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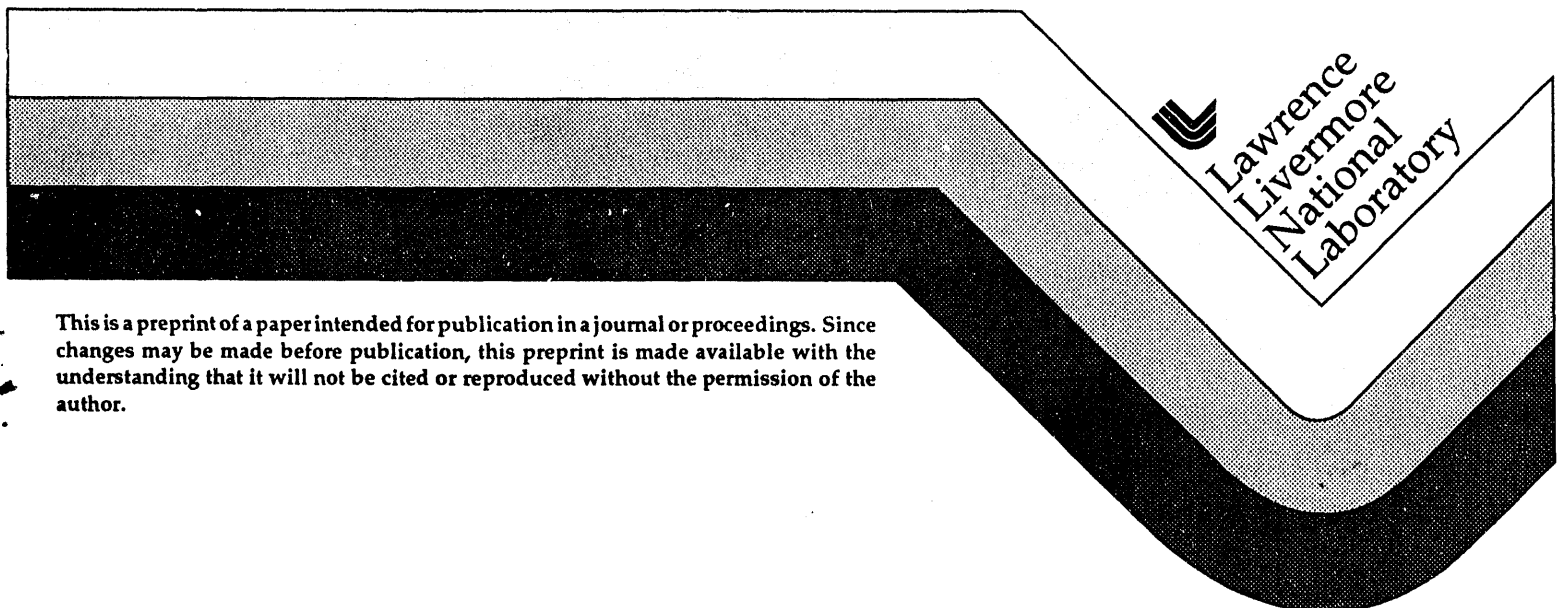
UCRL-JC-115308
PREPRINT

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Cloud Droplet Concentrations at a Marine Site**

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This paper was prepared for submittal to the
74th AMS Annual Meeting
Nashville, TN
January 23-28, 1994

October 1993



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ANTHROPOGENIC SULFATE AND ORGANIC AEROSOLS, CCN, AND
CLOUD DROPLET CONCENTRATIONS AT A MARINE SITE

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1. INTRODUCTION

The need to establish the relationships between the number concentration of cloud droplets, cloud condensation nuclei (CCN), and the mass concentrations of major aerosol species has been heightened by the results of recent modeling studies suggesting that anthropogenic sulfate (Charlson et al., 1992) and biomass smoke aerosols (Penner et al., 1992) may cause a globally averaged climate forcing comparable in magnitude but opposite in sign to the forcing due to "greenhouse" gases. In this paper we present the results of measurements of nonseasalt (nss) sulfate and organic carbon mass concentrations and mass size distributions, CCN, and cloud droplet number concentrations obtained in 1991 and 1992 on El Yunque peak, Puerto Rico (Novakov et al., 1993; Novakov and Penner, 1993). This peak (18°19'N, 65°45'W; elevation ~ 1000 m) is located at the eastern end of the island, directly exposed to the ocean winds and frequently covered with clouds.

Our results show that although CCN number concentrations (measured at 0.5% supersaturation) and nss sulfate mass concentrations are significantly correlated at this site, estimates based on measured mass size distributions of organic and sulfate aerosols indicate that the organic aerosols may account for the majority of CCN number concentrations. Droplet concentrations in the cumulus clouds do not show a discernible trend with nss sulfate mass concentrations. In stratocumulus clouds a small increase in droplet concentrations with nss sulfate mass concentrations was observed.

