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The effect of anthropogenic sulfate aerosols on marine cloud droplet concentrations

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ABSTRACT

Nonseasalt sulfate (nss SO_4^{2-}) mass concentrations, cloud condensation nuclei (CCN) number concentrations, and cloud droplet concentrations in warm cumulus and stratocumulus clouds were simultaneously measured in situ in marine air masses on El Yunque peak in Puerto Rico. Our results show that CNN number concentrations (measured at 0.5% supersaturation) and nss SO_4^{2-} mass concentrations (in the range of ~400–1700 ng m^{-3}) are significantly correlated at this site. Droplet concentrations in the cumulus clouds studied do not show a discernible trend with nss SO_4^{2-} mass concentrations (in the range of ~300–1400 ng m^{-3}). In stratocumulus clouds, a small increase in droplet concentration with nss SO_4^{2-} mass concentrations in the range of ~300–1100 ng m^{-3} was observed. We attribute the low sensitivities of the droplet number concentrations to nss SO_4^{2-} mass concentrations to the entrainment/mixing processes in these clouds. The magnitudes of the empirically derived sensitivities are considerably lower than those assumed in recent assessments of the effect of anthropogenic sulfate aerosols on cloud albedo.

1. Introduction

Atmospheric aerosols may influence climate directly by scattering and absorption of solar radiation and indirectly by affecting the number concentrations of cloud droplets and thus the cloud albedo (Twomey, 1974, 1977a). Charlson et al. (1992) have recently suggested that the direct and indirect effects of increased concentrations of anthropogenic sulfate (SO_4^{2-}) aerosols, resulting from industrial activity and fossil fuel combustion, may already have masked global greenhouse warming to a considerable degree. These authors have estimated that the indirect effect alone may decrease global shortwave radiative forcing (cooling effect) by ~1 W m^{-2} if increased anthropogenic SO_4^{2-} concentrations in the Northern Hemisphere were to cause a uniform average 30% hemispheric increase in droplet concentrations in marine stratus and stratocumulus clouds, i.e., an increase equal to the relative difference between average SO_4^{2-} mass concentrations observed in the Northern and Southern Hemispheres.

Quantification of the indirect forcing is difficult, in part because of the scarcity of empirically established relationships among mass concentrations of anthropogenic SO_4^{2-} aerosol, number concentrations of cloud condensation nuclei (CCN), and cloud droplet concentrations, particularly over oceanic regions. Limited data on marine stratus clouds over and near San Diego, California (with droplet concentrations ranging from ~300–500 cm^{-3}), show a qualitative relationship between CCN and cloud droplet concentrations (Hudson, 1983). In the cleaner Pacific Ocean air (off the coast of northwestern United States), with SO_4^{2-} concentrations rarely exceeding a

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few hundred ng m^{-3} and droplet concentrations between $\sim$20–80 cm^{-3}, significant correlations between mean stratus droplet concentration and below-cloud CCN concentration as well as between average CCN and nonseasalt (nss) SO_4^{2-} mass concentrations were observed (Hegg et al., 1991a). Also, in the Pacific air correlations among CCN concentrations, methane sulfonate, and dimethyl sulfide have been observed (Ayers and Gras, 1991; Hegg et al., 1991b).

In North American continental air masses characterized by high SO_4^{2-} mass concentrations and clouds with high droplet number concentrations, the relationship between aerosol SO_4^{2-} mass and cloud droplet number concentration was found to be roughly linear at low aerosol loadings (below $\sim 5\ \mu g\ m^{-3}$) but leveled out at higher loadings (Leaitch et al., 1986). In these anthropogenically influenced regions, relationships between droplet concentrations in both cumuliform and stratiform clouds (median concentration, 400 cm^{-3} and 250 cm^{-3} respectively) and cloud water SO_4^{2-} have been observed over a wide concentration range (Leaitch et al., 1992).

Empirical establishment of sulfate-droplet relationships in marine air is of particular interest in view of recent analyses suggesting that anthropogenic SO_4^{2-} emissions may enhance cloud albedos immediately adjacent to the east coast of the United States but not over the Northern Hemispheric ocean regions (Falkowski et al., 1992), in spite of evidence that these regions are influenced by anthropogenic sulfur emissions (Schwartz, 1988; Savoie and Prospero, 1989).

