



Chemical composition of marine stratocumulus clouds over the eastern Pacific Ocean

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[1] Samples of marine cloud water collected over the eastern Pacific Ocean have been analyzed for pH, major ions (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+}), hydrogen peroxide, formaldehyde, S(IV), Fe, Mn, and total organic carbon. The samples were obtained during the Dynamics and Chemistry of Marine Stratocumulus, Phase II (DYCOMS-II) field project in July 2001. These measurements represent a unique in situ description of cloud water composition for stratocumulus clouds residing in the remote marine boundary layer, a regime for which there are few published cloud water composition data. A wide range of concentrations was observed for each species of interest, including sodium (36–2784 μN), sulfate (15–905 μN), nitrate (3–205 μN), hydrogen peroxide (37.8–283.2 μM), formaldehyde (2.2–8.7 μM) and Fe (<MDL–85.9 $\mu\text{g L}^{-1}$). Chloride and potassium were present in expected seawater ratios while sulfate, magnesium, and calcium were enriched to varying degrees. Trends in cloud water concentrations with cloud liquid water content (LWC) and volume mean drop diameter show that dilution played a role in cloud drop solute concentration variations during individual flights and that solute concentrations are related to cloud drop size and ultimately to below-cloud aerosol number concentration. Air equivalent concentrations (the amount of a solute in cloud water per unit volume of air) were derived in order to eliminate concentration dependence on LWC and to allow comparison with previous aerosol, trace gas, and cloud water studies. The analysis indicates that background marine conditions were not always encountered during the DYCOMS-II mission as a result of anthropogenic or biogenic sources impacting the study region.

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1. Introduction

[2] Interest in cloud processing mechanisms such as the aqueous phase production of sulfate, the modification of the aerosol size distribution, and the removal of trace species from the atmosphere has motivated the collection and chemical analysis of cloud and fog water samples during a wide range of field studies. While the majority of these studies have focused on continental locations, a number of studies have also examined the composition of clouds in the marine environment. Solute concentrations from a variety of marine and coastal locations are therefore available in the published literature. However, studies have rarely been undertaken to directly sample clouds in the remote marine boundary layer, resulting in a limited record of cloud water solute concentrations from that environment.

[3] Marine cloud water studies have generally targeted stratiform clouds and have employed two approaches for

sample collection. Sampling has been carried out from coastal, ground-based locations that rely on high-elevation sites for cloud exposure. Alternatively, researchers have collected marine and coastal cloud water samples from aircraft, which are not limited to geographically fixed sampling sites. Many coastal, ground-based studies [e.g., Collett *et al.*, 2002; Rao and Collett, 1995, 1998; Bator and Collett, 1997; Munger *et al.*, 1989; Waldman *et al.*, 1985] and aircraft-based studies conducted near coastlines [e.g., Jaeschke and Gunther, 2002; Leitch *et al.*, 1996; Richards, 1995; Barth *et al.*, 1989; Hegg and Hobbs, 1981, 1986, 1988; Kelly *et al.*, 1985; Hegg *et al.*, 1984a; Daum *et al.*, 1984a, 1984b; Richards *et al.*, 1983] were not intended to document cloud water composition that was marine in origin. In many of these cases, cloud water samples were obtained from air masses suspected to be of continental origin or from air masses of unknown origin, making it difficult to determine if the reported composition data are representative of clouds in the marine environment or if sampled clouds simply exhibit direct continental or anthropogenic influences. The fact that sulfate and nitrate were the dominant ionic species in many of these studies suggests that the latter is often the case.

[4] Some cloud water samples have been classified as marine in origin, though not necessarily representative of

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pristine marine conditions, on the basis of surface weather maps, prevailing wind direction, or analyzed composition. These include ground-based samples from Puerto Rico [Weathers *et al.*, 1988; Lazrus *et al.*, 1970], the Oregon coast [Collett *et al.*, 2002; Bator and Collett, 1997], and the Canary Islands [Moore, 2001], and from aircraft flights over Western Washington [Hegg *et al.*, 1984b]. Though the evidence suggests that these samples were generally dominated by marine influences, local sources were not ruled out.

[5] A limited number of marine cloud water studies have included air mass trajectory analyses or streamline analyses to help evaluate the origin of sampled clouds. Vong *et al.* [1997] collected 102 stratiform cloud water samples along the coast of Washington State and selected samples that met back trajectory and concentration criteria to define a composite clean marine background composition. On the basis of their selection criteria, the composite case of Vong *et al.* [1997] may represent one of the best descriptions of unpolluted marine cloud water available. Borys *et al.* [1998] report on the composition of marine stratiform clouds intercepted on Tenerife. Back trajectories indicated that the majority of their sampled clouds resided over the Atlantic Ocean for a substantial duration; however, high concentrations of non sea salt sulfate (nssSO_4^{2-}) and nitrate coupled with high cloud drop number concentrations lead them to conclude that their sampling site was strongly influenced by polluted air masses. Air mass back trajectories were used by Menon *et al.* [2000] to categorize cloud water samples collected from Mount Mitchell Peak in North Carolina as marine, continental, or polluted. However, sulfate, nitrate, and ammonium constituted the major ionic components for even the marine samples, suggesting significant continental influences.

[6] Few cloud-sampling operations have obtained samples directly from clouds residing more than 200 km offshore. Observations of cloud water composition made in this environment, whether representative of pristine marine conditions or influenced by extensive biological or anthropogenic sources, have typically only included pH and ionic concentrations for a limited number of samples. Marine stratocumulus cloud water samples were collected in the Eastern Pacific as part of the aircraft-based Dynamics and Chemistry of Marine Stratocumulus (DYCOMS) field project [Lenschow *et al.*, 1988; Huebert *et al.*, 1988], though only the median and range of cloud water pH values were reported. Twohy *et al.* [1995] sampled cloud water within several hundred km of the Northern California coast and provide sulfate and nitrate concentrations for two sample periods. Additional composition data for cloud water samples collected in the marine boundary layer include ionic concentrations and pH for five samples obtained over the western Pacific Ocean during a period potentially impacted by Asian pollution [Watanabe *et al.*, 2001], ionic concentrations and pH for two cumulonimbus clouds residing 200 km upwind of Hawaii [Parungo *et al.*, 1982], and pH values for several samples collected more than 150 km from the Australian coast [Scott, 1978].

[7] A more comprehensive in situ composition data set is now available for stratocumulus clouds in the remote boundary layer. This data set is based on fifty cloud water samples that were obtained with an aircraft-based cloud

water collection system jointly developed at Colorado State University (CSU) and the National Center for Atmospheric Research (NCAR) [Straub and Collett, 2004]. The collector was deployed during the second Dynamics and Chemistry of Marine Stratocumulus (DYCOMS-II) field project, during which cloud water samples were collected over the eastern Pacific Ocean, approximately 400 km off the coast of southern California. The result is a unique description of marine cloud water solute composition that includes pH, and concentrations of major inorganic ions, trace metals, formaldehyde, peroxides, S(IV), and total organic carbon. Although the samples were all obtained well offshore, samples from each of the flights may not be representative of clean marine background conditions. Comparisons with previous cloud water, aerosol, and trace gas measurements made in the marine boundary layer suggest that some combination of continental sources and biogenic activity may have influenced the cloud water composition in the study region, although source apportionment was not possible with the available data. These comparisons, along with details regarding the deployment of the collection system during DYCOMS-II and a discussion of the factors controlling cloud water concentrations in the marine boundary layer will be the focus of this paper.

2. Experimental Methods

2.1. DYCOMS-II Field Campaign

[8] The DYCOMS-II field project took place during July 2001 [Stevens *et al.*, 2003] as a sequel to the original 1986 DYCOMS field campaign [Lenschow *et al.*, 1988]. The DYCOMS-II mission consisted of nine flights in the marine boundary layer over the Pacific Ocean and was based on the NSF/NCAR C-130 aircraft. The primary focus of DYCOMS-II was to study the turbulent mixing of free tropospheric air into the marine boundary layer (entrainment) and the production and influences of drizzle in marine stratocumulus cloud layers. Seven of the flights occurred during the nighttime (RF01–RF07) and two during the daytime (RF08 and RF09).