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2. MEASUREMENT METHODS

Total and size-resolved dry aerosol samples were collected through a vertical duct heated 10°C above the ambient temperature. Total aerosol was collected on Millipore filters with a low-volume sampler (in 1991 and 1992). Four 6-hr samples were collected daily. Size-resolved sampling was performed (in 1992) with an eight-stage Micro Orifice Uniform Deposit Impactor — MOUDI (MSP Corporation) having aerodynamic cutoff diameters D_{50} of 0.05, 0.11, 0.15, 0.37, 0.54, 1.0, 1.8 and 3.2 μm . The sampling for inorganic and organic species was done on alternate days using Teflon and aluminum substrates. The MOUDI was operated for approximately 22 hr during each sampling day. Impactor samples were analyzed at Desert Research Institute (DRI). Elemental analyses of Teflon substrates were performed by x-ray fluorescence (0700/8000 analyzer, Kevex Corp.). Organic carbon (OC) collected on aluminum substrates was analyzed by DRI's thermal-optical reflectance method (Chow et al., 1993). Millipore filters were analyzed by XRF at LBL. The CCN concentrations were measured (in 1992) with the M1 counter (DH Associates), which sampled air from a plenum equipped with a cyclone with a cutoff diameter D_{50} of 2.5 mm. Cloud droplet concentrations were measured with the CSASP 100 HV spectrometer (Particle Measurement Systems).

3. RESULTS

3.1 CCN-SO_4^{2-} -Organic Carbon Relationships

During the 1992 measurement period, clear air CCN (at 0.5% supersaturation) concentrations were measured.

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Average 6-hr (1200-1800 hr local time) CCN number concentrations, together with concurrently determined nss SO_4^{2-} mass concentrations, are given in Table 1 and, in the form of a graph, in Fig. 1. For these data the mean nss SO_4^{2-} concentration is 1197 ng m^{-3} , and the mean CCN concentration is 550 cm^{-3} . Linear regression analysis of the data shows that the CCN number concentrations and nss SO_4^{2-} mass concentrations co-vary (correlation coefficient $r = 0.77$, significant at better than 95% confidence level).

Table 1. Measured nss SO_4^{2-} and CCN concentrations.

Date	nss SO_4^{2-} (ng m^{-3})	CCN (cm^{-3})
3/28	1116	589
3/29	1241	407
3/30	941	485
3/30	925	561
3/31	572	319
4/01	1586	863
4/02	1763	736
4/09	1430	508
Average	1197(390)	558(170)

In the absence of readily available methods for direct determinations of the chemical composition of CCN, we used the mass size distributions measured by the MOUDI sampler to estimate the contributions of sulfate, organic, and seasalt mass concentrations to the CCN number concentrations. The mass distributions measured by impactors are determined by the true aerosol mass distribution and the collection efficiencies of the individual impactor stages. An approximation of the true mass size distribution can be obtained by

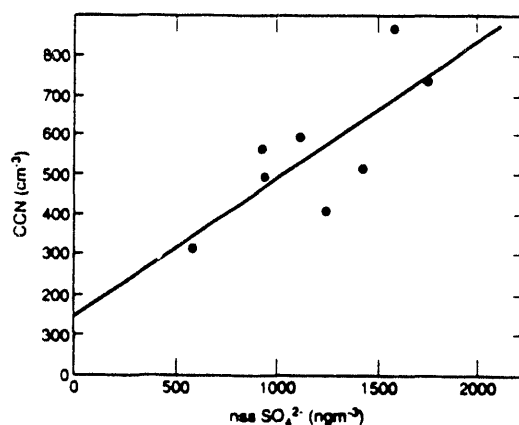


Figure 1. Dependence of clear sky CCN number concentrations measured at 0.5% supersaturation on nonseasalt sulfate mass concentrations.

using the Twomey inversion algorithm modified for multistage cascade impactors (Winklmayr et al., 1990). Inputs to the calculations consisted of aerosol OC (organic mass assumed to be $\text{OC} \times 1.2$ [Gray et al., 1984], with density of 1.0), Cl (assumed NaCl; density of 2.165) and S (assumed $(\text{NH}_4)_2\text{SO}_4$; density of 1.769) mass concentrations determined on the MOUDI stages. In deriving the mass and number size distributions, the measured aerodynamic particle diameters were converted to geometric diameters. The mass size distributions obtained in this way were used to calculate the aerosol number size distributions and aerosol number concentrations (details in Rivera-Carpio et al., 1993).