In this paper we report the results of simultaneous measurements at an anthropogenically influenced tropical site of nss SO_4^{2-} mass concentrations, CCN number concentrations, and droplet number concentrations of marine cumulus and stratocumulus clouds. Our results demonstrate that CCN number concentrations (measured at 0.5% supersaturation) and nss SO_4^{2-} mass concentrations (in the range of $\sim$400–1700 ng m^{-3}) are significantly correlated at this site. However, droplet concentrations in cumulus clouds studied do not show any discernible trend with nss SO_4^{2-} mass concentrations in the range of $\sim$270–1300 ng m^{-3}. In stratocumulus clouds a small increase in droplet concentration with nss SO_4^{2-} mass concentration in the range of $\sim$300–1100 ng m^{-3} may be inferred.

2. Measurement results

Simultaneous aerosol and cloud microphysical measurements in the same air mass were performed during July 1991 and March/April 1992 at a fixed point on El Yunque peak (18°19′N, 65°45′W) in Puerto Rico at an elevation of $\sim$1000 m above sea level. This peak is located on the eastern end of the island, directly exposed to winds from the ocean, and is frequently impacted by low, warm cumulus and stratocumulus clouds (Odum et al., 1970).

In our experiments, we measured in real time the cloud droplet concentration N_d and size distribution in the diameter range 2–32 μm (in 1991 and 1992) and CCN number concentrations (in 1992). Total aerosol filter samples were collected every day at 6-hr intervals (00–06; 06–12; 12–18; 18–24 h). Droplet concentration and size distribution were measured with the CSASP 100 HV spectrometer (Particle Measurement Systems). The horizontally positioned CSASP inlet horn was oriented into the direction of the prevailing wind. Measurements were taken with 10-, 5-, and 3-sec time resolutions. 5- and 3-second resolutions were used at higher droplet concentrations to prevent the "overflow" in channels with maximum counts. The CSASP data were analyzed using the manufacturer's calibration. CCN concentrations were measured with the M-1 counter (DH Associates), operated at a fixed supersaturation of 0.5%. The M-1 counter sampled the air fom a plenum (7.8 l volume) equipped with a cyclone (Bendix 240), through which the air was drawn at a flow rate of 113 l min^{-1}. The cyclone removes the cloud droplets from the air stream, so that during cloud events the interstitial aerosol is sampled. The cutoff diameter D_{50} of this cyclone for the flow rate used in our measurements was determined to be 2.5 μm from the results of Chan and Lippman (1977). Because of the small sample volume and the specific features of the M-1 counter, 17-min average CCN concentrations were recorded.

Aerosol samples were collected on Millipore filters (1.2 μm pore size) through a vertical stack (92 cm high, 5 cm diameter), heated to $\sim$10°C above ambient temperature at a flow rate of 42 l min^{-1}. The slight heating of the air in the stack evaporates the water condensed on the particles and prevents the wetting of the filter during

sampling. An inverted cylinder 19 cm wide and 8.5 cm high was mounted above the stack with the open end facing the stack inlet to prevent rain drops from entering the sampler. The stack inlet was positioned approximately at the same level as the open-end base of the rain shield.

According to the Agarwal-Liu criterion, the aspiration efficiencies of >0.95 through a vertically facing thin-walled tube in calm air are achieved for $St_c R_c < 0.05$ (Vincent, 1989). St_c is the Stokes number related to the entry velocity and R_c is the equivalent velocity ratio. For the dimension of the sampling stack and the flow rate used, the value of $St_c R_c$ is 0.017 for particles with aerodynamic diameter of 30 μm. Therefore, the Agarwal-Liu criterion is satisfied for particles of all sizes of interest. The effect of wind on the aspiration efficiency of the sampler is relatively small because of the low average wind speed on El Yunque, ~ 1.2 m s^{-1} (Odum et al., 1970). Sampling efficiencies for a horizontal wind velocity of 1 m sec^{-1}, estimated from eq. (6.26) in Vincent (1989) are 0.92, 0.83, and 0.74 for aerodynamic diameters of 10, 15, and 20 μm respectively. Because the CSASP measurements at this site show that droplets with diameters > 15 μm constitute typically about 5–6% of the total droplet number, the sampler should collect essentially all aerosol particles and most cloud droplets with reasonably high efficiency.

Aerosol filter samples were analyzed by X-ray fluorescence (XRF) for elemental composition, and by ion chromatography (IC) for major water-soluble anions and cations. The nss SO_4^{2-} mass concentrations were obtained by correcting the total SO_4^{2-} for seasalt SO_4^{2-} estimated from Na^+ and Cl^- concentrations determined by IC, and from Cl measured by XRF. The nss SO_4^{2-} concentrations estimated by using the corrections based on sodium, chloride, and chlorine concentrations differed on the average by less than 10%. Similar results were obtained by Ayers et al. (1991) at a different location. These results indicate that the aerosol at the site was not acidic enough to produce the loss of chloride by acid + NaCl = HCl(g) reaction. Martens et al. (1973) observed significant Cl^- loss from Puerto Rican marine aerosol in 1971, in contrast to our observations.

