant value for the efficiency is to be used, it should be the mass-weighted average over the aerosol column. Given that the scale height for aerosol mass for all but remote background conditions is on the order of 1–2 km (Jaenicke 1993) and that our data suggest a roughly similar scale height for the aerosol scattering efficiency, our 1-km data on sulfate-scattering efficiency would seem a better choice for use in radiative forcing calculations than previously measured surface values.

A decrease in the sulfate light-scattering efficiency with increasing altitude is to be expected, at least for strong aerosol source regions such as the eastern United States. This is because most of the aerosol mass of submicron size is at the lower end of the efficient light-scattering range and the mass mean aerosol diameter generally decreases with increasing altitude in such airsheds (Meszaros 1981; Jaenicke 1993). Aerosol size distribution data, derived from the batch sizing system aboard the C-131A aircraft, allow us to explore this idea further.

Aerosol size spectra were measured for each of the datasets listed in Table 2. The spectra shown are distance-weighted least squares (DWLS) fits to the data points. Such fits closely follow the actual data points, as can be seen from the example shown in Fig. 3. Aerosol volume distributions measured at two flight levels on 12 July are shown in Fig. 4, where it can be seen that there is more aerosol volume at the lower altitude. Furthermore, a slightly higher percentage of this volume is commonly in the effective light-scattering range, which extends from about 0.4- to 1.4- μm diameter at a wavelength of 550 nm. For example, in the 20 July case, shown in Fig. 5, 26% of the submicron mass is in the efficient light-scattering range at an altitude of 0.63 km, whereas, only 19% is in this size range at an altitude of 1.56 km.

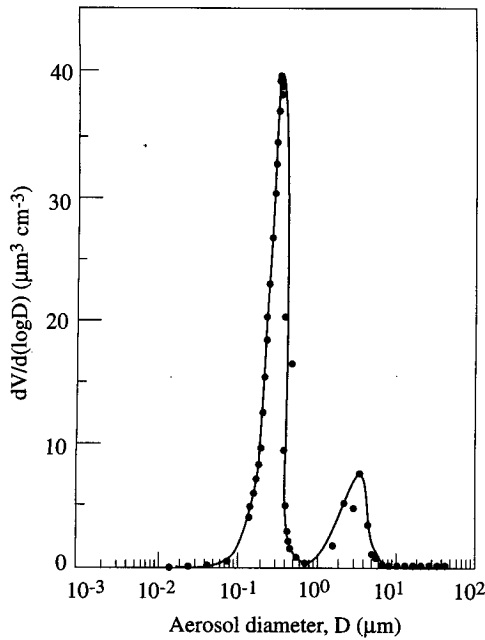


FIG. 3. Aerosol volume distribution at the altitude of 0.31 km for the flight of 12 July 1993. The curve shown is the distance-weighted least squares (DWLS) fit to the indicated data points.

An interesting variant on the monotonic decrease in the aerosol light-scattering efficiency with height is provided by the 25 July flight. Here the sulfate light-scattering efficiency decreased with height between 0.78 and 1.56 km, and then increased between 1.56 and

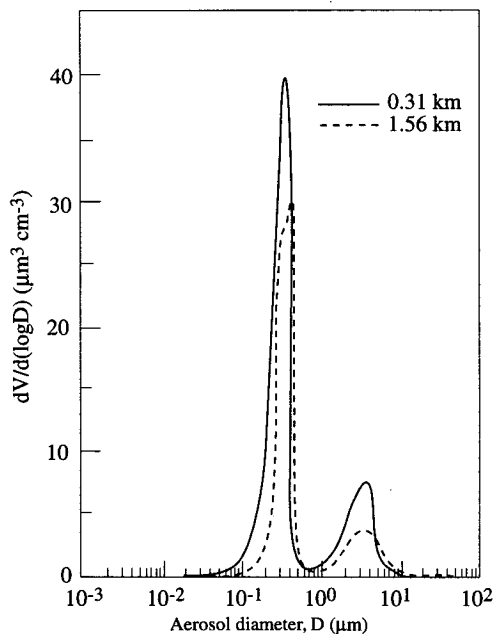


FIG. 4. Aerosol volume distributions (DWLS fits) at altitudes of 0.31 and 1.56 km for the flight of 12 July 1993.

