

ATMOSPHERIC SULFUR CHEMISTRY AND CLOUD CONDENSATION NUCLEI (CCN) CONCENTRATIONS OVER THE NORTHEASTERN PACIFIC COAST

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Abstract. Correlated measurements of dimethylsulfide (DMS), gas phase dimethylsulfoxide (DMSO), methanesulfonic acid (MSA)(g), sulfuric acid (H₂SO₄), and cloud condensation nuclei (CCN) were conducted in April 1991 at a Pacific coastal site in northern Washington. Measurements of SO₂, aerosol methanesulfonate (MSA)(p), and non-sea-salt sulfate (nss-SO₄) concentrations were also included. Maximum DMS concentrations between 100 and 240 pptv were observed when the measurement site (480 m above sea level) was embedded in clouds and air from the marine boundary layer was flowing upslope to the site. DMS levels measured in continental air and/or above the mixed layer were typically less than 20 pptv. The sulfur gases DMSO, H₂SO₄, and MSA(g) were measured in real time on a continuous basis (once every 60-150 s) using selected ion chemical ionization mass spectrometry. Corresponding concentrations ranged between <0.5-3.2 pptv, 0.001-1.19 pptv, and 0.002-0.19 pptv, respectively. All three sulfur gases showed significant diel variations mostly in phase with each other. Their corresponding lifetimes in the marine atmosphere are estimated to be of the order of a few hours. The results in connection with recent laboratory studies and model calculations suggest that dimethylsulfone (DMSO₂) was the dominant end product of DMS oxidation under the present conditions. CCN concentrations measured in marine air ranged roughly between 10-200 cm⁻³ and 200-400 cm⁻³ at 0.3% and 0.9% supersaturation, respectively. A statistical analysis using only data obtained in predominantly marine air and during non-fog/non-precipitation periods showed significant correlations between individual sulfur species and between CCN (0.3% ss) and H₂SO₄, and CCN (0.3% ss) and nss-SO₄. The results indirectly support a relationship between DMS and CCN concentrations. However, other observations also suggest that at higher supersaturations (0.9%), compounds less soluble than sulfate may become important in marine CCN formation.

1. Introduction

The potential link between the oxidation of dimethylsulfide (CH₃SCH₃; DMS), particle nucleation, and cloud condensation nuclei (CCN) formation in the marine

atmosphere represents a crucial component in the DMS-cloud-climate hypothesis [Charlson et al., 1987; Bigg et al., 1984; Shaw, 1983]. Although recent studies have shown indirect evidence for such a link [Hegg et al., 1991a, 1991b; Ayers and Gras, 1991; Ayers et al., 1991], the intricate mechanisms involved in each of these processes are still poorly understood. As discussed by Bates et al. [1989] and Quinn et al. [1993], a variety of factors control the relationships among the DMS sea-to-air flux, atmospheric DMS chemistry, and CCN formation making an experimental verification of the above hypothesis extremely difficult. In particular, large uncertainties still exist with respect to the relative yields of the end products of DMS oxidation, i.e., dimethylsulfone (CH₃S(O)₂CH₃; DMSO₂), methane sulfonic acid (CH₃S(O)₂OH; MSA(g)), and sulfuric acid (H₂SO₄). Of these three products only sulfuric acid is believed to contribute significantly to CCN formation [Lin et al., 1992; Kreidenweis et al., 1991; Twomey, 1971; Dinger et al., 1970]. Therefore a better understanding of the relative yield of H₂SO₄ from DMS oxidation is crucial for estimating the importance of the DMS-cloud-climate relationship.

Recently, Yin et al. [1990] proposed a detailed photochemical mechanism for atmospheric DMS oxidation based on available kinetic and mechanistic data. The most important DMS oxidation mechanism involves the hydroxyl radical, OH, which initially reacts with DMS either by addition or by H abstraction. Based on a reaction rate constant of $k_{298} = 0.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Hynes et al., 1986] and assuming a daytime average OH concentration of 10^6 cm^{-3} , the atmospheric lifetime of DMS with respect to OH is approximately 1.5 days. The branching ratio between the two initial reactions is temperature-dependent [Hynes et al., 1986]. The addition pathway dominates below 285 K, the abstraction pathway above 285 K. Yin et al.'s [1990] scheme suggests that DMSO₂ is the dominant end product of OH addition and that both DMSO₂ and its precursor dimethylsulfoxide (CH₃S(O)CH₃; DMSO) are produced only through the addition pathway. The formation of DMSO and its further oxidation by OH to DMSO₂ appears to be relatively straightforward. Conversely, the reactions following H abstraction from DMS and finally yielding H₂SO₄ and/or MSA(g) are far more complex. Yin et al. [1990] postulate a number of side-branching reactions for the abstraction mechanism involving several highly reactive intermediate species. The corresponding uncertainties in this scheme are substantial, for example, with respect to reactions involving NO_x or HO₂ and their relative importance in the marine atmosphere. Recently, Bandy et al. [1992] have proposed a modification of Yin et al.'s mechanism suggesting that under the low NO_x concentrations in the remote marine atmosphere, SO₃ instead of SO₂ is formed as the dominant precursor of sulfuric acid. The proposed SO₃ pathway not only bears significant consequences with respect to current mechanistic models of DMS chemistry but also with respect to CCN formation over remote oceanic regions. Based on recent calculations by Lin and Chameides [1993], the proposed SO₃ pathway is capable of generating significant numbers of new CCN due to the

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very efficient formation of H_2SO_4 from the reaction of SO_3 with water vapor. At the same time, assuming this pathway is indeed important, this would imply a strong coupling between DMS emissions and CCN concentrations in the marine atmosphere. For typical marine boundary layer conditions, Lin and Chameides [1993] estimate the production of H_2SO_4 from the $\text{SO}_3\text{-H}_2\text{O}$ reaction to be approximately 1 order of magnitude faster than from the $\text{SO}_2\text{-OH}$ reaction. With the SO_3 pathway taken into account, their calculations suggest a production rate of $24 \text{ cm}^{-3}\text{d}^{-1}$ for new CCN from DMS oxidation. On the other hand, if H_2SO_4 formation from DMS proceeds only via SO_2 , it follows from previous calculations [Lin et al., 1992; Raes and Dingenen, 1992; Chameides and Stelson, 1992] that DMS chemistry is rather inefficient in generating new CCN particles in the marine atmosphere. Lin et al.'s [1992] calculations show no formation of new CCN from the SO_2 pathway even for a period of 3 days. Virtually all of the H_2SO_4 generated through this pathway is scavenged by preexisting CCN unless the number of preexisting CCN is extremely low (about 1 cm^{-3}). In summary, depending on the relative yields of SO_2 and SO_3 from DMS oxidation, these model calculations suggest extremely different results with respect to the degree of coupling between DMS emissions and new CCN formation.