The average nss SO_4^{2-} concentrations measured at the site were 980 ($\pm$400) and 940 ($\pm$500) ng m^{-3} respectively for the 1991 (July 13–26) and 1992 (28 March–11 April) experiment. (The values in parentheses are standard deviations.) These values are within the range of the average nss SO_4^{2-} concentration of 750 ($\pm$600) ng m^{-3} measured over several years on the coast of Barbados, where it was also shown that sulfate aerosol is derived from a mixture of biogenic and long-distance transported anthropogenic sources (Savoie et al., 1989). The close agreement between the average SO_4^{2-} concentration measured at the two geographically close sites suggests that the aerosol sulfate observed on El Yunque is derived from a similar mix of sources. Anthropogenic influences at the site are also suggested by occurrences of relatively high droplet and CN concentrations. CN concentrations (measured by the TSI Condensation Particle Counter CPC-3022 for a purpose not directly related to this work) ranged from ~ 300 to ~ 3600 cm^{-3} during the course of the experiment.

The nss SO_4^{2-} concentrations for different 6-h sampling periods can be compared to the CCN concentrations and the average droplet concentrations detected on the same days during approximately similar counting periods (5–6 h). Such a comparison is shown in Fig. 1, where the clear sky CCN concentrations (full circles) are plotted against the nss SO_4^{2-} mass concentrations. (We note that at 0.5% supersaturation the CCN

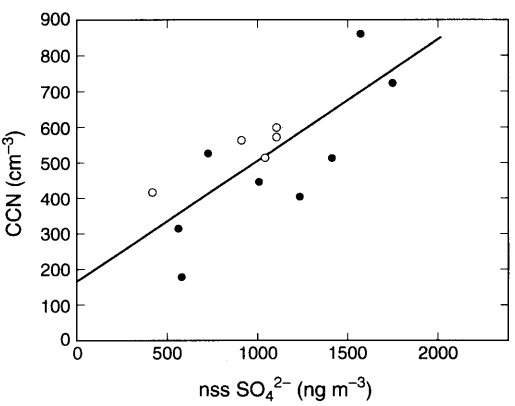

Fig. 1. Dependence of clear sky CCN number concentrations (full circles) and total (activated + nonactivated) CCN concentrations (open circles) measured at 0.5% supersaturation on nonseasalt sulfate mass concentrations. Correlation coefficients are 0.82 for clear sky and 0.76 for all points.

counter will count particles with diameters > 0.05 μm, assuming that they consist of pure ammonium sulfate.) For in-cloud periods, we show the points (open circles) representing the sum of interstitial CCN and droplet number concentrations (i.e., total activated and unactivated CCN concentrations). CCN number concentration (cm^{-3}) dependence on nss SO_4^{2-} mass concentration ($ng\,m^{-3}$) for the eight clear air points can be represented by the linear relationship $CCN = 0.39\ (\pm 0.11) \times SO_4^{2-} + 60.2\ (\pm 133.55)$ and a correlation coefficient of 0.82 (significant at better than 95% confidence level). The uncertainties in the linear regression coefficients in this and in subsequent relationships represent standard errors (The number of degrees of freedom was taken to be the number of data points minus two.). Linear regression analysis of all 13 points resulted in the relation $CCN = 0.33\ (\pm 0.08) \times SO_4^{2-} + 166.2\ (\pm 94.3)$. The correlation coefficient of 0.76 is significant at 99% confidence level. We conclude that at this site the CCN number concentrations and nss SO_4^{2-} mass concentrations co-vary and that nss SO_4^{2-} mass concentrations can be used as a surrogate for CCN number concentration.