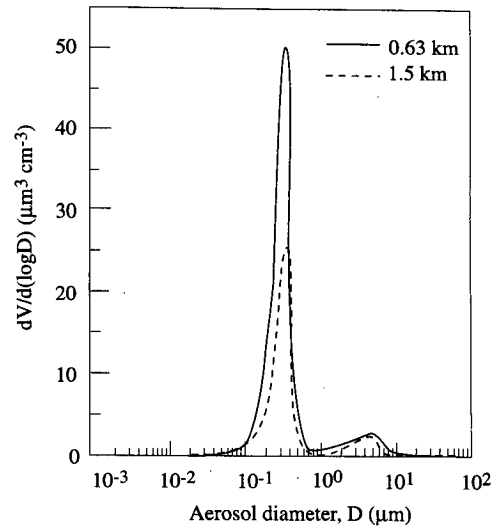


FIG. 5. Aerosol volume distributions (DWLS fits) at altitudes of 0.63 and 1.5 km for the flight of 20 July 1993.

2.19 km (Table 2). The aerosol volume distributions associated with these variations are shown in Fig. 6. The changes in aerosol volume over the light-scattering

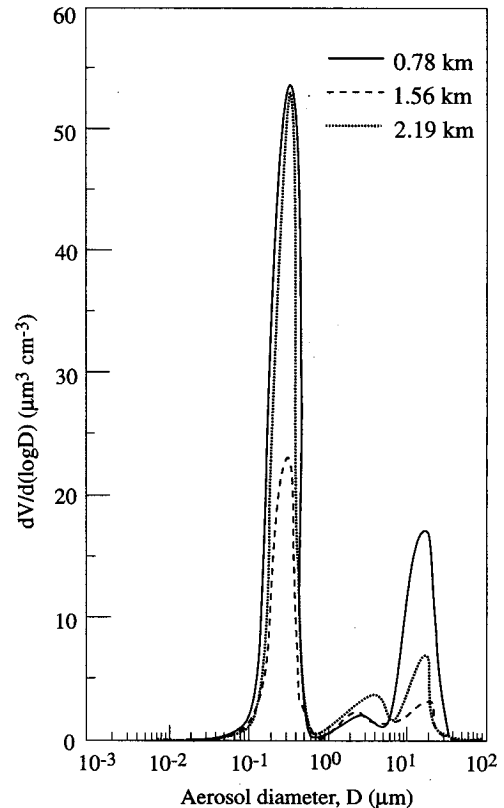


FIG. 6. Aerosol volume distributions (DWLS fits) at altitudes of 0.78, 1.56, and 2.19 km for the flight of 25 July 1993.

TABLE 3. Cloud condensation nucleus (CCN) concentration at 1% supersaturation and some ancillary parameters.

Date (1993)	Altitude (km)	[SO ₄ ²⁻] (μg m ⁻³)	Submicron aerosol mass (μg m ⁻³)	Total aerosol concentration (CN) (cm ⁻³)	CCN (cm ⁻³)	CCN/CN	k*
20 July	0.63	16.2	17.2	1211 ± 268	335	0.28	0.36
	1.56	9.1	10.4	1208 ± 486	344	0.28	0.71
25 July	1.56	14.4	16.0	701 ± 149	303	0.43	0.47
	2.19	4.7	12.4	946 ± 149	314	0.33	0.21

* Defined by $CCN(S) = c(S)^k$, where S (%) is the supersaturation of the air.

range are consistent with the measured changes in the aerosol light-scattering efficiency with altitude. In this case, there was a haze layer above 1.56 km. Such layers occurred several times during the course of our field study; they illustrate the danger of using surface aerosol data as representative of the atmospheric boundary layer, let alone the entire atmospheric column. The 28 July case (Fig. 7) is similar to the earlier cases.

b. Cloud condensation nuclei and sea-salt particles

Limited measurements of CCN were obtained during this study (Tables 1 and 3). The four measured values of the CCN concentrations at 1% supersaturation are quite similar, with a standard deviation less than 6% of the mean value of 324 cm^{-3} . As expected (because of the more polluted air), this value is much higher than that measured over the northeast Pacific Ocean (Hegg et al. 1991) and significantly higher than that measured over the northeast Atlantic Ocean under variable polluted conditions (Hegg et al. 1993a). On the other hand, these values are lower than some previous measurements in the same area under even more polluted conditions (e.g., Radke and Hobbs 1976). The values of k listed in Table 3 do not differ significantly from those measured in background marine air (e.g., Hegg et al. 1991).