The ultimate test of such mechanistic models and of the hypothesized DMS-CCN relationship must be provided by field measurements conducted under real atmospheric conditions. Assuming the relatively short time scale of CCN formation suggested by the DMS- $\text{SO}_3\text{-H}_2\text{SO}_4$ mechanism, such an experiment can be suitably conducted even at a stationary site (Eulerian system). However, even if the time scale for the DMS-CCN connection is of the order of only 1 day, an in-depth study of DMS chemistry in marine air still requires at least two to three consecutive days of continuous measurements under relatively stable meteorological conditions and without major changes in air mass trajectories, cloud formation, and daylight radiation. Any precipitation events or advection of continental air will seriously interfere with such a study.

Unfortunately, previous field measurements have been of relatively little help in revealing intricate mechanisms involved in atmospheric DMS chemistry. For example, the role of NO_x in determining the yield of MSA(g) is still controversial [Mihalopoulos et al., 1992; Ayers et al., 1991; Berresheim et al., 1990; Berresheim, 1987]. It seems clear, however, that NO_x is not the only parameter affecting the relative yields of the DMS oxidation products. A major shortcoming in previous field studies has been the lack of adequate detection techniques for some of the important reactant and product species involved in DMS oxidation. Recently, however, new techniques have been developed based on selected ion chemical ionization mass spectrometry (SI/CI/MS) which now make it possible to measure gas phase DMSO, H_2SO_4 , MSA(g), and other species in real time [Berresheim et al., 1993; Eisele and Berresheim, 1992; Eisele and Tanner, 1991; 1993]. As part of the Pacific Sulfur/Stratus Investigation (PSI-3) conducted in April/May, 1991, a combination of these techniques has been used for the first time in conjunction with measurements of DMS, aerosol sulfur species, and CCN particles to study atmospheric sulfur chemistry and the DMS-CCN relationship in the marine atmosphere. Unfortunately, only a rather limited data set could be obtained from the present measurements due to the exploratory design of the PSI-3 Cheeka Peak program and the relatively short measurement period (2 weeks). Measurements of species such as NO_x , CO, OH, and radon

required for a detailed model evaluation of the data were not included and only a very limited number of SO_2 measurements were made. Also, strong fluctuations in weather conditions and air mass character affected the overall consistency of the measurements. However, significant relationships between individual compounds were observed and a statistical evaluation of the results is given in the present paper.

2. Experiment

The present measurements were conducted at Cheeka Peak Research Station (480 m above sea level) located on the Washington Olympic Peninsula (near Cape Flattery) approximately 2 km inland from the Pacific coast. The distance between the site and the nearest major industrial sulfur sources in Port Angeles and Victoria is approximately 100 km. The following atmospheric sulfur compounds were measured: DMS using the gold wool adsorption/GC/FPD technique [Berresheim et al., 1991] and DMSO, H_2SO_4 , and MSA(g) using SI/CI/MS. Absolute MSA(g) concentrations were calculated from the corresponding measurements based on the assumption that MSA(g) reacts with NO_3^- ions at the collision rate [Eisele and Tanner, 1993]. Stacked filter units were used to sample SO_2 , aerosol non-sea-salt sulfate, and aerosol methanesulfonate, MSA(p), in air advected from the marine wind sector ($190^\circ\text{-}330^\circ$) when wind speeds were greater than 2 m s^{-1} and total particle counts less than 1000 cm^{-3} . Filter preparation, sampling, and analytical procedures used for the SO_2 and aerosol measurements have been described in detail by Quinn and Bates [1989]. Particles larger than $0.9\text{-}\mu\text{m}$ diameter were excluded from sampling by using a prefilter cyclone separator to prevent high loadings of sea salt on the filters. CCN concentrations were measured at 0.3% and 0.9% supersaturation with a static thermal diffusion chamber. Measurements of particle size distributions and size distributions of MSA(p) and nss- SO_4 during PSI-3 are discussed in detail in a separate paper by Quinn et al. [1993]. In the present work, MSA(p) and nss- SO_4 concentrations are reported as mole mixing ratios in parts per trillion (ppt) (10^{-12} mol of species/mol of air). At STP, 1 nmol m^{-3} corresponds to 22.4 ppt. Gas mixing ratios are given in parts per trillion by volume (pptv).

3. Results and Discussion

3.1. Meteorological Conditions

Table 1 presents an overview of the meteorological conditions encountered at the measurement site. Air mass trajectories were calculated for every 12-hour time point to terminate at Cheeka Peak at a fixed height of 480 m above sea level. Calculations were made for 0000 UT, 0600 UT, 1200 UT, and 1800 UT of each measurement day. A hybrid Eulerian and Lagrangian method [Draxler, 1992] based on medium-range forecast wind field data was used which allows the trajectories to follow the horizontal and vertical wind fields. A trajectory length of up to 3000 km distance and/or 5 days of transport time was assumed to have sufficient accuracy to characterize the origin and mixing of a specific air mass. Upper air soundings of meteorological parameters were provided twice a day by a coastal National Weather Service station in Quillayute approximately 40 km from the Cheeka Peak site. These soundings, along with direct observations made at the site, were used to analyze the daily variations of the marine boundary layer (MBL) height. The data in Table 1 show significant changes in the weather

TABLE 1. Significant Weather Conditions at Cheeka Peak Research Station

April 1991 Day	Time, PDT	Wind	Air Mass	MBL Height, m	Comments
16	1200-1430	W,<3	C	<480	above clouds
	1700-1930	W,<3	C/M	<480	above clouds
17	1200-1300	W,3	C/M	500	in/out of clouds
	1300-1600	W,6	C/M	<480	above clouds
	1730-2000	W,6	M	500	in cloud
18	0800-1000	calm	M/C	500	in cloud
	1100-1530	calm/E	C/M		fair; subsidence
	1800-1830	W,3	M/C		cloudy
	1930-2000	W,3	M/C	475	in cloud
19	0700-1900	E,3	C/M	<480	above cloud
20	1000-1630	E,9	C		fair, gusty
	2000-0000	NW,5	C/M		fair
21	0100-0000	SW/W,7	M	500	in cloud
22	0000-0000	W,4	M/C	1070	lifting fog
23	0200-2100	S/SE,8	C	---	front/precipitation
24	0730-2100	W,6	M	---	MBL air
25	0830-1130	W,<3	M	1300	intermittent sleet
	1300-2100	W,<3	M	1300	MBL air
26	0730-1200	SE/E,7	C		front/precipitation
	1630-2000	W,4	M	1380	MBL air
27	0730-1930	W,5	M	1380	MBL air
28	0000-0300	W,<3	M		
	0300-1230	S,7	C		snowfall
	1230-1310	W,7	M		front/precipitation
	1330-2130	W/NW,4	M	930	MBL air
29	0000-0400	W,5	M	930	MBL air
	0400-1100	E,4	C/M		
	1200-1900	W/NW,<3	M/C		
30	1900-0000	E,4	C		
	1030-1800	E,9	C		gusty

PDT is Pacific daylight time. Wind data are denoted by average direction and wind speed (m/s). Air mass is categorized as continental (C), marine (M), predominantly continental (C/M), and predominantly marine (M/C) air. MBL (marine boundary layer) data are taken from Quinn et al. [1993].

for most of the measurement period. Relatively undisturbed fair weather conditions with marine air being advected to the site prevailed only on two non-consecutive days (April 24 and 27). On other days with marine air influence, the measurements were complicated either by precipitation or in-cloud/fog events or by an alternation between marine and continental air masses or advection of mixed marine/continental air. Often when the measurement site was embedded in clouds, fairly clear conditions prevailed upwind over the open ocean. On the other hand, relatively fair weather conditions occurred at the site mostly in connection with easterly winds advecting continental air from the United States or Canada. As discussed in the following sections, the frequent weather changes encountered at the Cheeka Peak site during a relatively short measurement period imposed significant limits on the data interpretation.