Having demonstrated the proportionality between CCN number and nss SO_4^{2-} mass concentrations, we next examine the relationships between CCN, nss SO_4^{2-}, and droplet concentrations. In Table 1 we show the mean CCN and droplet number concentrations (N_d) measured on three days during the pre-cloud periods and the immediately following in-cloud periods. For these periods the pre-cloud CCN concentrations were essentially equal to the sum of in-cloud (interstitial) CCN and droplet concentrations. As expected, the decrease in CCN concentration, ΔCCN, from pre-cloud to in-cloud conditions closely matches the increase in cloud droplet concentration, ΔN_d, showing that a fraction of these CCN is involved in droplet formation. These results also demonstrate the consistency of number concentration measured by the two instruments. However, as shown in Table 1, the CCN scavenging ratios, ΔCCN/CCN (pre-cloud), can vary from 0.24 to 0.7 independently of pre-cloud CCN concentrations, indicating that a variable fraction of the aerosols (as defined by the CCN counter) forms cloud droplets.

The N_d values shown in Table 1 are total number concentrations of particles with radii greater than 1 μm measured by CSASP. These could include cloud droplets, dust particles, and unactivated haze particles with radii > 1 μm. The possibility that dust particles are included in N_d values is eliminated because, during prolonged cloud-free periods, the total particle concentrations detected by the CSASP were quite low, averaging less than 2 cm^{-3}. Unactivated haze particles may in principle fall into this size interval. The pre-cloud N_d concentrations between ~ 10 and $\sim 50\ cm^{-3}$, measured in the breaks between clouds (shown in Table 1), provide a conservative estimate of the contribution of haze particles. These concentrations are upper limits because some of the cloud droplets were undoubtedly present in the pre-cloud air. For comparison we note that directly measured number concentrations of particles and haze droplets with radii > 1 μm below cloud base of the more polluted California stratus were approximately between 10 and 20 cm^{-3} (Hudson, 1983). Additionally, we used SO_4^{2-} mass size distributions measured during

Table 1. *Pre-cloud and in-cloud CCN and droplet number concentrations; the decrease in CCN closely matches the number of droplets formed*

	Pre-cloud			In-cloud					
Date	local time	CCN[a] (cm^{-3})	N_d (cm^{-3})	local time	CCN[a,b] (cm^{-3})	N_d (cm^{-3})	ΔCCN	ΔN_d	ΔCCN/CCN
28 March 1992	1254–1438	531	37	1438–1639	406	192	125	155	0.24
30 March 1992	1347–1456	504	51	1456–1658	152	392	352	341	0.70
3 April 1992	1531–1639	337	9	1639–1806	193	164	144	155	0.43

[a] Measured at $\sim 0.5\%$ supersaturation.
[b] Interstitial CCN.

the 1992 experiment (details in Rivera-Carpio, C., Novakov, T., Chow, J. C. and Rogers, C. F., Lawrence Berkeley Laboratory Report LBL-33905, submitted to *J. Geophys. Res.*) to calculate the number concentrations of particles (assuming that these are ammonium sulfate) with critical radii > 1.0 μm. For sulfate mass concentration of 1000 ng m^{-3}, the calculated haze particle concentration was found to be $\sim$30 cm^{-3}. Based on the foregoing evidence, we may conclude that the unactivated haze particles contribute significantly less than 50 cm^{-3} to the N_d concentrations measured by the CSASP.

Unlike the CCN number concentrations, the cloud droplet number concentrations show a different relationship with SO_4^{2-} mass concentration. This is evident from Fig. 2, where the mean droplet concentrations for 16 cloud events are plotted against the corresponding nss SO_4^{2-} mass concentrations. The data fall into two groups: those with lower (155 cm^{-3}) and higher (310 cm^{-3}) average N_d concentrations. To calculate the average N_d concentrations, only the data points with concentrations exceeding 20 cm^{-3} were used. These data were obtained from 13 through 26 July 1991, and from 28 March through 11 April 1992. During these 23 days, we encountered 16 periods of cloud impacts of sufficient duration for which the 6-h SO_4^{2-} concentrations could be compared with droplet concentrations averaged over similar time periods (4–6 h). The cloud microphysical data and nss SO_4^{2-} concentrations for individual days are summarized in Table 2. Here we list the average droplet number concentrations (N_d), liquid water content (LWC), and effective droplet radius (r_{eff}), defined as $\int r^3 n(r)\,dr / \int r^2 n(r)\,dr$, all derived from the CSASP measurements.

As the data in Table 2 indicate, during the 1991 measurement period, all clouds sampled had relatively low droplet concentrations ($\sim$160–220 cm^{-3}) and average LWC ($\sim$0.07 g m^{-3}). In 1992, 5 out of 8 cloud events had approximately two times higher N_d concentration ($\sim$350–420 cm^{-3}) and average LWC ($\sim$0.15). By comparing the appearance of the clouds at the site with photographs of typical marine clouds (WMO, 1987), we conclude that low N_d and LWC clouds are in the cumulus category (fair weather humilis or fractus; mediocris or congestus). The high N_d and LWC clouds were of considerable spatial extent, visually denser (very low visibility at the site) and had the appearance of stratocumulus (cumulogenitus) clouds. For the purpose of this discussion, we shall refer to this cloud type simply as "stratocumulus". These two general cloud categories most commonly impact El Yunque peak, with the former occurring more frequently (Odum et al., 1970).