The ratios of CCN (at 1% supersaturation) to total particle concentrations (CN) listed in Table 3 average 0.33. This value is similar to that found by Hegg et al. (1991) over the northeast Pacific Ocean, and it is only slightly lower than values calculated by Hegg et al. (1991) from measurements made at Cape Grim, Australia, by Gras (1987, 1989). The sulfate CCN nucleation efficiency is also of interest. In previous studies (cf. Hegg et al. 1993a) we had sufficient data to regress CCN concentrations onto sulfate masses to derive an estimate of the sulfate CCN nucleation efficiency. We found this efficiency to be significantly less in the relatively polluted air encountered over the Atlantic Ocean than in cleaner air over the northeast Pacific Ocean. Furthermore, a substantially higher percentage of the CCN over the Atlantic Ocean were nonsulfate. While the data for the present study are insufficient to permit a formal analysis, it is interesting to note that

a change in sulfate mass of about a factor of 3 produced essentially no change in CCN concentrations. This suggests that most of the CCN that we measured over the northeastern Atlantic coast of the United States were not sulfate. Recent measurements of CCN composition in the Caribbean, which suggest a large organic contribution to CCN, are consistent with this hypothesis (Novakov and Penner 1993).

Our measurements of sea-salt particle number concentrations measured just off the Atlantic coast in this study ranged from a few tenths to about 2 cm^{-3} (Table 4), which are similar to measurements made over the

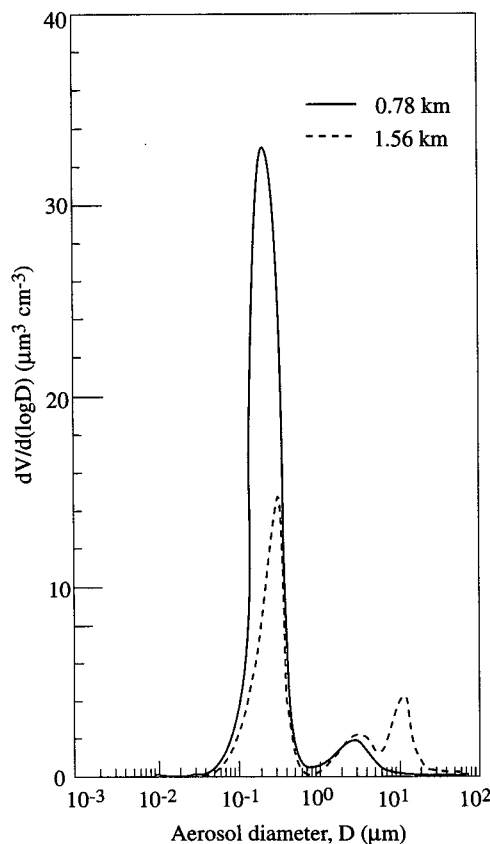


FIG. 7. Aerosol volume distributions (DWLS fits) at altitudes of 0.78 and 1.56 km for the flight of 28 July 1993.

Pacific Ocean by Hobbs (1971). Discounting the low-altitude value measured on 16 July, which was over freshwater, there was a general decrease in sea-salt particle concentrations with increasing altitude (Fig. 8). The data in Table 4 also shows that less than 2% of the total particles greater than $0.11 \mu\text{m}$ were sea salt, which is also similar to the results obtained by Hobbs (1971). These measurements indicate a lesser role for sea-salt CCN than that suggested by various surface-based analyses (e.g., Meszaros and Vissy 1974; Parungo et al. 1986; O'Dowd and Smith 1993). However, the dependence of sea-salt number concentrations on wind speed (which was low during our measurements) precludes any definitive conclusions from being drawn from the limited data available.