3.2. Temporal Variations of Individual Species

Figure 1a shows the results of the DMS measurements. Conspicuously high DMS concentrations (>100 pptv) were observed between April 17 and 18, April 21 and 22, and April 28 and 29. The corresponding measurements show a relatively sharp increase and decline of DMS levels. The onset of the high DMS levels during the first of these

episodes was induced by a transition from free tropospheric to marine boundary layer air reaching the measurement site. At daytime the mixed layer height increased to approximately 500 m which caused the site to be mostly embedded in clouds during this time. DMS levels were lower again early on April 18 due to subsiding air masses and relatively low winds from easterly (continental) directions. The highest DMS concentrations (up to 240 pptv) were measured during the second episode with winds turning westerly early on April 21. Again, the Cheeka Peak site was mostly in clouds until mid-morning of the following day when the mixed layer increased to about 1 km (Table 1) and wind trajectories indicated a mixture of coastal MBL air and continental air advected from Canada. Similar conditions were also encountered during the third episode, however, with more variable weather (occasional easterly winds, precipitation, and a frontal passage on midday, April 28). Relatively clear conditions with MBL air reaching the site contributed to elevated DMS levels (up to 50 pptv) on April 24-25 and April 27. The daytime mixed layer height during these two periods extended up to approximately 1400 m or higher, thus causing a considerable dilution of DMS in the MBL. DMS levels in the free troposphere or in continental air were typically less than 20 pptv.

Continuous field measurements of gas phase DMSO without preconcentration were made for the first time using

the SI/CI/MS technique described by Berresheim et al. [1993]. The results smoothed to 10-min average values are shown in Figure 1b. As discussed by Berresheim et al., negative values were occasionally obtained due to short-term variations of the background signal which were not resolved by the measurements. In future experiments these uncertainties can be eliminated by using standard addition of isotopically labeled DMSO. The DMSO detection limit of the present method is conservatively estimated to be 0.5 pptv. The results show a significant diel variation of DMSO, except on April 23 due to heavy precipitation on that day. DMSO concentrations ranged between $0.5\text{--}3.2\text{ pptv}$. Typically, DMSO levels were significantly higher than MSA(g) and H_2SO_4 values (Figures 1c and 1d) consistent with the relatively higher vapor pressure of DMSO [Watts and Brimblecombe, 1987].

Figures 1c and 1d show the results of the H_2SO_4 and MSA(g) measurements, respectively, smoothed to 20-min (10 data point) averages. These measurements started on April 19. Individual breaks in both data plots correspond to periods when the measurements were interrupted for more than 2 hours. The plots shown in Figures 1c and 1d represent 433 average data points each. Corresponding median values for H_2SO_4 and MSA(g) were 0.011 pptv and 0.009 pptv, respectively, with total concentration ranges of

0.001-1.19 pptv and 0.002-0.19 pptv. As shown, maximum levels of both compounds were observed in the beginning of the measurements on April 19. Trajectories calculated for this day indicate advection of aged marine air mixed with continental air from western Canada (Table 1). Relatively gusty winds were prevalent on April 20 changing from easterly to northwesterly directions, again suggesting advection of mixed marine/continental air to the study site. Both H_2SO_4 and MSA(g) showed a strong diel behavior indicative of significant in situ production of both compounds. On both April 19 and April 20, relatively sunny, clear weather conditions were prevalent and potentially high OH concentrations were present in this air mass. Ozone levels typically ranged between 50 and 80 ppbv. As can be seen from Figure 1a, DMS values were extremely low on both days. A clear diel variation of both H_2SO_4 and MSA(g) was observed almost every day except on days with in-cloud conditions or precipitation events (April 21, 23, 26, and early 28; see Table 1). For both compounds a significant daytime production is evident from the measurements on April 27 (marine air) and April 29 (mixed marine/continental air) although the average MBL height was rather high (Figures 1c and 1d; Table 1). On the same days, DMS levels were also elevated, as discussed earlier (Figure 1a).