The mass size distributions of SO_4^{2-} , NaCl, and organic aerosols (collected on April 9 and 10, 1992) are shown in Fig. 2a; and the derived aerosol number size distributions are shown in Fig. 2b. A comparison of the two figures shows that organic aerosols contribute significantly more than sulfate

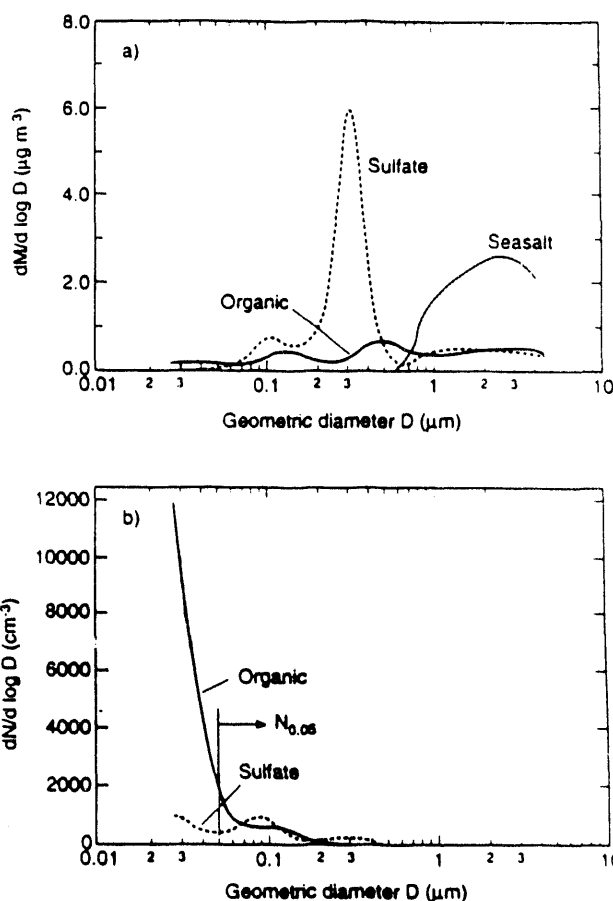


Figure 2. a) Mass size distributions of sulfate, seasalt (NaCl), and organic aerosol measured on April 9 (inorganic) and April 10 (organic), 1992. b) Derived number size distributions. Vertical line indicates the lower integration limits used to compute $N_{0.05}$ number concentrations.

aerosols to the number concentrations of small particles ($D < 0.08 \mu\text{m}$), despite the fact that the sulfate mass concentration (1362 ng m^{-3}) is two times higher than the organic aerosol mass (628 ng m^{-3}). The seasalt contribution to aerosol number concentration could not be estimated because the Cl concentrations on the lowest size impactor stages were below detection.

From the aerosol number size distributions, the number concentrations $N_{0.05}$ of sulfate and organic aerosol with diameters $> 0.05 \mu\text{m}$ can be calculated. Ammonium sulfate particles in this size range are expected to be activated at 0.5% supersaturation and therefore counted as CCN. For the reasons discussed below, we assume that the same criterion can be used to estimate the organic CCN concentrations. The $N_{0.05}$ number concentrations calculated from impactor data are shown in Table 2. The uncertainty in the $N_{0.05}$ values caused by the analytical errors in sulfate and OC determinations are indicated by the numbers in parentheses.

Table 2. Measured SO_4^{2-} and OC aerosol mass concentrations and derived number concentrations.

	Date	Mass (ng m^{-3})	$N_{0.05}$ (cm^{-3})
Sulfate	3/30-3/31	954	162(147-178)
	3/31-4/01	936	259(237-279)
	4/07-4/08	984	95(82-107)
	4/09-4/10	1362	334(308-359)
	Average	1059	212(193-230)
Organic	4/01-4/03	556	369(251-487)
	4/04-4/05	896	413(290-536)
	4/08-4/09	568	314(206-422)
	4/10-4/11	628	371(249-492)
	Average	662	366(249-484)

Mass concentrations of sulfate as SO_4^{2-} and organic carbon as C. Numbers in parentheses are uncertainty ranges.

These calculated values can be compared with the measured CCN concentrations shown in Table 1. The rationale for this comparison is based on the fact that the mean nss SO_4^{2-} concentration of 1197 ng m^{-3} shown in Table 1 is within 13% of the mean MOUDI SO_4^{2-} concentration of

1059 ng m^{-3} (Table 2) and on the assumption that the mean OC concentration during the 6-hr events was comparable to the mean of 662 ng m^{-3} obtained from impactor samples. Comparison of the data in Tables 1 and 2 shows that the average measured CCN concentration of 556 cm^{-3} is in remarkably good agreement with the sum of 578 cm^{-3} of the average estimated concentrations of $N_{0.05}(\text{S}) = 212$ and $N_{0.05}(\text{O}) = 366 \text{ cm}^{-3}$. The excellent agreement between measured CCN and derived values strongly suggests that both sulfate and organic aerosol contribute to the CCN number concentration. We note that the calculated $N_{0.05}$ number concentrations do not depend critically on the assumed mixing state (external vs. internal) of the aerosol components.