[9] The targeted region was approximately 400 km southwest of San Diego, CA (approximately 29–32°N, 120–123°W). The majority of research flight tracks consisted of a ferry flight to the target location followed by a series of hour long legs flown at five different levels: above cloud, below cloud, at the surface, just below cloud top and just above cloud base. At each level, the flight track consisted of one 30 min clockwise circle and one 30 min counterclockwise circle, each approximately 60 km in diameter. Between horizontal flight legs, rapid traverses from the surface to the free troposphere provided profiles of the entire marine boundary layer. An attempt was made for the flight tracks to advect with the mean wind in order to sample the same air mass over the duration of the flight. However, the flights were not truly Lagrangian because of wind shear in the boundary layer.

[10] The marine boundary layer was well mixed throughout the duration of the DYCOMS-II project, as indicated by profiles of total water content and liquid water potential temperature [Stevens *et al.*, 2003]. The well-mixed layer was topped by a strong inversion, below which the stratocumulus cloud layer formed. The cloud layer appeared to be

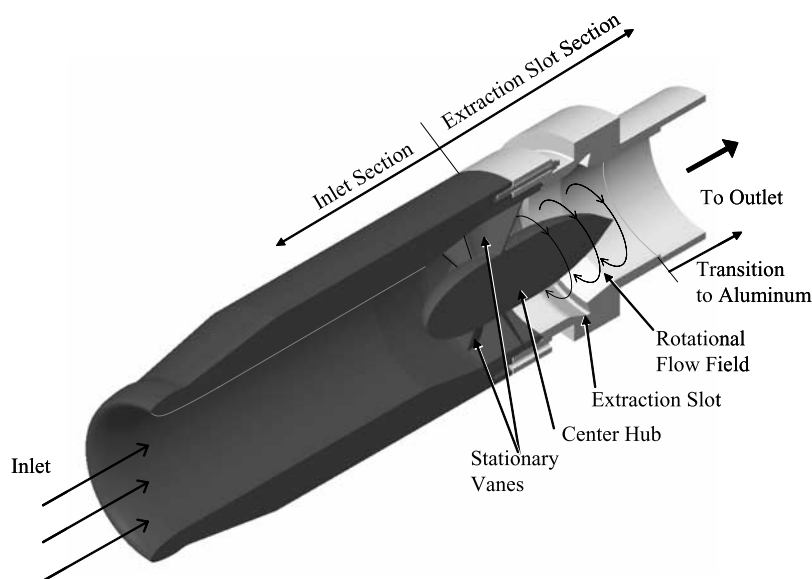


Figure 1. Cut-away view of the axial-flow cyclone cloud water collector inlet. The inlet and extraction slot sections are machined from polycarbonate, and the curved vane assembly is fabricated from glass filled nylon. The inlet is 6 cm in diameter.

relatively homogeneous throughout each of the research flights; however, variability in drizzle, cloud liquid water content (LWC), dimethyl sulfide (DMS) concentrations, particle concentrations, and other parameters were observed from flight to flight and across individual flight circles [Stevens *et al.*, 2003, 2005]. Cloud drop number concentrations also varied substantially from flight to flight, ranging from 50 cm^{-3} to over 300 cm^{-3} during individual cloud water sample periods.

[11] The cloud layer was generally 300 to 500 m in depth with cloud tops ranging between 600 and 1100 m during the study. LWC increased from cloud base to cloud top, typically ranging between 0.1 and 0.2 g m^{-3} during the cloud base flight legs and 0.5 to 0.8 g m^{-3} during the legs near cloud top. Winds were predominantly from the north-northwest and average horizontal wind speeds varied from 5 to 12 m s^{-1} at flight level. Drizzle was encountered on all flights, although the drizzle intensity varied from flight to flight and over the course of individual flight circles [van Zanten *et al.*, 2005].

2.2. Instrumentation

[12] Cloud water samples were obtained during DYCOMS-II with the NCAR/CSU airborne cloud water collector [Straub and Collett, 2004]. The collector features an axial-flow cyclone for the separation of cloud drops from the airstream (Figure 1). The cyclone consists of a 6 cm inner diameter duct that is placed on the exterior of the aircraft and exposed to the airflow. Ram pressure drives air and cloud drops into the duct and through a fixed vane unit that creates a rotational flow field. Centrifugal action quickly moves cloud drops to the duct wall where they accumulate and flow into a circumferential extraction slot. Cloud water is drawn out of the extraction slot and directed to one of seven individual sample bottles.

[13] The entire collection system was housed in a Particle Measurement Systems (PMS) canister, which was mounted

on the instrumentation pod located below the right wing of the NSF/NCAR C-130 during the DYCOMS-II mission. The wetted surfaces of the collection system were cleaned with deionized water prior to every flight and an inlet cover prevented contamination during periods when sampling was not occurring.

[14] Computational fluid dynamics (CFD) analysis and an experimental laboratory calibration were used to evaluate the collection characteristics of the axial-flow cyclone [Straub and Collett, 2004]. The overall D_{p50} , the diameter at which 50% of the drops are collected, is approximately $8 \mu\text{m}$. The CFD analysis indicates that sampling is subisokinetic as freestream velocities are reduced from 115 m s^{-1} to approximately 30 m s^{-1} in the interior of the collector. Mass transfer calculations addressing compressional heating effects in the collector show that evaporation of cloud drops suspended in the air stream should be negligible for drop sizes of interest. Additional calculations place an upper limit on potential evaporation from wall surfaces at less than 10% for operation in clouds with LWC greater than 0.2 g m^{-3} [Straub and Collett, 2002].

[15] The first operational use of the collection system occurred during the DYCOMS-II mission at which time the cloud water collection rate was found to be lower than anticipated. Evidence presented by Straub and Collett [2002, 2004] suggests that while cloud drops are efficiently separated from the airstream as expected, the accumulated sample is inefficiently removed from the interior wall of the axial-flow cyclone for storage. Because the accumulated cloud drops should be well mixed, extraction of any portion of this available water still provides a sample representative of the composition of the entire population of collected cloud drops. The observed collection rate varied between 0.07 and 1.2 g min^{-1} .

[16] Sample volumes collected during the first research flight, RF01, were insufficient for complete chemical analysis and no results from that flight are reported. In order to

Table 1. Sample Durations, Collected Sample Volumes, and Microphysical Parameters Averaged for Cloud Base and Cloud Top Sample Periods for Individual DYCOMS-II Flights

Flight	Takeoff Date/Time, UTC	Flight Leg	Number of Samples	Sample Duration, min	Volume Collected, mL	Height Above Cloud Base, ^a m	Volume Mean Diameter, ^b μm	Cloud Drop Number Concentration, ^b cm^{-3}	Average LWC, ^c g m^{-3}
RF02	11 Jul 2001, 0624	cloud base	1	11.3	0.8	176	16.6	49	0.14
RF02	11 Jul 2001, 0624	cloud top	5	12.9	9.4	232	22.7	65	0.34
RF03	13 Jul 2001, 0618	cloud base	2	16.0	5.0	17	10.6	279	0.25
RF03	13 Jul 2001, 0618	cloud top	5	11.7	3.5	170	13.1	260	0.46
RF04	17 Jul 2001, 0622	cloud base	2	26.0	5.1	94	10.6	211	0.21
RF04	17 Jul 2001, 0622	cloud top	5	12.3	11.6	358	17.5	177	0.64 ^d
RF05	18 Jul 2001, 0619	cloud base	1	41.2	4.7	87	N/A ^e	N/A ^e	0.13
RF05	18 Jul 2001, 0619	cloud top	3	20.1	3.7	89	N/A ^e	N/A ^e	0.26
RF06	20 Jul 2001, 0539	cloud base	2	16.1	1.4	102	N/A ^e	N/A ^e	0.17
RF06	20 Jul 2001, 0539	cloud top	4	9.2	5.7	329	N/A ^e	N/A ^e	0.50
RF07	24 Jul 2001, 0553	cloud base	2	30.2	5.6	134	14.4	132	0.29
RF07	24 Jul 2001, 0553	cloud top	5	12.6	13.7	381	19.5	137	0.62
RF08	25 Jul 2001, 1945	cloud base	0 ^f	N/A	N/A	N/A	N/A	N/A	N/A
RF08	25 Jul 2001, 1945	cloud top	7	16.8	4.7	178	16.6	118	0.39
RF09	27 Jul 2001, 1816	cloud base	2	37.3	3.6	68	9.2	244	0.13
RF09	27 Jul 2001, 1816	cloud top	4	16.1	5.1	205	12.7	233	0.39

^aCloud base approximated from C-130 sounding leg data.