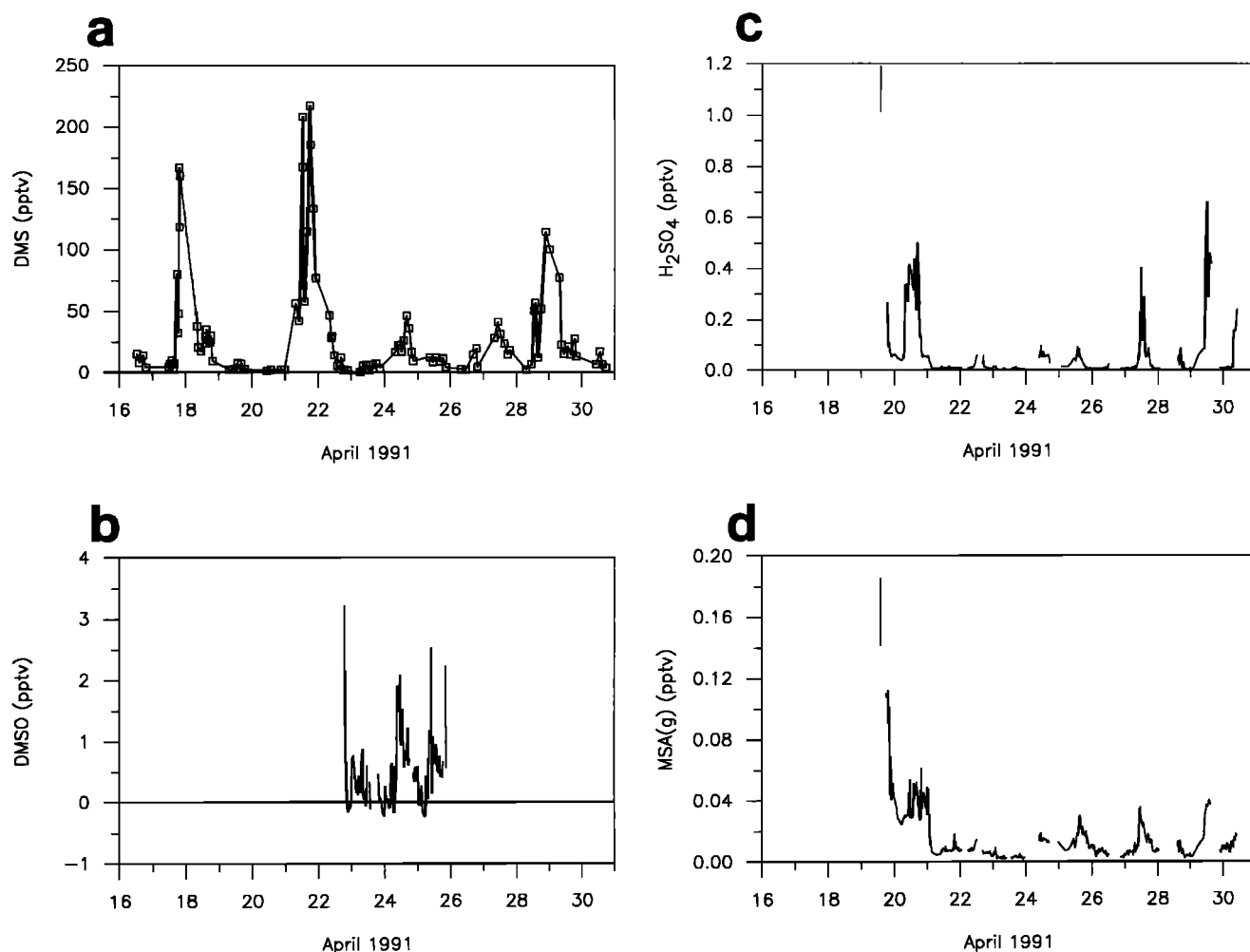


Fig. 1 Mixing ratios of (a) DMS, (b) gas phase DMSO, (c) gas phase H_2SO_4 , and (d) gas phase MSA(g) measured at Cheeka Peak during PSI-3. The DMSO and both the H_2SO_4 and MSA(g) data have been smoothed by 10-min and 20-min averaging, respectively. Negative DMSO values are discussed in the text.

Both MSA(g) and H₂SO₄ are rapidly removed from the gas phase either by deposition to existing particles or by condensation forming new particles. Model calculations [Hegg et al., 1992; Kreidenweis et al., 1988; 1991; Shaw, 1989] and recent field observations [Covert et al., 1992; Eisele and Tanner, 1993] suggest that both compounds have typical atmospheric lifetimes ranging from minutes (continental air) to a few hours (marine air). Their loss rates are largely dependent on the corresponding sticking coefficients and on the number and size distribution of preexisting particles. To the contrary, DMSO has a sufficiently high vapor pressure to be able to exist predominantly in the gas phase [Watts et al., 1990; 1987]. However, DMSO is readily attacked by OH to form DMSO₂. Recent laboratory studies by Hynes et al. [1992] show that the DMSO+OH reaction ($k_{298} = 1.0 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) proceeds approximately 20 times faster than the DMS+OH reaction at room temperature. Assuming a daytime average OH concentration of 10^6 cm^{-3} , the results reported by Hynes et al. suggest an atmospheric lifetime of DMSO of approximately 3 hours which is comparable to the lifetimes estimated for MSA(g) and H₂SO₄ in the marine atmosphere.

In contrast to the DMS+OH reaction the rate constant of the DMSO+OH reaction varies only slightly with temperature (A. Hynes, personal communication, 1992). Ambient temperatures at the Cheeka Peak site typically ranged between 5–10°C during the PSI-3 experiment. At these temperatures, the rate constant of the DMS+OH reaction is approximately $1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and about 60% of the reaction proceeds through the OH addition channel [Hynes et al., 1986]. Therefore the production of DMSO may have been further intensified due to the prevailing temperatures at the site. Based on the median concentrations of DMSO (0.71 pptv), MSA(g) (0.014 pptv), and H₂SO₄ (0.043 pptv) measured between April 22 and 25 and assuming similar atmospheric lifetimes for all three compounds, we calculate a relative yield of DMSO from DMS oxidation approximately 16 times that of H₂SO₄ and 50 times that of MSA(g). This estimate is, of course, very crude. However, as shown in more detail in section 3.3.1, the present results suggest that DMSO₂ may be the dominant end product of DMS oxidation in marine air at this latitude.

Preceding measurements of DMSO and DMSO₂ made at Cheeka Peak with 6 to 12-hour time resolution (G. Harvey, personal communication, 1992) support this conclusion. On both April 18 and April 21 when maximum values of DMS were observed, Harvey measured significantly elevated levels of DMSO (6–14 pptv) and DMSO₂ (7–31 pptv), respectively. Previous measurements by Pszenny et al. [1990] of DMSO and DMSO₂ mixing ratios of up to several hundred pptv over the North Atlantic also support our present conclusion. Unfortunately, a rigorous intercomparison between the two DMSO techniques used at Cheeka Peak was not possible.

At Cheeka Peak, only six long-term (1–2 days) integrated SO₂ filter samples were collected from the marine wind sector (Figure 2a). Four relatively low values (all approximately 17 pptv) were obtained on days with precipitation events and/or in free tropospheric air. The higher values (31–39 pptv) measured between April 26 and 29 are consistent with elevated concentrations of H₂SO₄ (Figure 1c) and nss-SO₄ (Figure 2a) observed during the same period. However, as discussed earlier it has recently been questioned whether DMS oxidation is the major source of SO₂ in the marine atmosphere [Bandy et al., 1992]. Because of the relatively low number of samples collected,

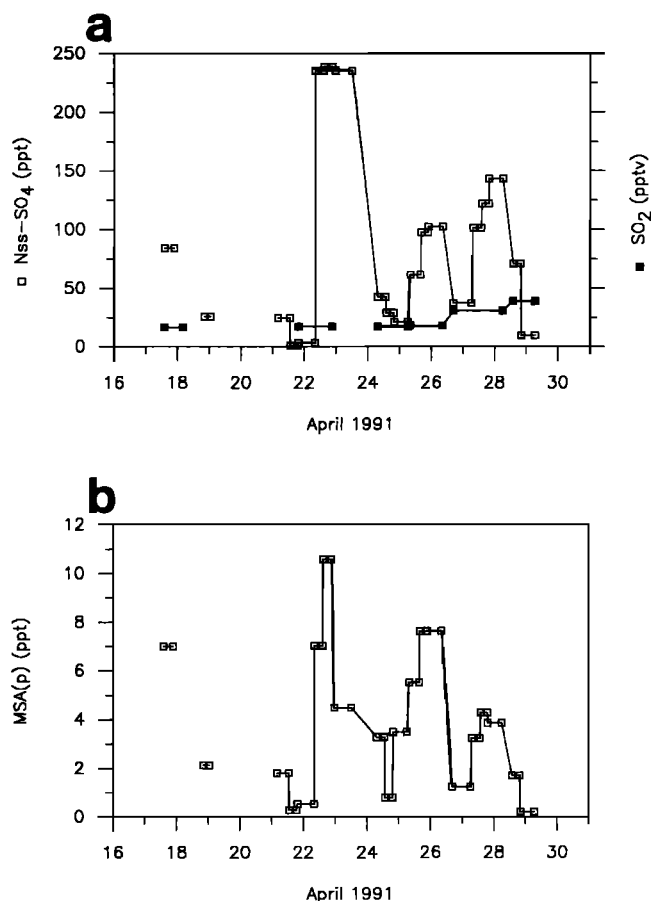


Fig. 2 Mixing ratios of (a) SO₂ and nss-SO₄ and (b) MSA(p) measured at Cheeka Peak during PSI-3. For definition of "ppt" see text.

we refrain from further interpretation of the SO₂ data obtained in the present study.