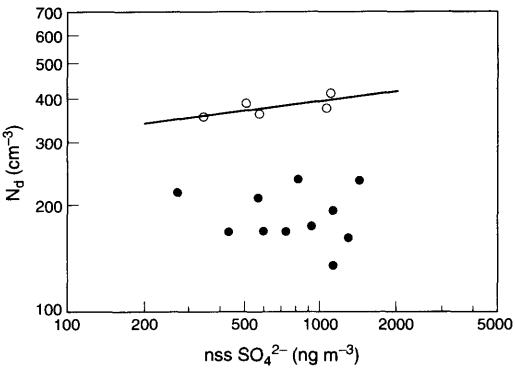

Fig. 2. Mean droplet number concentrations plotted against the average nss SO_4^{2-} mass concentrations determined for the duration of the individual cloud events. Data points shown with full circles are for cumulus clouds for which no dependence of N_d on nss SO_4^{2-} is seen. Open circles represent the data for stratocumulus clouds. The slope of the log(N_d) versus log(nss SO_4^{2-}) linear regression defines the sensitivity of the relative change in N_d to relative change in nss SO_4^{2-} mass concentration.

When in cumulus clouds, the site was $\sim$100 m to $\sim$230 m (average, $\sim$150 m) above the cloud base; for stratocumulus clouds, the cloud base was $\sim$300 m below the site. (The height of the cloud base was recorded on a number of occasions with an altimeter during the trips to and from the site.) We note that the relatively small droplet radii of $\sim$5 μm (Table 2) observed in our study are not unusual for marine clouds at such heights above the cloud base. Similar droplet radii were observed in the first few hundred meters above cloud base in some marine stratocumulus clouds (Slingo et al., 1982), as well as in trade wind and fair weather cumulus clouds (Stephens and Platt, 1987). The values of the liquid water content listed in Table 2 could be lower than actual because these were derived from CSASP measurements, which tend to underestimate LWC (Stephens and Platt, 1987).

As the data in Fig. 2 show, the droplet concentrations in the two cloud types may differ by a

Table 2. *Cloud droplet number concentrations, liquid water content, effective radius, and aerosol nss SO_4^{2-} concentrations, measured in 1991 and 1992*

Date	n[b]	N_d (cm^{-3})	LWC ($g\,m^{-3}$)	r_{eff} (μm)	nss SO_4^{2-} ($ng\,m^{-3}$)[d]
13 July 1991	476	163 (120)[c]	0.188 (0.198)	6.7 (1.0)	1283
14 July 1991	1118	235 (101)	0.079 (0.046)	4.7 (0.7)	1411
17 July 1991	1666	236 (99)	0.091 (0.048)	4.8 (0.6)	816
19 July 1991[a]	639	218 (124)	0.039 (0.030)	3.7 (0.7)	269
19 July 1991	799	210 (105)	0.049 (0.038)	4.0 (1.5)	563
24 July 1991[a]	488	170 (62)	0.075 (0.029)	5.2 (0.7)	594
26 July 1991[a]	584	170 (69)	0.077 (0.046)	5.2 (0.6)	730
26 July 1991	1733	136 (74)	0.068 (0.054)	5.3 (0.7)	1116
28 March 1992	1976	194 (122)	0.085 (0.078)	5.0 (0.5)	1116
30 March 1992	3067	417 (166)	0.140 (0.088)	4.6 (0.7)	1105
3 April 1992	1362	175 (91)	0.051 (0.039)	4.2 (0.7)	925
4 April 1992[a]	2747	355 (229)	0.112 (0.087)	4.5 (0.6)	341
4 April 1992	1723	168 (77)	0.076 (0.075)	5.0 (0.8)	433
8 April 1992[a]	2347	360 (127)	0.175 (0.100)	5.2 (0.8)	575
8 April 1992	5257	379 (149)	0.175 (0.095)	5.1 (0.7)	1052
11 April 1992	2545	390 (136)	0.145 (0.074)	4.8 (0.6)	505