^bSPP-100 data; only partial data available for RF03 and RF04.

^cPVM-100A data.

^dHot wire LWC used for three cloud top sample periods.

^eSPP-100 data unavailable for RF05 and RF06.

^fAll in-cloud flight legs during RF08 were at midcloud or cloud top.

compensate for the lower than expected sample retention by the system, collection times were increased during subsequent flights to an average of 25 min for cloud base samples and 13 min for cloud top samples. During each flight, two samples were typically collected near cloud base and five samples were collected at cloud top. Fifty total samples were obtained during flights RF02–RF09; a summary of these sample collection periods is shown in Table 1.

[17] The NSF/NCAR C-130 was outfitted with a range of in situ and remote sensing instruments for the measurement of aerosol and cloud microphysics, trace gases (DMS, O₃, CO, and CO₂), and meteorological and aircraft state parameters. An overview of the DYCOMS-II instrumentation suite is given by *Stevens et al.* [2003]; a brief description of those instruments most relevant to the cloud water composition measurements and analyses is included here. A PVM-100A (Gerber Scientific, Inc.) provided measurements of cloud LWC for drop diameters in the range of 4 to 45 μm with a reported LWC measurement uncertainty of 5–10% [*Gerber et al.*, 1994]. The PVM-100A LWC data was used for all of the analyses in this work except for three sample periods during RF04 when PVM-100 data were unavailable. During those periods, LWC data were obtained from one of the two available hot wire probes [*King et al.*, 1985]. Cloud drop size distributions were obtained with an SPP-100, a version of a Forward Scattering Spectrometer Probe (FSSP-100) upgraded by Droplet Measurement Technologies (DMT), which is sensitive to drops between 2 and 47 μm and has reported measurement uncertainties of 20–28% for size and 16–27% for concentration [*Baumgardner*, 1989, 1996]. Data from the SPP-100 were unavailable for flights RF05 and RF06, thus cloud water solute trends with volume mean diameter or drop number concentration do not include these flights. Size distributions for aerosol particles between 0.1 and 3.0 μm were measured with a Particle

Measurement Systems Passive Cavity Aerosol Spectrometer Probe (PCASP) with electronics upgraded by DMT.

2.3. Analytical Methods

[18] Immediately after returning from each flight, the sample storage bottles were removed from the cloud water collector and individually weighed to determine the mass of collected water. Cloud water samples were analyzed for pH using an Orion model 250A meter calibrated with pH 4.01 and pH 7.00 buffer solutions. This was followed by the preparation of separate sample aliquots for each analytical protocol to be applied. When sufficient sample was available, aliquots were prepared for analysis of inorganic ions, S(IV), peroxides, trace metals, formaldehyde, and total organic carbon (TOC). Aliquots were stored on site at 4°C until postcampaign analysis could be performed at Colorado State University.

[19] Anions and cations were analyzed on parallel Dionex DX500 ion chromatograph (IC) systems equipped with AS4A and CS12 separation columns, AG4A and CG12 guard columns, self-regenerating suppressors, and conductivity detectors. Anion concentrations (Cl⁻, NO₃⁻, and SO₄²⁻) and cation concentrations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) were measured for all 50 sample periods. Ammonium concentrations were below the minimum detection limit (MDL) in 13 samples and are reported to be one half the MDL in those cases to provide an unbiased estimate of the study average concentration.

[20] Aliquots for total S(IV) were prepared in the field by stabilizing S(IV) as hydroxymethanesulfonate (HMS). At the time of analysis, the HMS was decomposed to free S(IV) and formaldehyde and quantified by the pararosaniline method [*Dasgupta et al.*, 1980] using a Hach DR/4000V spectrophotometer. Of the 38 total samples analyzed for

Table 2. Analytical Uncertainty for the DYCOMS-II Cloud Water Sample Analyses^a

	MDL	RSD, %
H ₂ O ₂ , μM	0.91	2.06
HCHO, μM	0.79	3.18
Fe, $\mu\text{g L}^{-1}$	11.63	2.43
Mn, $\mu\text{g L}^{-1}$	0.41	1.48
S(IV), μM	0.87	8.39 ^b
Na ⁺ , μN	2.12	2.75
NH ₄ ⁺ , μN	0.99	8.69
K ⁺ , μN	0.19	4.21
Mg ²⁺ , μN	8.65	2.93
Ca ²⁺ , μN	8.00	5.89
Cl ⁻ , μN	10.01	2.95
NO ₃ ⁻ , μN	1.10	1.4
SO ₄ ²⁻ , μN	1.18	2.28

^aMinimum detection limits (MDL) at the 95% confidence level were calculated from preflight blanks and relative standard deviations (RSD) were calculated from replicate sample analyses.

^bRSD calculated from standard replicates.

S(IV), 22 had concentrations below the MDL and are reported as one half the MDL.

[21] Following the procedure of *Lazrus et al.* [1985], aliquots for total soluble peroxides were created by adding *p*-hydroxyphenylacetic acid (POPHA) to react with available peroxides to form a stable dimer. The dimer concentration was then determined with a Shimadzu RF-1501 spectrofluorophotometer. This analysis technique does not differentiate hydrogen peroxide from organic peroxides, resulting in a measure of total soluble peroxides in the cloud water. Although organic peroxides have been measured as a significant fraction of total gas phase peroxides [e.g., *Heikes et al.*, 1996a; *Heikes*, 1992; *Weller et al.*, 2000], aqueous phase measurements are usually dominated by H₂O₂ because of the lower solubility of organic peroxides [e.g., *Olszyna et al.*, 1988; *Kelly et al.*, 1985; *Daum et al.*, 1984b]. However, sizable contributions from organic peroxides have also been measured in a few continental cloud water samples [*Kelly et al.*, 1985], thus the presence of organic peroxide cannot be ruled out entirely.

[22] A single aliquot was prepared for the measurement of total soluble manganese and total soluble iron by acidifying a portion of cloud water sample with concentrated HNO₃. The analysis of the DYCOMS-II trace metal samples was performed on a Varian model 640Z Zeeman-corrected graphite furnace atomic absorption spectrometer. No trace metal concentrations are reported from RF03 because of possible contamination indicated by one of the blanks. Of the 20 analyzed samples, 8 Fe and 10 Mn samples were below the MDL and are therefore reported as one half the MDL.

[23] Formaldehyde was stabilized as HMS for storage by adding bisulfite. Just before analysis, HMS in the aliquot was decomposed back to formaldehyde and quantified through a fluorescence technique [*Dong and Dasgupta*, 1987].

[24] Because of limited sample volumes, only two 15 mL TOC aliquots were prepared. Cloud water from two individual cloud top sample periods during RF07 was combined in equal proportions to create each aliquot. The TOC analysis was performed on a Shimadzu model 5000A Total Organic Carbon Analyzer.

[25] For each measured species, the MDL at the 95% confidence level was determined from blank analyses taken before every flight. When sufficient sample was available, replicate analyses were completed in order to determine relative standard deviations (RSD). Excess sample was unavailable for replicate S(IV) analysis; therefore the RSD was based on replicate analyses of low concentration standards. Table 2 shows the MDL and RSD for each analyzed species.

3. Results and Discussion

[26] The composition of the DYCOMS-II cloud water samples will first be presented in terms of aqueous phase concentrations in order to establish a data set of cloud water composition for the study region and to describe factors that control aqueous phase concentrations. Air equivalent concentrations, representing the amount of cloud drop solute present in a given volume of air, will then be presented in order to compare the DYCOMS-II findings with aerosol, gas phase, and cloud water measurements from past field studies conducted in marine environments.

3.1. Cloud Water Solute Concentrations

[27] The pH of the 50 cloud water samples collected during DYCOMS-II ranged between 3.26 and 4.82, with a median of 4.01. These values are consistent with cloud water pH measurements obtained during the original DYCOMS mission, which ranged between 3.71 and 5.06 with a median of 4.02 [*Lenschow et al.*, 1988]. Mean cloud water pH values between 4.0 and 5.0 have been observed for cloud water in other marine stratiform environments as sampled from ground-based sites [*Collett et al.*, 2002; *Moore*, 2001; *Borys et al.*, 1998; *Vong et al.*, 1997; *Weathers et al.*, 1988] and from aircraft [*Hegg et al.*, 1984b; *Watanabe et al.*, 2001; *Parungo et al.*, 1982].