The results of the sub-micrometer aerosol nss-SO₄ and MSA(p) measurements (less than 12 hours sample integration) are shown in Figures 2a and 2b. Mass size distributions of both compounds have been discussed in detail by Quinn et al. [1993]. As shown in both figures, the highest concentrations were measured between April 22 and 23. Corresponding back trajectories indicate a change in air mass from a mixed marine/continental type (April 22) to predominantly continental air (April 23). Although the high values for MSA(p) on April 22 were measured approximately one day after a period with high DMS levels (Figure 1a), a significant increase in H₂SO₄ and MSA(g) concentrations was not observed (Figures 1c and 1d). However, this was probably due to the presence of drifting fog on midday of April 22 (see Table 1) which forced a temporary shutdown of the measurements. It is possible that the daytime maxima of both compounds had been missed due to this interruption. The conditions encountered on April 22 are further discussed below with respect to the DMS and DMSO data obtained on the same day. Measurements made during other periods with high MSA(p) and nss-SO₄ levels, in particular on April 25–26 and 27–28, are consistent with the presence of predominantly marine air at the site (Table 1). Both the MSA(p) and the nss-SO₄ peak values observed during these periods occurred within a few hours following peak values measured for MSA(g) and H₂SO₄ (Figures 1c and 1d). Again, these results suggest atmospheric lifetimes of a few

hours for both MSA(g) and H_2SO_4 in marine air. Figure 3 shows a time series of CCN concentrations measured in predominantly marine air at 0.3% and 0.9% supersaturation. Maximum levels were observed on April 21 and 22 just below cloud base or between cloud pockets.

3.3. Statistical Relationships Between Measured Species

At Cheeka Peak, both weather conditions and air mass origin varied considerably during the measurements. The results obtained from measurements in continental air and measurements associated with in-cloud and/or precipitation events have been excluded from the following data analysis.

3.3.1. Gaseous sulfur species. No significant correlations were found between DMS and H_2SO_4 or DMS and MSA(g) even if only daytime data were used. This is not surprising in view of the complexity of atmospheric DMS chemistry, the time lag involved in the DMS reaction with OH, and the frequent fluctuations in air mass origin and daytime solar radiation encountered at Cheeka Peak. Assuming a consistent presence of marine air at the measurement site one would have expected to observe a phase shift between DMS peaks and MSA(g) and H_2SO_4 peaks depending on the time lag involved in DMS oxidation. However, even when such a time lag was taken into account (up to 48 hours), the present data set as a whole showed no significant correlations. On the other hand, a comparison of the results obtained on a single day, April 27 (Figures 1a, 1c, and 1d), with relatively clean marine conditions and no precipitation (Table 1), suggests a correlation between DMS and both H_2SO_4 and MSA(g). Unfortunately, the corresponding number of DMS data was insufficient to obtain statistical significance for such a correlation. Since the data on April 27 show a time difference of only 1 hour between the maximum values of DMS and its product species, the presumed correlation would indicate an extremely low lifetime of DMS in marine air.

In contrast to these results a significant correlation between DMS and DMSO (95% confidence level) was obtained from measurements made on April 24 (Figure 4a). As mentioned earlier, meteorological conditions were favorable on that day to study DMS chemistry. However, corresponding data pairs obtained for DMS and both MSA(g) and H_2SO_4 were too scarce to permit a statistical evaluation. The relatively good correlation between DMS and DMSO in

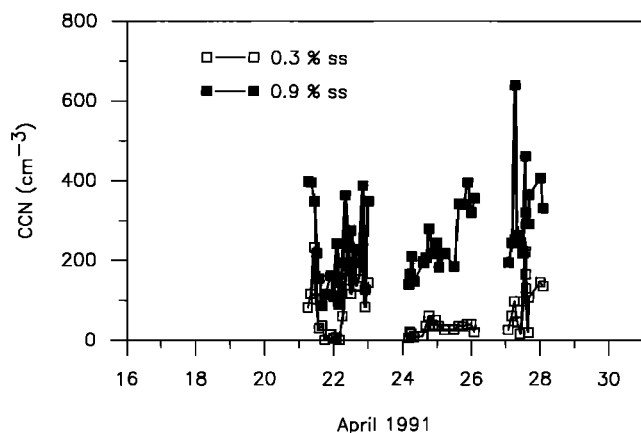


Fig. 3 Cloud condensation nuclei (CCN) particle concentrations measured at two different supersaturation (ss) levels. All data shown were obtained in predominantly marine air.

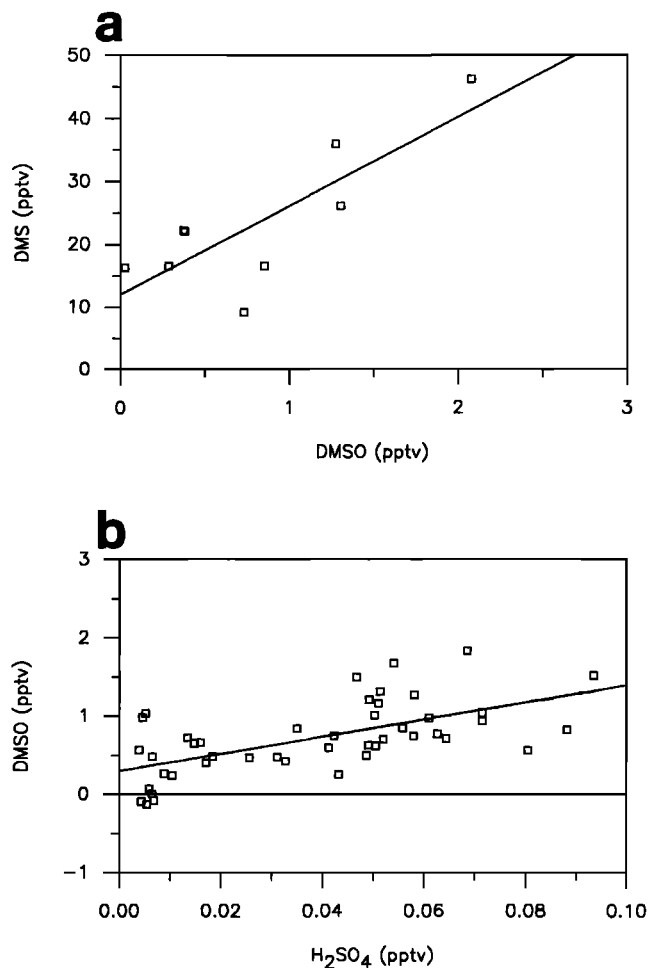


Fig. 4 Correlation between (a) DMS and DMSO on April 24 (adjusted for time lag of 5 hours; see text; $y = 14.09x + 12.03$, $r^2 = 0.64$, $n = 9$) and (b) DMSO and H_2SO_4 ($y = 10.91x + 0.30$, $r^2 = 0.38$, $n = 45$). Only data obtained during marine/non-fog/non-precipitation conditions were used.