4. Conclusions

Analysis of airborne data from the northeast Atlantic seaboard of the United States has yielded values for several important parameters related to radiative forcing by aerosols. Concurrent measurements of aerosol light-scattering, total submicron aerosol mass, and sulfate mass have been used to derive the light-scattering efficiencies of the submicron aerosol and of sulfate (measured at a relative humidity of about 40% or less). The sulfate light-scattering efficiency (assumed a priori to be equivalent to the submicron aerosol mass scattering efficiency) at a wavelength of 550 nm was found to lie in the range $2.2\text{--}3.2 \text{ m}^2 \text{ g}^{-1}$, which is considerably less than values used in recent estimates of radiative forcing by anthropogenic sulfate (cf. Charlson et al. 1991, 1992). We have related some of the variability in the sulfate light-scattering efficiency to changes in the aerosol size distribution. A particularly important facet of the variability in the sulfate light-scattering efficiency is its dependence on altitude. Our measurements suggest that the sulfate light-scattering efficiency generally decreases with altitude, although exceptions

TABLE 4. Sea-salt particle concentrations and some ancillary parameters over the ocean off the northeast Atlantic seaboard of the United States.

Date (1993)	Altitude (km)	Sea-salt particle concentrations (cm^{-3})	Concentration of particles with diameter $\geq 0.11 \mu\text{m}$ (from DMPS) (cm^{-3})
16 July	0.2	0.65*	1142
	0.5	2.10	1262
	1.1	1.24	908
	1.8	1.91	89
19 July	0.06	1.61	717
	0.48	1.30	1346
	1.30	0.48	—
25 July	0.5	0.56	—
	1.5	0.16	535

* Over Delaware River.

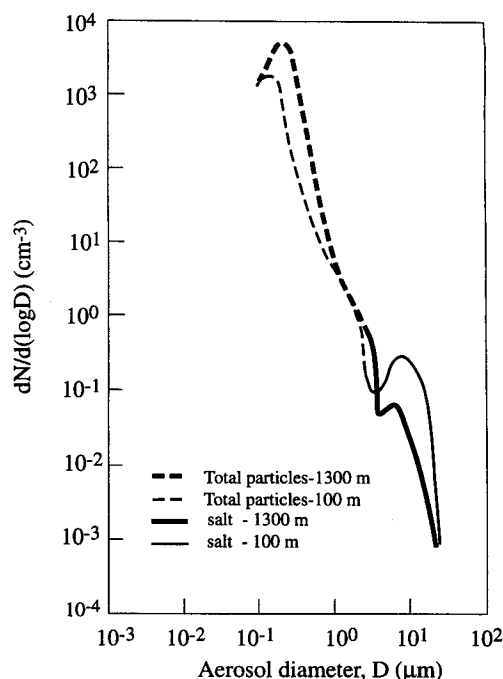


FIG. 8. Aerosol number distributions (DWLS fits) at altitudes of 0.1 and 1.3 km for the flight of 19 July 1993. The solid curves are sea-salt particles and the dashed curves total aerosol particles.

may occur due to haze layers aloft. The variations with altitude of the sulfate light-scattering efficiency could have a major impact on assessments of global radiative forcing by anthropogenic sulfate and should be investigated more fully.

Limited data obtained in this study suggest that most of the CCN were not sulfate. Earlier measurements over the northeast Atlantic Ocean led to a similar conclusion (Hegg et al. 1993a). Measurements to establish the major chemical components of CCN should receive high priority in future field studies.