[28] The average ionic cloud water composition is illustrated in Figure 2. Sodium and chloride accounted for approximately two thirds of total ions in solution. An ionic charge balance was constructed for each sample with H⁺ and OH⁻ concentrations computed from measured pH values. Carbonate and bicarbonate concentrations were calculated

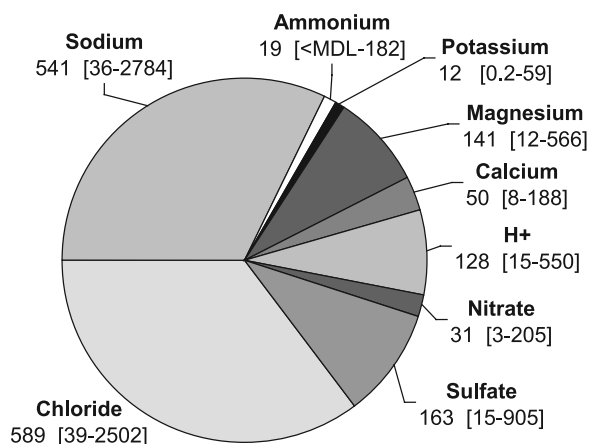


Figure 2. Average DYCOMS-II cloud water ion concentrations. Average concentrations in μN follow species name, and the range in μN appears in brackets.

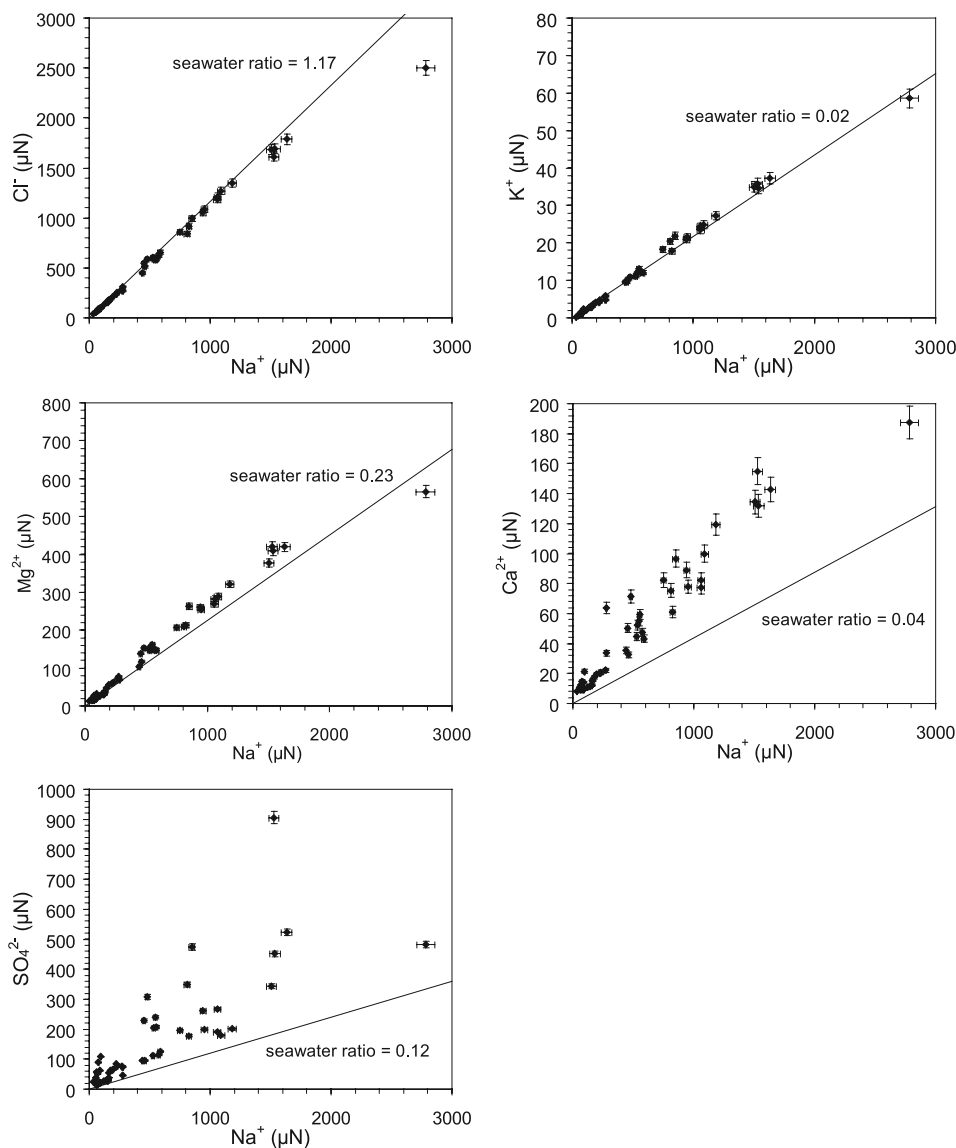


Figure 3. Cloud water concentrations of Cl^- , K^+ , Mg^{2+} , Ca^{2+} , and SO_4^{2-} plotted as a function of Na^+ concentration. Solid lines represent the ratio observed in seawater, and error bars indicate one sigma analytical uncertainty.

on the basis of an assumed equilibrium with background $\text{CO}_2(\text{g})$ concentrations. Calculated anion to cation charge ratios ranged between 0.71 and 0.95, with an average of 0.85. Because organic acids were not preserved in the field, their contribution to the ion balance is not included, partially contributing to a ratio less than 1.0. Some release of acetic acid from a sealant used in the system downstream of the sample flow path may have also contributed to a charge balance below 1.0, and we cannot rule out some effect on the pH of some samples. The lowest charge balance ratios were observed when total ion concentrations were low (less than approximately 300 μN).

[29] Many of the ions typically associated with sea salt were observed in proportions similar to those found in seawater (Figure 3), suggesting sea salt aerosol produced at the ocean surface as their source. No significant chloride deficit was observed in the cloud water samples, unlike

observations for polluted marine aerosols in which acid displacement reactions occur [e.g., *Munger et al.*, 1989; *Parungo et al.*, 1987]. HCl displaced by NO_3^- , SO_4^{2-} , and organic acids in deliquesced, concentrated sea salt aerosols resides in the gas phase and can be reabsorbed by dilute cloud drops [*Munger et al.*, 1989; *Bator and Collett*, 1997; *von Glasow and Sander*, 2001].

[30] Potassium was present at seawater proportions while magnesium was slightly enriched and calcium was substantially enriched. Other researchers have observed calcium enrichment in cloud water [*Moore*, 2001], aerosols [*Parungo et al.*, 1987], and rainwater [*Keene et al.*, 1986] collected in the marine boundary layer. It has been noted [*Fitzgerald*, 1991; *Raemdonck et al.*, 1986] that soil or mineral components are nearly always identified in coarse mode marine aerosols as a result of transport from continental locations. The measurement of dissolved Fe and Mn in the

Table 3. Average, Minimum, and Maximum Concentrations of Nonionic Species in the DYCOMS-II Cloud Water Samples

	Samples	Average	Minimum	Maximum
HCHO, μM	30	4.7	2.2	8.7
H ₂ O ₂ , μM	44	114.1	37.8	283.2
S(IV), μM	38	1.0	<MDL	3.7
Fe, $\mu\text{g L}^{-1}$	20	22.3	<MDL	85.9
Mn, $\mu\text{g L}^{-1}$	20	0.7	<MDL	2.7
TOC, ppm	2 ^a	0.847	0.841	0.853

^aCombined samples from RF07.

DYCOMS-II cloud water samples supports the presence of a soil component as Fe and Mn have a negligible marine source (as measured by the molar ratios of these species to Na⁺ which are both $<1 \times 10^{-8}$) but a substantial crustal source. Alternatively, calcium and magnesium enrichment may occur as sea salt aerosols are formed from an ocean surface layer enriched in calcium and magnesium, potentially as a result of biogenic processes [Sievering *et al.*, 1999].

[31] Sulfate was also significantly enriched in the DYCOMS-II cloud water samples. This is consistent with the routine observation of excess sulfate in aerosols residing globally in the marine boundary layer [Heintzenberg *et al.*, 2000; Fitzgerald, 1991]. Non-sea-salt sulfate was found in every cloud water sample and accounted for 27% to 90% of the total sulfate concentration and averaged 58% of the total. The origin of nssSO₄²⁻, which has biological oceanic and anthropogenic sources, will be discussed further below.