The apparent ability of organic aerosol to serve as CCN can have two possible explanations. The first is that the organic aerosols are inherently inactive and that condensation of H_2SO_4 vapor, or some other water-soluble species, onto these particles renders them active CCN. As a consequence of this process, organic particles with the same diameters as sulfate will be CCN active. The second explanation is that a fraction of the chemically complex organic aerosol material is hydrophilic.

3.2 Cloud Droplet-CCN-Sulfate Relationship

In Table 3 we show the mean CCN and cloud droplet number N_d concentrations measured on three days during the pre-cloud periods and during the immediately following in-cloud periods. As expected, the decrease in CCN concentration, ΔCCN , from the pre-cloud to in-cloud conditions closely matches the increase in droplet concentration, ΔN_d . However, as shown in Table 3, the CCN scavenging ratios $\Delta\text{CCN}/\text{CCN}$ can vary from 0.24 to 0.7 independently of pre-cloud CCN concentrations, indicating that a variable fraction of the aerosol (as defined by the CCN counter) forms cloud droplets.

In Fig. 3 the mean cloud droplet concentrations for 16 cloud events are plotted against the corresponding aerosol nss SO_4^{2-} mass concentrations. The data fall into two groups — those with lower (155 cm^{-3}) and higher (310 cm^{-3}) average number concentrations. By comparing the appearance of the clouds at the site with photographs of typical marine clouds (WMO, 1987), we conclude that low N_d clouds are in the cumulus category (fair weather humilis or fractus; mediocris or congestus). The high N_d clouds had the appearance of stratocumulus (cumulogenitus) clouds. As the data in Fig. 3

Table 3. Pre-cloud and in-cloud CCN and droplet number concentrations.

Date	Local time	Pre-cloud		In-cloud		ΔCCN	ΔN_d	$\Delta\text{CCN}/\text{CCN}$
		CCN ^a (cm^{-3})	N_d (cm^{-3})	Local time	CCN ^{a,b} (cm^{-3})			
3/28	1254-1438	531	37	1438-1639	406	125	155	0.24
3/30	1347-1456	504	51	1456-1658	152	352	341	0.70
4/3	1531-1639	337	9	1639-1806	193	144	155	0.43

a: Measured at $\sim 0.5\%$ supersaturation; b: Interstitial CCN.

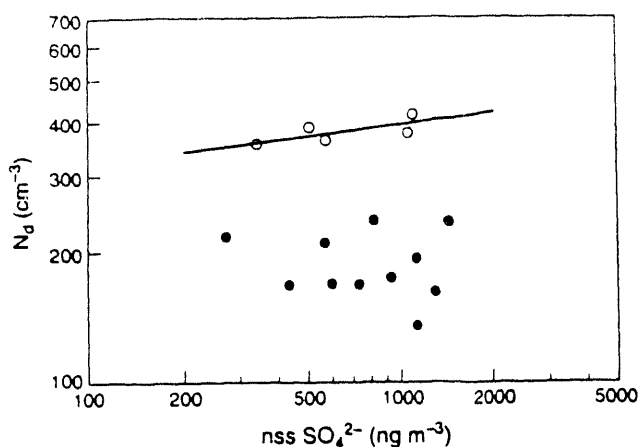


Figure 3. Mean droplet number concentrations plotted against the average nss SO_4^{2-} mass concentrations determined for individual cloud events. Data points shown with full circles are for cumulus clouds and with open circles are for stratocumulus clouds.

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

4. CONCLUSIONS

The results presented above show that about 37% of the CCN number concentrations measured at the site can be accounted for by sulfate and the remaining 63%, by the organic aerosol mass concentration. If the organic aerosol is inherently CCN active, the production of these particles will determine the organic CCN concentration. If, however, the condensation of H_2SO_4 vapor renders the organic particles active, then the number concentration and surface area of these particles, together with the existing sulfate particles, will control the total number of CCN. Therefore, the organic aerosol should contribute to the total CCN concentration irrespective of the mechanism that governs their nucleation properties.

Although nss SO_4^{2-} mass concentration appears to be a good surrogate for CCN, the droplet number concentration in cumulus clouds was found to be insensitive to changes in nss SO_4^{2-} mass loading. For stratocumulus clouds a weak dependence of droplet concentration on sulfate may exist. These results suggest that aerosol SO_4^{2-} mass alone is not the principal parameter that determines the droplet concentrations of marine clouds studied.

5. ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Health and Environmental Research, Environmental Sciences Division under contract no. DE-AC03-76SF00098 at Lawrence Berkeley Laboratory and no. W-7405-ENG-48 at Lawrence Livermore National Laboratory. C.F. Rogers was partially supported by Desert Research Institute during his stay at LBL.

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