[a] Morning data; all others are for afternoons.
[b] Number of measurements used to derive the average N_d, LWC, and r_{eff}. Measurement frequency, 10 s in 1991; and 3–5 s in 1992.
[c] Numbers in parentheses are standard deviations.
[d] Analytical error, $\pm 4\%$.

factor of two for the same nss SO_4^{2-} concentrations. For cumulus (low N_d) clouds, increasing the nss SO_4^{2-} mass concentrations from ~ 270 to $\sim 1400\,ng\,m^{-3}$ did not result in a discernible increase in droplet concentrations. The droplet concentrations in stratocumulus (high N_d) clouds could be construed as showing a slight increase when nss SO_4^{2-} concentration increases from ~ 300 to $\sim 1100\,ng\,m^{-3}$.

The apparent sensitivity (S) of the relative droplet concentration change to the relative change in nss SO_4^{2-} mass concentration can be estimated from the regression relationship $\log(N_d) = a \times \log(SO_4^{2-}) + b$, where the constant $a = S = (\Delta N_d/N_d)/(\Delta SO_4^{2-}/SO_4^{2-})$. The dependence of N_d on nss SO_4^{2-} concentration for stratocumulus clouds observed at the site can be expressed by the relationship $\log(N_d) = 0.091\ (\pm 0.053) \log(SO_4^{2-}) + 2.323\ (\pm 0.149)$ with a correlation coefficient of 0.71. This correlation coefficient, because of the small number of points, is only significant at 80% confidence level. A similar analysis of the cumulus cloud data points yielded $\log(N_d) = -0.056\ (\pm 0.113) \log(SO_4^{2-}) + 2.430\ (\pm 0.326)$ and a correlation coefficient of -0.16. Therefore the sensitivities of droplet number concentration to the relative change in nss SO_4^{2-} mass concentration for marine stratocumulus clouds and cumulus clouds at our site are $\sim 0.1 \pm 0.05$ and ~ 0, respectively. We note for comparison that the sensitivity for anthropogenically influenced continental cumuliform clouds was found to be 0.186 ± 0.038, about a factor of two higher than for our marine stratocumulus clouds; and the sensitivity of continental stratiform clouds was determined to be 0.257 ± 0.052 (Leaitch et al., 1992).

3. Discussion

Before discussing the possible explanations of the observed dependence (or lack of it) of the cloud droplet number concentrations to the changes in nss SO_4^{2-} mass concentrations, we note that our measurements were taken on the average between 150–300 m above the cloud base. At an average updraft velocity of $2\,m\,s^{-1}$, about 75–150 s are available for droplet activation and growth. Detailed calculations in a closed air parcel

have shown that the activation takes place in a few tens of meters above the cloud base (Lee and Pruppacher, 1977). Thus, because significant CCN-nss SO_4^{2-} correlation was found, a noticeable dependence of droplet number on nss SO_4^{2-} mass concentration should be observed if the nonadiabatic effects on droplet concentrations are negligible.

We have used Twomey's approximate analytical expression (eq. (4.15) in Twomey, 1977b) to estimate the droplet number concentration expected from adiabatic air parcel theory. The droplet concentrations were calculated from CCN number concentrations, derived from our measured CCN-nss SO_4^{2-} relationship, for several values of updraft velocities W and values of the parameter k (k is the value of the exponent in the relation $CCN = cS^k$, which describes the dependence of CCN on supersaturation S). The calculated N_d-CCN dependencies are shown in Fig. 3, together with measured mean droplet concentrations. The calculated droplet concentrations show a spread (~ 100–$400\ cm^{-3}$) similar to our observations for a realistic range of W (1–3 m s^{-1}) and k (0.5–1.0). However, for cumulus clouds the expected trend of increasing N_d with increasing CCN concentration is not seen in the measured data. To explain this disagreement, we would have to assume that both the updraft velocity and the sulfate size distribution (and thus the values of k) change with CCN concentration and in a systematic manner that obscures the expected relationship between N_d and nss SO_4^{2-} or CCN. We also note that sulfate size distributions (alluded to above) measured on a number of days were remarkably similar, suggesting approximately constant k values. To explain the stratocumulus data, very high, possibly unrealistic, updraft velocities would have to be assumed; however, these possibilities seem unlikely.