[32] Concentrations of nonionic species are listed in Table 3. Cloud water peroxide concentrations were considerable throughout the DYCOMS-II mission, averaging 114.1 μM and ranging between 37.8 and 283.2 μM . These levels are not unexpected as peroxides are formed through peroxy radical recombination which is positively correlated with increased solar radiation, water vapor concentrations, and temperature [Lee *et al.*, 2000]. Enhanced peroxide concentrations are also expected when nitrogen oxide levels are low, which is typically the case in the marine boundary layer [Weller *et al.*, 2000; Martin *et al.*, 1997].

[33] The cloud water formaldehyde concentration represents dissolved formaldehyde, formaldehyde present in solution as the gem diol form, and any formaldehyde complexed with dissolved S(IV) as HMS. Formaldehyde concentrations between 2.2 and 8.7 μM were observed while the average concentration was 4.7 μM . Methane oxidation, followed by the formation and photolysis of methylhydroperoxide, is the main source of formaldehyde in the marine boundary layer [Ayers *et al.*, 1997; Heikes *et al.*, 2001]. Formaldehyde can be directly emitted from anthropogenic sources; however, its photochemical lifetime is on the order of hours making long-range transport into the remote marine boundary layer negligible [Weller *et al.*, 2000].

[34] The majority of DYCOMS-II samples had S(IV) concentrations below the MDL. This result is not surprising given the presence of abundant H₂O₂ and the ability of H₂O₂ to rapidly oxidize S(IV) in the aqueous phase. It is often observed that very little S(IV) is detected in clouds in which excess H₂O₂ is found [Daum *et al.*, 1984b; Kelly *et al.*, 1985; Macdonald *et al.*, 1995]. S(IV) concentrations

occasionally measured above the detection limit, primarily on flights RF03 and RF09, may indicate the presence of HMS in the cloud drops. HMS provides a more stable S(IV) reservoir that is not easily oxidized [Rao and Collett, 1995; Richards *et al.*, 1983]. During sample periods when both species were measured above the detection limit, sufficient HCHO was always present to support this assumption.

[35] Two TOC aliquots were prepared from cloud water obtained during the RF07 cloud top flight leg. As discussed below, RF07 was characterized by lower air equivalent cloud water concentrations of sea salt species, sulfate, nitrate, and ammonium than observed on many of the other flights. Accordingly, it is possible that TOC concentrations from RF07 are lower than those present (but not measured) in clouds sampled on other flights.

[36] Aqueous phase cloud water concentrations of all species varied widely from sample to sample and from flight to flight during DYCOMS-II. As pointed out by Daum *et al.* [1984a] and Vong *et al.* [1997], variations in cloud water solute concentrations not only reflect changing source concentrations, dispersion, and chemical processing, but also changes in cloud LWC. LWC has typically been observed to increase with height in marine stratocumulus, resulting from condensational growth of existing drops rather than additional drop activation [Martin *et al.*, 1994]. This suggests that nonvolatile solute concentrations in a bulk cloud water sample should dilute at the rate LWC increases, subject to other factors such as the scavenging of interstitial particles. Accordingly, during individual DYCOMS-II flights cloud water solute concentrations tended to decrease as LWC increased from cloud base to cloud top. For each flight, the relationship between nonvolatile solute concentrations and LWC was generally consistent with that expected for simple dilution, with deviations attributable to small sample populations obtained from clouds that were not individually tracked from cloud base to cloud top and to cloud processes other than dilution.

[37] Cloud water solute concentrations also varied widely from flight to flight. For example, the average sodium concentration during RF08 was very low (69 μM) compared to the averages for RF03 (1015 μM) or RF05 (1293 μM). When solute concentrations are plotted as a function of cloud drop volume mean diameter rather than LWC, a single relationship emerges for each species as seen in Figure 4. Two effects are captured in the graphs in Figure 4. First, as drop diameter increases from cloud base to cloud top during an individual flight, dilution reduces solute concentrations. Second, mean drop diameters varied in general from flight to flight. Flights with smaller mean drop diameters typically exhibited higher solute concentrations and flights with larger mean drop diameters exhibited lower solute concentrations.

[38] Consistent with previous microphysical studies of marine stratocumulus [e.g., Hudson and Svensson, 1995], cloud drop size was inversely correlated with cloud drop number concentration during DYCOMS-II (Figure 5). Higher cloud drop number concentrations were generally associated with smaller mean drop diameters and, as described above, higher solute concentrations. Twohy *et al.* [2005] have shown that the number of cloud drops observed during the DYCOMS-II flights was significantly correlated with the particle number concentration present below cloud. This suggests that flight to flight variability in the below

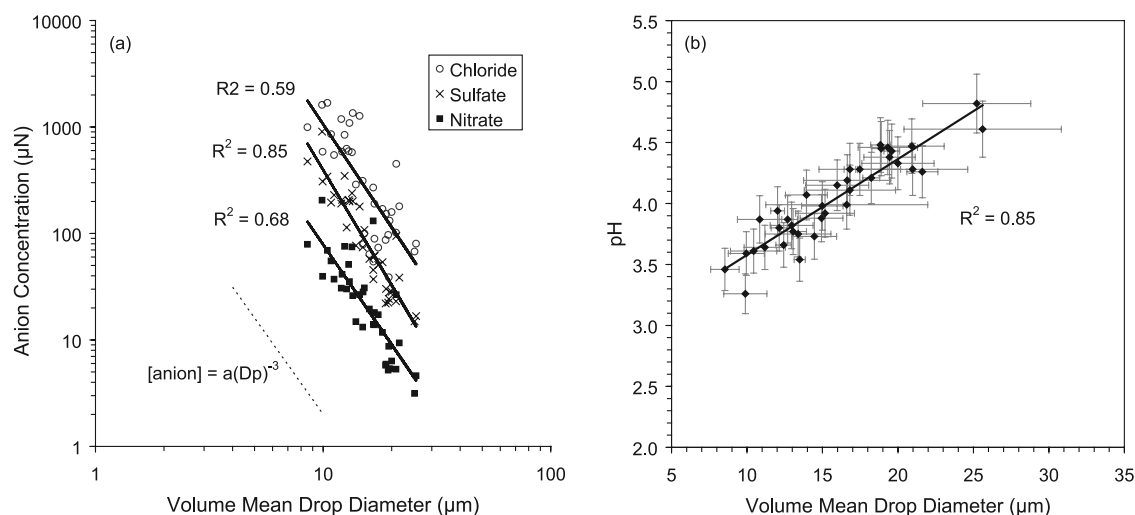


Figure 4. Variations in (a) cloud water concentrations of Cl^- , SO_4^{2-} , and NO_3^- and (b) pH with volume mean diameter for individual cloud water sample periods during DYCOMS-II flights RF02–RF04 and RF07–RF09. In Figure 4a, the expected decrease in concentration with drop size due to simple dilution is indicated by the dashed line. In Figure 4b, horizontal error bars represent one standard deviation from the mean for each sample period, and vertical error bars represent $\pm 5\%$ uncertainty in the pH measurement. Volume mean drop diameters were calculated from SPP-100 drop size distributions.

cloud aerosol number concentration, in conjunction with condensational growth from cloud base to cloud top, represent major controls on the cloud water ion concentrations observed during DYCOMS-II.

[39] The cloud water concentrations of dissolved gas phase species, such as H_2O_2 and HCHO , also varied during individual flights and between flights. In this case the concentrations did not decrease as rapidly with increasing mean drop diameter as was the case for low volatility ionic species (Figure 6). For species that partition between the gas and aqueous phase, dilution can be partially offset by additional uptake of these species from the gas phase. Theoretical calculations that assume Henry's law equilibrium in a closed system suggest that this was the case [Straub and Collett, 2002]. The observed trends in aqueous phase trace gas concentrations could also reflect an increase in the gas phase concentration of these species that happens to be coincident with smaller, more numerous cloud drops that are representative of a less pristine air mass. Unfortunately, convoluting factors such as the complexation of HCHO with S(IV) and the depletion of H_2O_2 due to S(IV) oxidation makes a complete explanation of these trends difficult without concurrent trace gas measurements.

3.2. Air Equivalent Concentrations

[40] Cloud water concentrations were converted to air equivalent concentrations to remove the effects of variations in LWC and facilitate comparisons with results from previous marine-based studies. Air equivalent concentrations representing the amount of each species present within the cloud drops in a given volume of air (Table 4), were obtained by multiplying the cloud water solute concentration by the average LWC measured during the sample period.