Figure 4a resulted from overlapping the observed peaks of both compounds by using the peak maxima as anchor points. During the relatively sunny conditions on April 24, DMS was initially depleted resulting in high DMSO levels during the daytime. With decreasing daylight and more cloudiness in the afternoon, DMSO production declined and DMS levels increased. The corresponding time lag between the peak maxima observed for both compounds was approximately 5 hours. A time lag of this order was also observed in the beginning of the DMSO measurements on April 22, however with high DMSO values following earlier high DMS levels. The meteorological conditions on this day were different than on April 24 (see Table 1). The April 22 trajectories suggest a mixing of continental air from Canada with relatively local MBL air. This mixture probably caused a rapid local production of DMSO from elevated DMS levels observed earlier in the same MBL air mass. The short time scale for DMSO production suggested by the present measurements indicate an atmospheric DMS lifetime of the order of a few hours to one day. In support of our previous discussion the regression data shown in Figure 4a also indicate the important role of DMSO and DMSO_2 as products of the DMS oxidation.

DMSO was also significantly correlated with H_2SO_4 as shown in Figure 4b. As discussed in the previous section,

this result is consistent with the assumption of similar atmospheric lifetimes for both compounds. In this context the slope of the regression line represents the relative yield ratio of DMSO/H₂SO₄ from DMS oxidation. The value obtained here (11) is close to that (16) derived from median concentrations in the previous section. To test the above assumption more quantitatively, the atmospheric lifetime of H₂SO₄ in marine air was calculated based on data obtained on April 24. The same calculation scheme as described by Eisele and Tanner [1993] was used. The data set consisted of aerosol size spectra measured every 15 min using a TSI model 3071 differential mobility analyzer in combination with a TSI model 3760 particle counter. In each measurement cycle, particle concentrations were recorded in 17 consecutive channels covering a size range of 20-600 nm. A first-order reaction rate constant for the reaction of H₂SO₄ with particles detected in this size range was calculated for each measurement cycle. A reaction probability (sticking coefficient) of 1.0 was assumed to obtain a minimum estimate for the H₂SO₄ lifetime. Based on this procedure, a diel variation of the 1/e lifetime of H₂SO₄ with respect to heterogeneous particle nucleation was obtained. The corresponding values ranged between 50-85 min resulting in a median value of 63±8 min. Corresponding total particle concentrations (20-600 nm diameter) measured on April 24 were typically between 150-300 cm⁻³. Concurrent measurements of ultrafine (>3 nm) aerosol (TSI model 3025) indicated no significant formation of new particles from homogeneous nucleation. Measurements of coarse mode aerosol (0.8-10 μm; TSI model 3300) showed relatively low particle surface area concentrations suggesting that H₂SO₄ removal due to particle scavenging was negligible in this size range. Therefore the estimate derived here for the atmospheric lifetime of H₂SO₄ is representative for the total particle spectrum observed on April 24. The minimum value of approximately 1 hour calculated for the H₂SO₄ lifetime is in reasonable agreement with the corresponding value obtained earlier for DMSO (3 hours) in view of the many uncertainties still inherent in this comparison (e.g., sticking coefficient, OH concentration). This further supports our conclusion that DMSO₂ was the dominant DMS oxidation product in marine air at Cheeka Peak. In contrast to DMSO and H₂SO₄ the correlation between DMSO and MSA(g) was barely significant at the 95% level ($r^2=0.10$, $n=46$). The lack of a better correlation between the two data sets was mainly due to a bifurcation in the data at higher DMSO and MSA(g) values which may reflect changes in the relative yields of both compounds in association with different air masses.

A highly significant correlation was found between gas phase MSA(g) and H₂SO₄ (Figure 5a). The positive intercept (0.008±0.005) is consistent with the relatively higher vapor pressure of MSA(g) compared to H₂SO₄ [Hoppel, 1987; Kreidenweis and Seinfeld, 1988]. The value of 0.07 obtained for the slope is surprising. Although the result may be somewhat fortuitous, it compares very well with a similar value (0.065) assumed to represent the average mole ratio of the corresponding aerosol species in the remote temperate and low-latitude marine atmosphere [Saltzman et al., 1983]. Interestingly, this ratio also results from recent calculations by Lin and Chameides [1993] assuming that the DMS-SO₃-H₂SO₄ pathway dominates sulfuric acid formation in marine air. On the other hand, the data in Figure 5a would be better fitted by an asymptotic curve than by a straight regression line. The data with H₂SO₄ concentrations higher than 0.3 pptv were obtained on April 29 when local

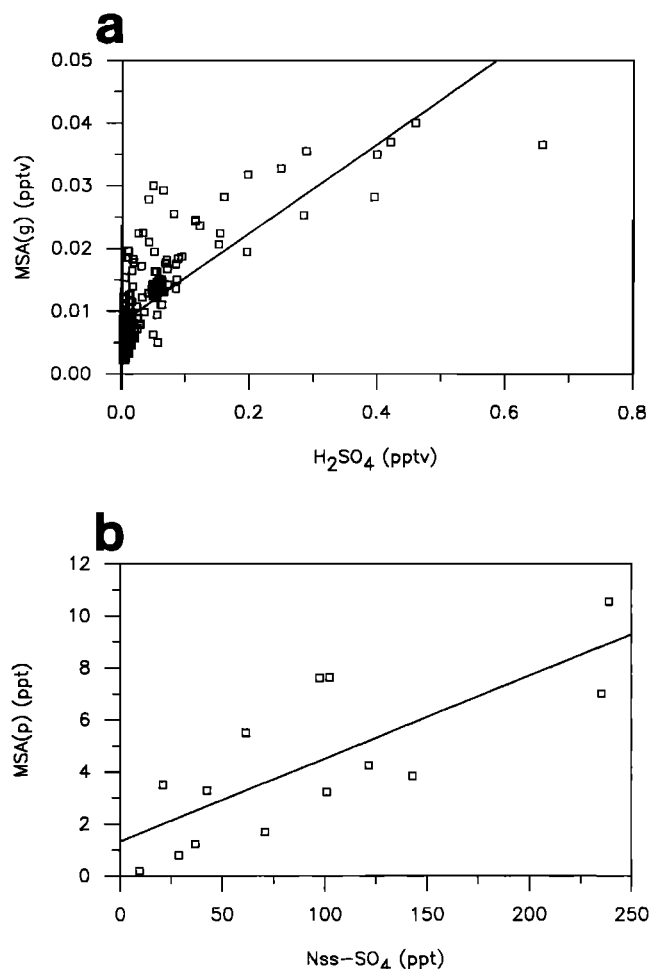


Fig. 5 Correlation between (a) gas phase MSA(g) and H₂SO₄ ($y = 0.071x + 0.008$, $r^2 = 0.60$, $n = 171$) and (b) aerosol MSA(p) and nss-SO₄ mixing ratios ($y = 0.032x + 1.32$, $r^2 = 0.59$, $n = 14$). Only data obtained during marine/non-fog/non-precipitation conditions were used.

air masses became increasingly more mixed with continental air (Table 1). By omitting these data, a slope of 0.10 results from the first-order regression of the data.