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REFERENCES

- Anderson, T. L., R. J. Charlson, W. H. White, and P. H. McMurry, 1994: Comment on "Light scattering and cloud condensation nucleus activity of sulfate aerosol measured over the northeast Atlantic Ocean." *J. Geophys. Res.*, **99**, 25 948–25 950.
- Charlson, R. J., J. Langer, H. Rodhe, C. B. Leovy, and S. G. Warren, 1991: Perturbation of the Northern Hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols. *Tellus*, **43**(AB), 152–163.
- , S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley Jr., J. E. Hansen, and D. J. Hofmann, 1992: Climate forcing by anthropogenic aerosols. *Science*, **255**, 423–430.
- Ferek, R. J., D. A. Hegg, J. Herring, and P. V. Hobbs, 1991: An improved filter pack technique for airborne measurement of low concentration SO_2 . *J. Geophys. Res.*, **96**, 22 373–22 378.

- Gras, J. L., 1987: Particulates. *Baseline Atmospheric Program (Australia) 1985*. B. W. Forgan and G. P. Ayers, Eds., Australian Bureau of Meteorology and CSIRO Division of Atmospheric Research, 4.11–4.12.
- , 1989: Particulates. *Baseline Atmospheric Program (Australia) 1987*. B. W. Forgan and G. P. Ayers, Eds., Australian Bureau of Meteorology and CSIRO Division of Atmospheric Research, 47–48.
- Hanel, G., 1976: The properties of atmospheric aerosol particles as function of the relative humidity at thermodynamic equilibrium with the surrounding moist air. *Adv. Geophys.*, **19**, 73–188.
- Hegg, D. A., L. F. Radke, and P. V. Hobbs, 1991: Measurements of Aitken nuclei and cloud condensation nuclei in the marine atmosphere and their relationship to the DMS cloud-climate hypothesis. *J. Geophys. Res.*, **96**, 18 727–18 733.
- , ———, and ———, 1993a: Light-scattering and cloud condensation nucleus activity of sulfate aerosol measured over the northeast Atlantic Ocean. *J. Geophys. Res.*, **98**, 14 887–14 894.
- , ———, and ———, 1993b: Aerosol size distributions in the cloudy atmospheric boundary layer of the North Atlantic Ocean. *J. Geophys. Res.*, **98**, 8841–8846.
- , ———, and ———, 1994: Reply to “Comment on light scattering and cloud condensation nucleus activity of sulfate aerosol measured over the northeast Atlantic Ocean” by Anderson et al. *J. Geophys. Res.*, **99**, 25 951–25 954.
- Hobbs, P. V., 1971: Simultaneous airborne measurements of cloud condensation nuclei and sodium-containing particles over the ocean. *Quart. J. Roy. Meteor. Soc.*, **97**, 263–271.
- , L. F. Radke, L. H. Lyons, R. J. Ferek, and D. J. Coffman, 1991: Airborne measurements of particle and gas emissions from the 1990 volcanic eruptions of Mount Redoubt. *J. Geophys. Res.*, **96**, 18 735–18 752.
- Jaenicke, R., 1993: Tropospheric aerosols. *Aerosol–Cloud–Climate Interactions*. P. V. Hobbs, Ed., Academic Press, 1–27.
- Kiehl, J. T., and B. P. Briegleb, 1993: The relative roles of sulfate aerosols and greenhouse gases in climate forcing. *Science*, **260**, 311–314.
- Kvalseth, T. O., 1985: Cautionary note about R^2 . *Amer. Stat.*, **39**, 279–285.
- Liu, P. S. K., W. R. Leitch, J. W. Strapp, and M. A. Wasey, 1992: Response of particle measuring systems airborne ASASP and PCASP to NaCl and latex particles. *Aerosol Sci. Technol.*, **16**, 83–95.
- Malm, W. C., J. L. Sisler, D. Huffman, R. A. Eldred, and T. A. Cahill, 1994: Spatial and seasonal trends in particle concentration and optical extinction in the United States. *J. Geophys. Res.*, **99**, 1347–1370.
- Meszáros, E., 1981: *Atmospheric Chemistry*. Akademiai Kiado, 114–124.
- , and K. Vissy, 1974: Concentration, size distribution and chemical nature of atmospheric aerosol particles in remote oceanic areas. *J. Aerosol Sci.*, **5**, 101–110.