[41] The variability in cloud LWC, particle concentrations, and other parameters across individual flight leg

circles noted by Stevens *et al.* [2003] was also observed in cloud water air equivalent concentrations. This was most obvious during RF07 when five cloud water sample periods covered three distinct sections of the cloud top flight circle. While the duplicate samples agreed quite well, variations greater than 60% were observed across the individual sections of the flight circle (Figure 7). Sample period timing was not as consistent on the remaining flights, making it difficult to define separate sections of the flight circle for comparison purposes. However, sample to sample varia-

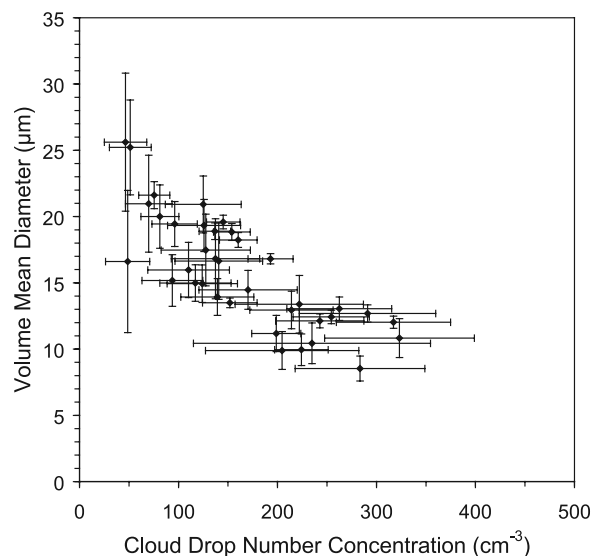


Figure 5. Cloud drop volume mean diameter as a function of cloud drop number concentration measured by the SPP-100 during individual cloud water sample periods. Error bars represent one standard deviation from the mean for each sample period.

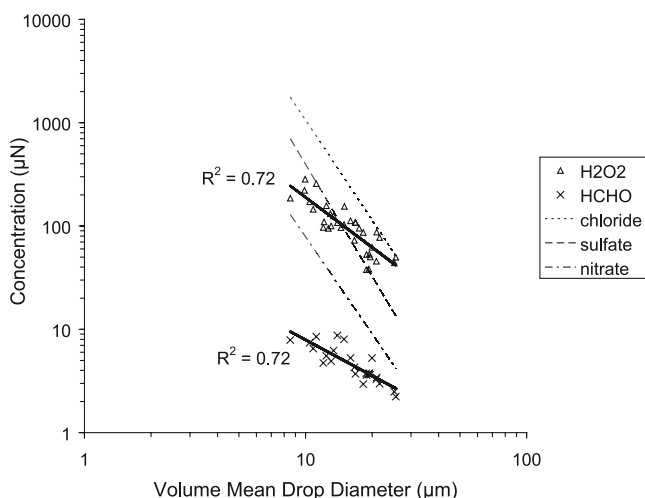


Figure 6. Measured concentrations of cloud water H_2O_2 and HCHO as a function of volume mean diameter. The decrease in concentration with drop size for chloride, sulfate, and nitrate are included for comparison. The regression equations have power law exponents of -1.61 for H_2O_2 and -1.15 for HCHO.

tions of a factor of two or more were observed during individual in-cloud flight legs.

[42] The air equivalent concentrations of most cloud water species also varied considerably from flight to flight. While separate daytime and nighttime flights were conducted during DYCOMS-II, it was not possible to attribute variations in any of the measured species to diurnal effects such as photochemistry or biological activity. Diurnal variations were most likely obscured by the substantial flight to flight changes in background conditions experienced during DYCOMS-II. Flight averaged air equivalent

concentrations of nssSO_4^{2-} and NO_3^- tended to increase as the number concentration of particles below cloud increased (Figure 8). Particle concentrations in this case were derived from PCASP measurements and represent particles larger than $0.1 \mu\text{m}$, which appear to be primarily responsible for cloud drop nucleation during DYCOMS-II [Twohy et al., 2005]. Air equivalent NH_4^+ concentrations follow a similar trend with particle concentration ($R^2 = 0.80$, not shown). Previous cloud water studies conducted in continental locations have also revealed positive correlations between cloud water derived air equivalent sulfate concentrations and particle number concentrations [Leitch et al., 1986, 1996] with the inference that sulfate is strongly associated with cloud drop nucleation. A number of studies have also sought to quantify the relationship between sulfate mass concentrations and cloud condensation nuclei (CCN) or cloud drop number concentrations, in some cases to establish a causal link between sulfate mass loadings and changes in radiative forcing. Van Dingenen et al. [1995] compiled data from 10 cloud water and aerosol studies in settings ranging from polluted to clean marine and presented a nonlinear regression that defines CCN or cloud drop number concentrations (depending on the type of study) as a function of sulfate mass for the entire data set. A similar regression based on air equivalent sulfate mass and cloud drop number concentrations during individual DYCOMS-II sample periods is in good agreement with that of Van Dingenen et al. (Figure 9).

3.3. Comparison to Previous Studies in the Clean Marine Boundary Layer

[43] Particle concentrations have been used as one measure of anthropogenic or continental influence in the marine boundary layer, with lower particle concentrations suggestive of “pristine” or “background” marine conditions and higher concentrations indicative of air masses being “polluted” or “continental” in origin. On the basis

Table 4. Summary of DYCOMS-II Cloud Water Air Equivalent Concentrations^a

	Average	Minimum	Maximum	RF02	RF03	RF04	RF05	RF06	RF07	RF08	RF09
Cl^- , $\mu\text{g m}^{-3}$	6.64	0.66	23.27	2.11	15.87	4.62	11.32	9.52	2.67	0.93	8.08
NO_3^- , $\mu\text{g m}^{-3}$	0.57	0.07	2.02	0.37	0.89	0.57	0.47	0.24	0.22	0.43	1.37
SO_4^{2-} , $\mu\text{g m}^{-3}$	2.32	0.25	7.17	0.58	3.68	2.24	3.92	2.45	0.83	1.03	4.61
nssSO_4^{2-} , $\mu\text{g m}^{-3}$	1.34	0.08	5.17	0.25	1.41	1.57	2.27	1.01	0.44	0.88	3.38
Na^+ , $\mu\text{g m}^{-3}$	3.89	0.39	13.39	1.31	9.03	2.68	6.56	5.74	1.56	0.58	4.87
NH_4^+ , $\mu\text{g m}^{-3}$	0.10	<MDL	0.54	0.02	0.20	0.05	0.07	<MDL ^b	0.02	0.07	0.31
K^+ , $\mu\text{g m}^{-3}$	0.15	0.004	0.53	0.04	0.35	0.09	0.25	0.21	0.05	0.02	0.20
Mg^{2+} , $\mu\text{g m}^{-3}$	0.54	0.06	1.81	0.16	1.26	0.40	0.93	0.74	0.20	0.10	0.72
Ca^{2+} , $\mu\text{g m}^{-3}$	0.31	0.06	0.96	0.12	0.70	0.24	0.49	0.37	0.14	0.10	0.43
H^+ , $\mu\text{g m}^{-3}$	0.04	0.01	0.12	0.01	0.07	0.05	0.05	0.03	0.02	0.03	0.07
HCHO, ^c ppb	0.05	0.02	0.08	0.03	0.05	0.06	N/A ^d	0.04	0.06	0.05	0.05
H_2O_2 , ^c ppb	1.01	0.39	1.78	0.55	1.09	1.62	1.11	0.76	0.72	0.96	1.08
S(IV), $\mu\text{g m}^{-3}$	0.025	<MDL	0.059	<MDL ^b	0.034	0.020	0.038	<MDL ^b	0.026	0.020	0.039
Fe, ng m^{-3}	7.10	<MDL	36.91	5.86	N/A ^e	6.34	1.79	<MDL ^b	4.55	4.19	21.68
Mn, ng m^{-3}	0.23	<MDL	1.16	0.24	N/A ^e	0.18	0.06	<MDL ^b	0.13	<MDL ^b	0.72
TOC, ^f $\mu\text{g m}^{-3}$	0.537	0.526	0.547	N/A	N/A	N/A	N/A	N/A	0.537	N/A	N/A

^aAverage, minimum and maximum columns are based on all sample periods, and the remaining columns show individual flight averages.