3.3.2. Aerosol compounds and gas/particle interactions. Figure 5b shows the correlation between MSA(p) and nss-SO₄ in sub-micrometer particles sampled from the marine wind sector. As shown by Quinn et al. [1993], approximately 80-90% of the MSA(p) and nss-SO₄ mass occurred in the sub-micrometer particle size range at Cheeka Peak. The slope of the regression line agrees well with a value of 0.034 calculated for the median MSA(p)/nss-SO₄ ratio and is consistent with the results reported by Quinn et al. [1993] for the size-separated data. It is also smaller than the slope in Figure 5a, presumably due to the different gas/particle partitioning of MSA and H₂SO₄ (see below). Assuming a range for the biogenic MSA(p)/nss-SO₄ ratio of 0.065-0.10 (see previous section) the regression slope of 0.032 in Figure 5b suggests that a major fraction of the nss-SO₄ (54-68%) sampled from the marine sector was associated with non-biogenic sulfur sources.

Figures 6a and 6b describe the relationships between gas phase and aerosol sulfur species. Both correlations are significant at the 95% confidence level and are consistent with a rapid gas/particle partitioning of both gases as

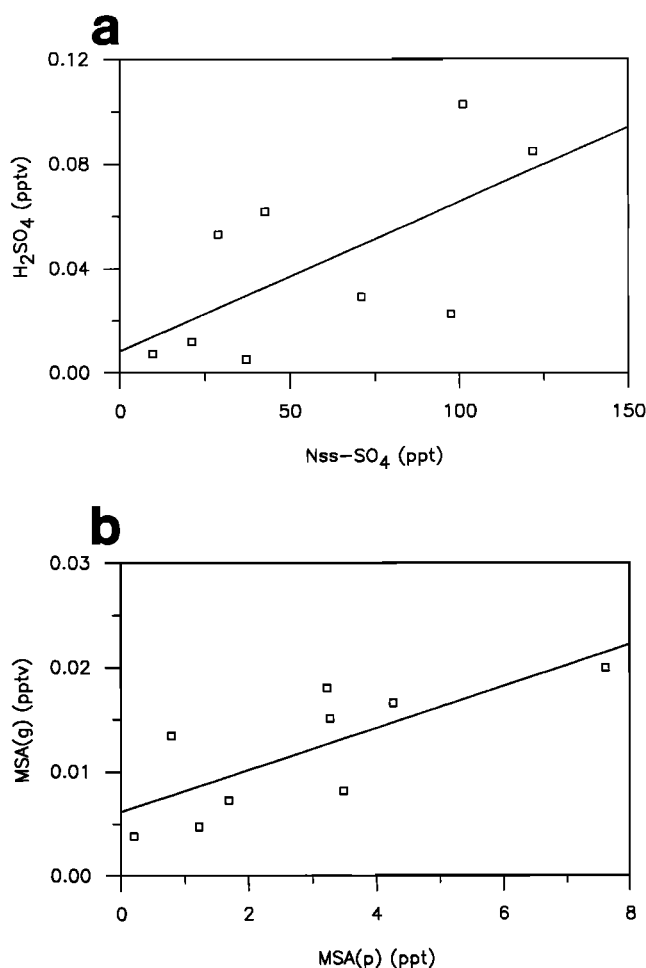


Fig. 6 Correlation between (a) gas phase H_2SO_4 and aerosol nss-SO_4 ($y = 0.00057x + 0.0084$, $r^2 = 0.42$, $n = 9$) and (b) gas phase MSA(g) and aerosol MSA(p) ($y = 0.002x + 0.006$, $r^2 = 0.56$, $n = 9$). Only data obtained from the marine wind sector were used.

discussed earlier. The difference of a factor of 3.5 between the slopes obtained in Figure 6a ($5.69\text{E-}04 \pm 2.55\text{E-}04$) and Figure 6b ($2.00\text{E-}03 \pm 6.65\text{E-}04$) indicates a relatively higher gas/particle partition ratio for MSA(g) compared to H_2SO_4 . Based on calculations by Hoppel [1987] and typical observed relative humidities of 70–90%, the data in Figure 6b suggest that gas phase MSA(g) levels were unsaturated with respect to preexisting particles by 1 to 2 orders of magnitude. However, Hoppel's calculations were based on the assumption of particles non-reactive to MSA(g) . The above factor of 3.5 and the small intercept obtained in Figure 5a suggest a relatively minor difference in the gas-to-particle removal rates of MSA(g) and H_2SO_4 . A more detailed case study of the particle removal of both compounds is given in the paper by Eisele and Tanner [1993]. We conclude that most of the data in Figures 6a and 6b represent partitioning ratios based on the scavenging of both gases by preexisting particles.

3.3.3. Relationships between CCN and other species. No significant correlation was found between CCN and DMS concentrations based on 22 simultaneous measurements made during marine/non-fog episodes. On the other hand, omitting four relatively high CCN values obtained on April 25 and

April 27 from the data set would yield a highly significant (99% confidence level) correlation between DMS and CCN at 0.9% supersaturation ($r^2 = 0.41$, slope = 2.5, intercept = 184, $n = 18$). Trajectories calculated for both days suggest a downward mixing of CCN from higher-altitude clouds which may justify excluding those days from the data regression. However, we believe that an interpretation of the DMS-CCN relationship based on DMS and CCN data alone is too speculative. The number of chemical and physical transformation steps involved is too large to suggest a simple linear correlation between both parameters. However, as shown in the discussion below, other measurements made for the first time in the present study significantly help to reveal the intricate processes involved in the DMS-CCN relationship.