- Novakov, T., and J. E. Penner, 1993: Large contribution of organic aerosols to cloud-condensation-nuclei concentrations. *Nature*, **385**, 823–826.
- O’Dowd, C. D., and M. H. Smith, 1993: Physicochemical properties of aerosols over the Northeast Atlantic: Evidence for wind-speed-related submicron sea-salt aerosol production. *J. Geophys. Res.*, **98**, 1137–1149.
- Quimette, J. R., and R. C. Flagan, 1982: The extinction coefficient of multicomponent aerosols. *Atmos. Environ.*, **16**, 2405–2419.
- Parungo, J. P., C. T. Nagamoto, and J. M. Harris, 1986: Temporal and spatial variations of marine aerosols over the Atlantic Ocean. *Atmos. Res.*, **20**, 11–22.
- Penner, J. E., and Coauthors, 1993: Quantifying and minimizing uncertainty of climate forcing by anthropogenic aerosols. DOE Report DOE/NBB-0092T UC-402, 1–53. [Available from NTIS, 5285 Port Royal Rd., Springfield, VA 22161.]
- Radke, L. F., 1983: Preliminary measurements of the size distributions of cloud interstitial aerosol. *Precipitation Scavenging, Dry Deposition and Resuspension*, H. R. Pruppacher, R. J. Semonin, and W. G. N. Slinn, Eds., Elsevier, 1037–1046.
- , and P. V. Hobbs, 1976: Cloud condensation nuclei on the Atlantic seaboard of the United States. *Science*, **193**, 999–1002.
- , J. H. Lyons, D. A. Hegg, and P. V. Hobbs, 1984: Airborne monitoring and smoke characterization of prescribed fires on forest lands in western Washington and Oregon. United States EPA Report 600-X-83-047, 1–122. [Available from Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. EPA, Las Vegas, NV 89114.]
- Reischl, G. P., 1991: Measurement of ambient aerosols by the differential mobility analyzer method: Concepts and realization criteria for the size range between 2 and 500 nm. *Aerosol Sci. Technol.*, **14**, 5–24.
- Slinn, W. G. N., L. F. Radke, and P. C. Katen, 1983: Inland transport, mixing, and dry deposition of sea-salt particles. *Precipitation Scavenging, Dry Deposition, and Resuspension*, H. R. Pruppacher, R. J. Semonin, and W. G. N. Slinn, Eds., Elsevier, 1037–1046.
- Sloane, C. S., 1984: Optical properties of aerosol of mixed composition. *Atmos. Environ.*, **8**, 871–878.
- , 1986: The effect of composition on aerosol light scattering efficiencies. *Atmos. Environ.*, **20**, 1025–1037.
- , and G. T. Wolff, 1985: Prediction of ambient light scattering using a physical model responsive to relative humidity: Validation with measurements from Detroit. *Atmos. Environ.*, **19**, 669–680.
- Trägårdh, C., 1982: Air chemistry measurements in the lower atmosphere over Sweden—Data evaluation. *Atmos. Environ.*, **16**, 1–7.
- Twomey, S., 1991: Aerosols, clouds and radiation. *Atmos. Environ.*, **25**(A), 2435–2442.
- Waggoner, A. P., and R. E. Weiss, 1980: Comparison of fine particle mass concentration and light scattering extinction in ambient aerosol. *Atmos. Environ.*, **14**, 623–626.
- White, W. H., 1986: On the theoretical and empirical basis for apportioning extinction by aerosols: A critical review. *Atmos. Environ.*, **20**, 1659–1672.
- , 1990: Contributions to light extinction. *Visibility: Existing and Historical Conditions—Causes and Effects*. NAPAP Report 24, 24–85. [Available from NTIS, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.]
- Winklmayer, W., G. P. Reischl, A. O. Lindner, and A. Berner, 1991: A new electromobility spectrometer for the measurement of aerosol size distributions in the size range from 1 to 1,000 nm. *J. Aerosol Sci.*, **22**, 289–296.
- Zhang, X., B. J. Turpin, P. H. McMurry, S. V. Herring, and M. R. Stolzenburg, 1994: Mie theory evaluation of species contributions to 1990 wintertime visibility reduction in the Grand Canyon. *J. Air Waste Manage. Assoc.*, **44**, 153–162.