^bAll samples less than the MDL.

^cAqueous phase contribution only.

^dNo HCHO samples analyzed for RF05.

^eFe and Mn are not reported for RF03 because of sample contamination indicated by blank analyses.

^fOnly two TOC samples analyzed because of limited sample volume.

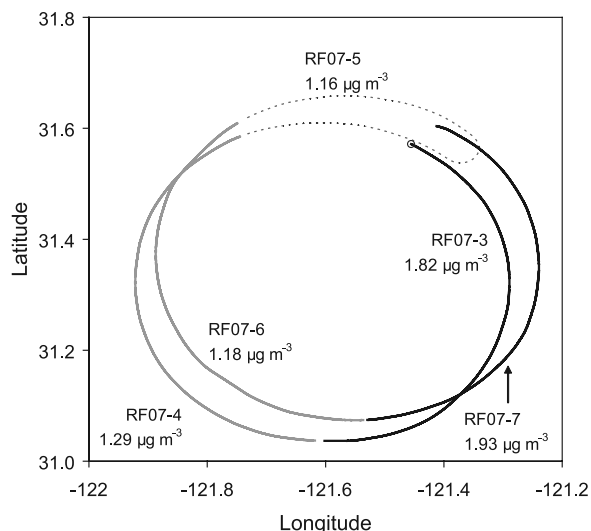


Figure 7. RF07 flight track showing the five cloud top sample periods and associated air equivalent Na⁺ concentration for each period. The open circle denotes the start of the in-cloud flight leg. To show replicate sample periods more clearly, the flight track has been shifted to account for aircraft drift with the mean wind during the flight leg.

of comparisons between flight averaged below-cloud particle concentrations and global averages for the marine environment, *Twohy et al.* [2005] categorize DYCOMS-II flights 1, 2, 6, 7, and 8 as “clean”; flights 3, 4, and 5 as “intermediate”; and flight 9 as “polluted.” Air equivalent concentrations of cloud water species such as nssSO₄²⁻, NO₃⁻, NH₄⁺, and trace metals can provide additional insight into the state of the marine environment during the DYCOMS-II research flights.

[44] *Leaich et al.* [1992] chose a total air equivalent SO₄²⁻ threshold of 0.72 μg m⁻³ to differentiate between background and polluted cloud water sample periods. On the basis of this criterion, only DYCOMS-II flight RF02 would

represent background conditions. Similarly, the mean cloud water air equivalent concentrations of nssSO₄²⁻ for the clean marine case of *Vong et al.* [1997] was 0.38 μg m⁻³, lower than all DYCOMS-II flight averages except RF02. In contrast, a much higher average air equivalent nssSO₄²⁻ concentration of 3.7 μg m⁻³ was reported for cloud water samples obtained in a polluted marine location [*Borys et al.*, 1998]. Although incomplete aerosol scavenging by clouds makes direct comparisons between clear air aerosol nssSO₄²⁻ concentrations and cloud water derived nssSO₄²⁻ concentrations difficult, a compilation of remote marine aerosol studies by *Fitzgerald* [1991] indicates that nssSO₄²⁻ concentrations are generally lower than the air equivalent nssSO₄²⁻ concentrations measured during DYCOMS-II. However, ship based measurements of aerosol nssSO₄²⁻ by *Parungo et al.* [1987] show that concentrations much higher than those considered to be background levels can be found off the west coast of the United States as a result of biogenic emissions and anthropogenic pollution. An extensive database of maritime aerosol chemical and physical measurements places the global marine nssSO₄²⁻ average at 1.01 μg m⁻³ with much higher meridional average concentrations at 30° to 40°N [*Heintzenberg et al.*, 2000].

[45] Similar to nssSO₄²⁻, air equivalent NO₃⁻ concentrations measured during DYCOMS-II were generally higher than studies reporting clean marine conditions but lower than marine studies strongly influenced by anthropogenic and continental sources. The average air equivalent NO₃⁻ concentration for the clean marine case of *Vong et al.* [1997] was 0.26 μg m⁻³, about half the 0.57 μg m⁻³ DYCOMS-II average. In contrast, air equivalent NO₃⁻ concentrations from cloud water collected in considerably polluted marine air masses averaged 2.1 μg m⁻³ [*Borys et al.*, 1998]. Aerosol studies in the remote marine boundary layer suggest that background NO₃⁻ concentrations may be 0.2 μg m⁻³ or less [*Fitzgerald*, 1991; *Savoie et al.*, 1989].

[46] The air equivalent concentrations of NH₄⁺ on flights RF02 and RF04–RF08 are all less than 0.07 μg m⁻³. Samples from these flights compare favorably to the aver-

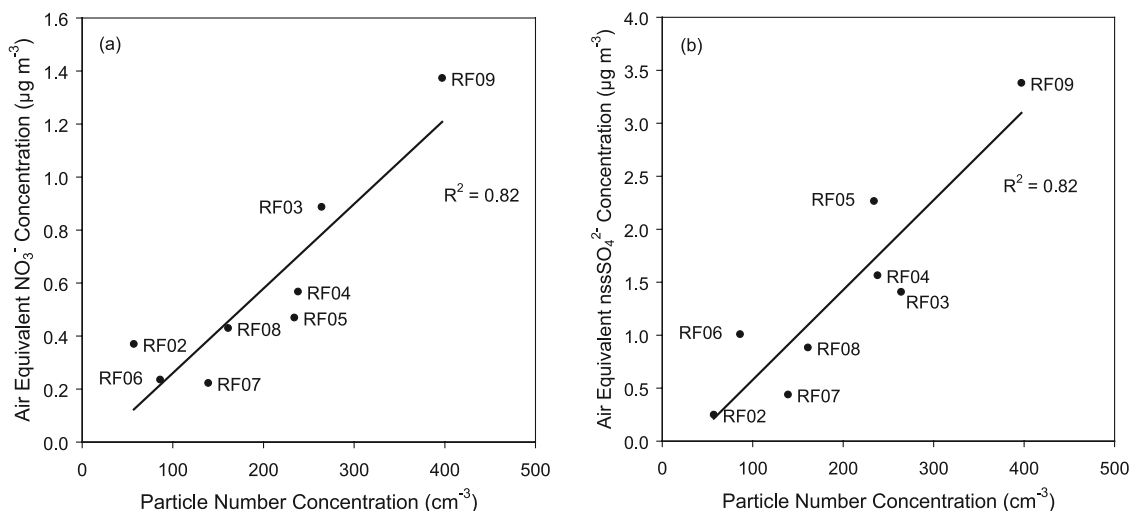


Figure 8. Flight averaged air equivalent concentrations of (a) NO₃⁻ and (b) nssSO₄²⁻ versus below cloud particle number concentration ($D_p > 0.1 \mu\text{m}$) derived from PCASP measurements.

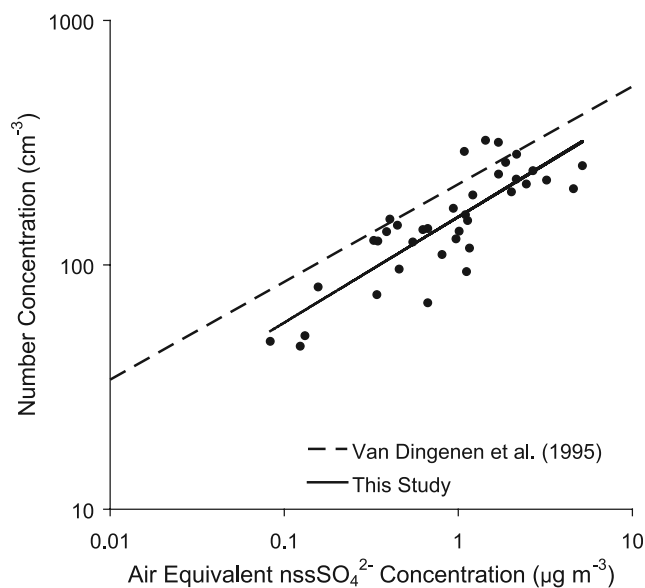


Figure 9. Cloud drop number concentration versus air equivalent nssSO_4^{2-} concentration for individual sample periods during DYCOMS-II flights RF02–RF04 and RF07–RF09. Regression equations are $\log(N) = 2.20 + 0.43\log[\text{SO}_4^{2-}]$ $R^2 = 0.69$ (this study) and $\log(N) = 2.33(\pm 0.07) + 0.40(\pm 0.11)\log[\text{SO}_4^{2-}]$ $R^2 = 0.42$ [Van Dingenen et al., 1995].

age air equivalent NH_4^+ concentration of $0.05 \mu\text{g m}^{-3}$ derived from the pristine marine cloud water samples collected by Vong et al. [1997]. For comparison, gas phase ammonia concentrations in air of strictly marine origin at Cape Grim have been found to average $0.06 \mu\text{g m}^{-3}$ [Ayers and Gras, 1980, 1983]. Higher NH_4^+ concentrations were measured during flights RF03 and RF09, with flight averaged values of 0.19 and $0.29 \mu\text{g m}^{-3}$, respectively.