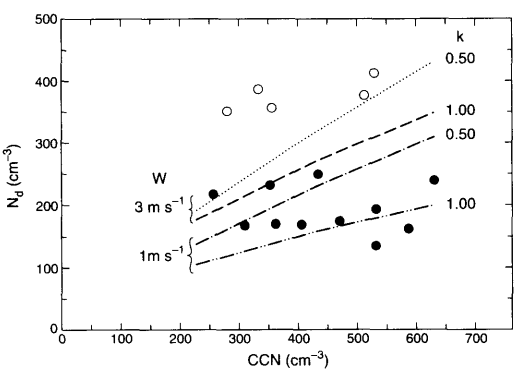

Fig. 3. Droplet number concentrations calculated from the approximate analytical expression (eq. (4.15) in Twomey, 1977b) as a function of CCN number concentrations (at 0.5% supersaturation). CCN concentrations are derived from measured nss SO_4^{2-} mass concentration and the regression relationship $CCN = 0.33 \times SO_4^{2-} + 166.2$. Theoretical results for two updraft velocities $W = 1$ and 3 m s^{-1} and 2 values of parameter k (0.5, 1.0) are shown. Measured droplet concentrations for cumulus (full circles) and stratocumulus (open circles) clouds are indicated for comparison.

An alternative explanation of our results involves the effects of entrainment and mixing that can influence the response of droplet concentrations to the changes in CCN and nss SO_4^{2-} concentrations. Recent experimental and modeling studies by Bower and Choularton (1992) have shown that cumulus clouds are strongly affected by entrainment and very inhomogeneous mixing at all levels and that, as the result of entrainment, the droplet concentration and size are only weakly affected by the CCN population.

When mixing is homogeneous, all droplets in a mixed parcel containing cloud-base and entrainment air are, at any time, exposed to identical conditions of supersaturation or undersaturation. In contrast, under conditions of extreme inhomogeneous mixing, droplets immediately adjacent to the infiltrating filaments, or blobs of undersaturated air, are drastically affected while those more remote may be unaffected (Latham and Reed, 1977; Baker et al., 1980).

If the mixing is inhomogeneous, a strong linear correlation between high frequency LWC and droplet number concentration is expected; if the mixing is homogeneous, LWC variations are mainly due to changes in droplet radius and are therefore weakly correlated with droplet number concentration (Slingo et al., 1982). The dependence of LWC on drop concentrations for all 16 cloud events reveals two qualitatively different patterns, examples of which are shown in Fig. 4. The essentially linear relationships exemplified by the plots in the upper part of Fig. 3 (a, b), suggestive of inhomogeneous mixing, were found for all 11 cumulus cloud events. This observation is consistent with the notion that cumulus clouds are strongly affected by entrainment and inhomogeneous mixing at all levels (Bower and