Strong correlations (99% confidence level) were observed between CCN (0.3% ss) and both H_2SO_4 (Figure 7a) and nss-SO_4 (Figure 7b) in marine air. Correlations between CCN and MSA(g) or MSA(p) were not significant at the 95% confidence level. This is consistent with the previous discussion suggesting that MSA(g) mixing ratios measured at the present location were too low to induce particle growth or new particle nucleation. MSA(g) levels are likely much higher over polar and subpolar oceanic regions due to a relatively higher MSA(g) yield from DMS oxidation [e.g.,

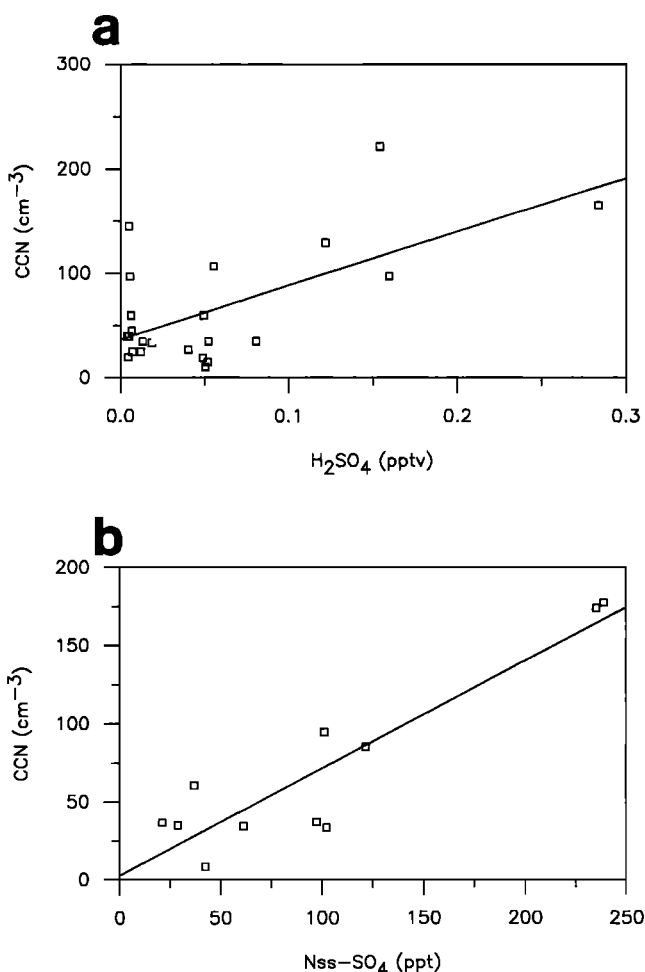


Fig. 7 Correlation between (a) CCN (0.3% ss) and H_2SO_4 measured on April 24–27 ($y = 514x + 37$, $r^2 = 0.40$, $n = 23$) and (b) CCN (0.3% ss) and nss-SO_4 ($y = 0.69x + 2.64$, $r^2 = 0.83$, $n = 11$). Only data obtained during marine/non-fog/non-precipitation conditions were used.

Ayers et al., 1991; Berresheim et al., 1990; Berresheim, 1987]. Future experiments are planned involving the techniques used in the present study to explore the possible contribution of MSA(g) to CCN formation over these regions. With respect to the present work the data in Figures 7a and 7b document the important role of H₂SO₄ as a precursor for CCN formation in the marine atmosphere. This is further supported by the relatively small intercept observed in the CCN-Nss-SO₄ data comparison (Figure 7b). Quinn et al. [1993] report a corresponding negative intercept which, however, resulted from only four long-term-averaged data pairs including also nss-SO₄ contributions from super-micrometer size sea-salt particles. Although a linkage between DMS and CCN (0.3% ss) levels is not directly evident from the present data, the relatively good correlations obtained between CCN and H₂SO₄ on one hand (Figure 7a) and between DMSO and H₂SO₄ (Figure 4b) and DMS and DMSO (Figure 4a) on the other support a DMS-CCN relationship. Interestingly, at 0.9% supersaturation no significant correlations between CCN and both H₂SO₄ and nss-SO₄ were observed. Earlier results by Hegg et al. [1991b] obtained from airborne measurements offshore of the Washington coast showed a weak correlation ($r^2=0.27$, $n=16$) between CCN and nss-SO₄ levels at 1% supersaturation. Although a supersaturation of 0.3% may be more typical for marine stratus clouds [Hoppel et al., 1986; Pruppacher and Klett, 1978], the present results suggest that the formation of marine CCN involving compounds less soluble than sulfate may not be negligible at higher supersaturation levels.

4. Summary and Conclusion

Simultaneous gas and particle phase measurements aimed at a field evaluation of the DMS-CCN relationship have been conducted at Cheeka Peak Research Station during the Pacific Sulfur/Stratus Investigation (PSI-3) in April 1991. Aerosol mass and size distribution data also obtained at Cheeka Peak are discussed in detail in a separate paper by Quinn et al. [1993]. The present study reports for the first time measurements of DMSO in ambient air obtained at high time resolution (2-3 min) and without preconcentration. Real-time measurements of H₂SO₄ and gas phase MSA(g) are also reported. Significant correlations between individual species were observed supporting a causal relationship between DMS and CCN (0.3% ss) in the marine atmosphere with H₂SO₄ representing the major linking species. Also, the present results in combination with recent kinetic studies [Hynes et al., 1992] suggest that DMSO₂ was the dominant end product of the DMS+OH reaction. Atmospheric lifetimes of 1-3 hours have been estimated for DMSO, H₂SO₄, and MSA(g) in marine air based on the present measurements. With respect to the DMS-CCN relationship our present results also suggest that at elevated supersaturation levels (0.9% ss) compounds less soluble than nss-SO₄ may become important in the formation of marine CCN.

While the present results will help to improve current model studies of atmospheric DMS oxidation and the DMS-CCN relationship they must still be regarded as being preliminary. The present study was limited to only a very short time period (2-3 weeks). During this period, frequent fluctuations in weather patterns, including fog and precipitation events at the study site, put considerable restraints on the measurement program and made the data evaluation very difficult. Moreover, fluctuations in air mass transport may have been responsible for the lack of

correlation observed between some of the species measured at different time resolutions. For example, no correlation was found between DMS and MSA(p) concentrations in contrast to previously reported measurements made at Cape Grim, Tasmania [Ayers et al., 1991], which had been conducted over the course of several seasons. At the Cheeka Peak site we frequently observed mixing of local MBL air with relatively aged air masses which had been transported from the Pacific Ocean area over Canada before reaching the site. This mixing of different air masses, possibly accompanied by relatively high NO_x and oxidant levels contained in continental air may explain the observed lack of correlation between DMS and MSA(p), similar to results obtained previously over the Atlantic Ocean [Berresheim et al., 1991]. In addition, previous airborne measurements over the northeastern Pacific coast [Andreae et al., 1988] have shown that long-range transport of continental air from Asia may have a significant impact on SO₂ and nss-SO₄ levels in this region. Although the Cape Grim site is also occasionally subject to continental air advection, it appears that contributions from continents other than Australia are relatively small over the Tasmanian coast [Berresheim et al., 1990]. In conclusion, we agree with Quinn et al. [1993] stating that a careful selection of measurement sites and of the types of measurements to be made is required in the planning of future experiments to achieve a better quantification of the DMS-CCN relationship. An adequate time period for the corresponding field measurements (of the order of at least 1 month) is also essential.

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