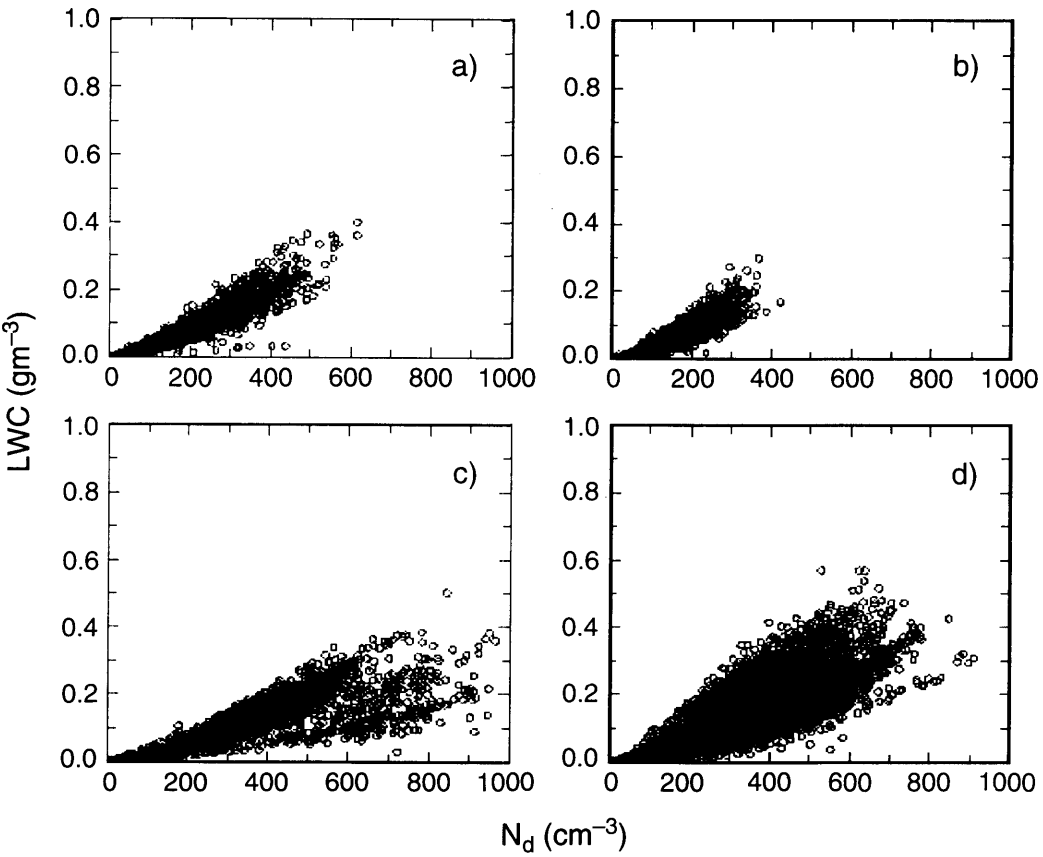

Fig. 4. Examples of LWC versus N_d dependencies for cumulus clouds (a, b) and stratocumulus (c, d). The data were obtained with 5- or 3-s time resolution. Sampling dates, time intervals (local time), and number of acquired data points (n) were (a) 28 March 1992, 1200–1652, $n = 3254$; (b) 4 April 1992, 1200–1626, $n = 3066$; (c) 4 April 1992, 0929–1200, $n = 2296$; and (d) 8 April 1992, 1200–1702, $n = 5490$.

Choularton, 1992). For this set of clouds (Fig. 2), no correlation between droplet number and nss SO_4^{2-} was observed. Plots of the type shown in the lower part of Fig. 3 (c, d) show a considerably higher scatter, greater complexity, and apparent deviations from linearity and could be a qualitative indication of different mixing in these clouds. That differences in mixing in these two cloud types can be expected is suggested by the results of Bower and Choularton (1992), who found that, in contrast to cumulus clouds, dry air entrainment has very little effect on continuous sheets of stratocumulus clouds and that the droplet sizes and number concentrations in such clouds are determined by the CCN entering the cloud base. Although the stratocumulus clouds encountered at our site do not appear as continuous sheets, it is possible that these clouds are less affected by the mixing than cumulus clouds, and because of this the N_d dependence on nss SO_4^{2-} may become more apparent (Fig. 2).

Clearly, the above discussion assumes that CCN are principally sulfate particles. Non-sulfate CCN, if present in sufficient concentrations, would obviously influence both the theoretically predicted and the observed nss SO_4^{2-}-N_d relationship. The possible existence of such CCN is suggested by the positive non-zero intercept in the CCN-nss SO_4^{2-} correlation observed at our site (Fig. 1) and over the Pacific Ocean (Hegg et al., 1991).

Measurements at Cape Grim (Ayers and Gras, 1991) show that a considerable fraction of CCN may originate from unidentified sources.

4. Conclusions

The results obtained in this study show that the CCN number concentrations and nss SO_4^{2-} mass concentrations at this site are significantly correlated. Although nss SO_4^{2-} mass appears to be a good surrogate for CCN, the droplet concentration in cumulus clouds was found to be insensitive to changes in nss SO_4^{2-} loadings. For stratocumulus clouds a weak dependence of droplet concentration on SO_4^{2-} mass may exist. These results suggest that aerosol SO_4^{2-} mass alone is not the principal parameter that determines the response of the microphysics of the marine clouds studied to anthropogenic influences. Entrainment and mixing processes in these clouds appear to be the principal factors that reduce the sensitivity of cloud droplet number concentrations on sulfate mass concentrations.

Limited evidence for marine clouds obtained in this work and the results of others (Leaitch et al., 1992) for continental clouds suggest that the empirically derived sensitivities for both marine and continental anthropogenically influenced clouds are significantly lower than 1, assumed in estimating the indirect forcing by anthropogenic sulfate aerosols (Charlson et al., 1992) and by aerosols resulting from biomass burning (Penner et al., 1992). Clearly, if sensitivities < 1 apply to anthropogenically influenced marine stratus and stratocumulus clouds, the magnitudes of these estimated forcings would have to be correspondingly reduced. Assuming for the purpose of illustration that the sensitivity for marine stratocumulus and stratus clouds to anthropogenic sulfate is ~ 0.3 (i.e., similar to the value of 0.26 for continental stratiform clouds), then the estimates of the indirect forcing by anthropogenic sulfate and by biomass aerosols would each be reduced from -1 W m^{-2} to about -0.3 W m^{-2}.

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