[47] If the nssSO_4^{2-} observed in the DYCOMS-II cloud water samples is assumed to originate from fine-mode precursor aerosols in which NH_4^+ is the primary neutralizing cation, then insufficient NH_4^+ was present for full neutralization of the nssSO_4^{2-} . The average molar ratio of NH_4^+ to nssSO_4^{2-} ranged from 0.76 during RF03 to near 0 during RF06 when ammonium concentrations were below the detection limit for all samples. This would indicate that the precursor aerosol particles contained sulfate in forms ranging between ammonium bisulfate and sulfuric acid. The DYCOMS-II NH_4^+ to nssSO_4^{2-} ratios are lower than the average ratio of 1 reported for fine-mode aerosol samples obtained from the North Pacific [Covert, 1988], but consistent with ratios that varied between 0 and 1 in the remote central Pacific [Clarke et al., 1987].

[48] The highest trace metal concentrations were encountered during RF09 while much lower concentrations were measured on all other flights (excluding RF03 for which concentrations are not reported). During flights RF02–RF08, the average air equivalent cloud water concentrations of Mn and Fe were 0.14 ng m^{-3} and 4.5 ng m^{-3} , respectively. For comparison, Mn concentrations in the clean marine cloud water samples of Vong et al. [1997] averaged 0.3 ng m^{-3} . No air equivalent cloud water Fe concentrations have been reported for the remote marine environment;

however, a summary of aerosol measurements in the remote marine boundary layer by Raemdonck et al. [1986] place the background total Fe concentration in the range of 3.3 to 10 ng m^{-3} .

[49] In order to evaluate H_2O_2 and HCHO measurements, total concentrations of these species (i.e., aqueous phase plus gas phase concentrations) were derived by adding the air equivalent concentration residing in the cloud water to a calculated equilibrium gas phase concentration. Although mass transport limitations and other effects may prevent cloud drops from reaching equilibrium with the gas phase, estimated total concentrations are presented here to enable general comparisons to past gas phase measurements in the marine boundary layer. Total gas phase H_2O_2 concentrations for the DYCOMS-II sample periods ranged from 0.54 to 2.47 ppb and averaged 1.42 ppb. These values appear to be in line with previous gas phase H_2O_2 observations made within the marine boundary layer [e.g., Weller et al., 2000; Martin et al., 1997; Heikes et al., 1996a]. Most notably, aircraft-based gas phase measurements made in the North Pacific by Heikes et al. [1996b] show average concentrations of approximately 1.5 ppb for altitudes and latitudes comparable to those for the DYCOMS-II study.

[50] Similarly, the average estimated total DYCOMS-II formaldehyde concentration of 0.32 ppb is consistent with previous gas phase studies in the remote marine boundary layer. An average daytime maximum of approximately 0.45 ppb and a nighttime minimum of approximately 0.3 ppb have been recorded at Cape Grim [Ayers et al., 1997]. Aircraft-based measurements in the central Pacific indicate that the highest formaldehyde concentrations were recorded in the 0 to 1 km surface layer with a median value of approximately 0.35 ppb for a latitude/longitude box near the DYCOMS-II target location [Heikes et al., 2001].

[51] The cloud water air equivalent concentrations described above, and nssSO_4^{2-} in particular, suggest that conditions were not always representative of the background marine environment during the DYCOMS-II mission. Although it is not possible to uniquely identify the origin of the nssSO_4^{2-} on the basis of the DYCOMS-II measurements, sources in the marine boundary layer may include the oxidation products of biological emissions, ship exhaust, and transport from continental locations. Elevated levels of nssSO_4^{2-} have been measured in regions of upwelling which support enhanced biological activity and DMS emissions [Clarke et al., 1987; Parungo et al., 1986, 1987] and occur off the west coast of the United States. Ooki et al. [2003] have attributed a nine fold increase in nssSO_4^{2-} mass above background north Pacific levels to biological production. Compared to the global DMS sulfur flux, ship emissions have been estimated to be about 20% , although ship emissions may equal or exceed the DMS contribution in the Northern Hemisphere [Corbett et al., 1999]. Shipping has also been found to increase NO_x concentrations by a factor of two in the remote boundary layer and by a factor of 100 or more in shipping lanes [Lawrence and Crutzen, 1999]. The transport of SO_4^{2-} and its precursors from the North American and Asian continents may have also contributed to measured nssSO_4^{2-} in the DYCOMS-II samples. Radon measurements made during the original DYCOMS field project provide strong evidence of transport from continental sources to the study

region [Lenschow *et al.*, 1988]. Results from the First ISCCP Regional Experiment (FIRE) also demonstrate that the signature of anthropogenic continental sources can be observed more than 500 km off the coast of California [Hudson and Frisbie, 1991]. Studies have also shown that nitrate concentrations in the remote marine boundary layer are strongly influenced by transport from continents [Savoie *et al.*, 1989], while Prospero and Savoie [1989] estimate that continental sources are responsible for 40 to 70% of nitrate over the North Pacific. Air parcel back trajectories for each DYCOMS-II flight indicate that air masses arriving at the study location were predominantly from the northwest, at times skirting the North American coastline. Although the various air equivalent concentrations observed during DYCOMS-II do not appear to be associated with particular air mass histories, the back trajectories do suggest that continentally influenced air may have been present at the DYCOMS-II study location.

[52] In contrast to nssSO_4^{2-} , NO_3^- , NH_4^+ , and trace metals, concentrations of sea salt species depend primarily on surface wind speeds and as such there is no sea salt concentration that is representative of background conditions in the remote marine boundary layer [Fitzgerald, 1991]. The average DYCOMS-II sodium concentration was $3.9 \mu\text{g m}^{-3}$. Other marine cloud water studies have yielded average air equivalent sodium concentrations of $1.6 \mu\text{g m}^{-3}$ [Vong *et al.*, 1997] and $3.5 \mu\text{g m}^{-3}$ [Borys *et al.*, 1998] while the global average sodium concentration is $3.6 \mu\text{g m}^{-3}$ according to a compilation of marine aerosol measurements [Heintzenberg *et al.*, 2000]. The air equivalent concentrations of sea salt species measured in the DYCOMS-II cloud water samples are not as highly correlated with flight averaged below cloud particle concentrations as nssSO_4^{2-} and NO_3^- (Figure 10). This can be attributed to the fact that large sea salt particles influence aerosol mass concentrations much more so than number concentrations [Katoshevski *et al.*, 1999].

3.4. S(IV) Oxidation

[53] Aqueous phase reactions are important in the generation of aerosol mass, most notably through the absorption of gas phase SO_2 followed by oxidation to nonvolatile sulfate. Mass addition due to aqueous phase sulfate production has been measured in laboratory experiments [Hoppel *et al.*, 1994] and field studies [Husain *et al.*, 2000; Rattigan *et al.*, 2001; Reilly *et al.*, 2001; Birmili *et al.*, 1999; Liu *et al.*, 1993; Hegg and Hobbs, 1986, 1988] and predicted in modeling studies [Bower and Choulaton, 1993; Feingold *et al.*, 1998]. The production of sulfate in cloud drops tends to acidify the drops and the production of new aerosol mass can influence radiative forcing and future cloud cycles. In the remote marine boundary layer, DMS produced through biological activity is considered a significant source of SO_2 which can ultimately be oxidized to sulfate. For these reasons, evidence of aqueous phase sulfate production in remote marine stratocumulus clouds was of interest.

[54] An examination of air equivalent nssSO_4^{2-} concentrations for each flight reveals no systematic increase from cloud base to cloud top that would provide an indication of in-cloud sulfate production [Straub and Collett, 2002]. However, there are several reasons that a strong sulfate production signal could be absent. Sulfate production may

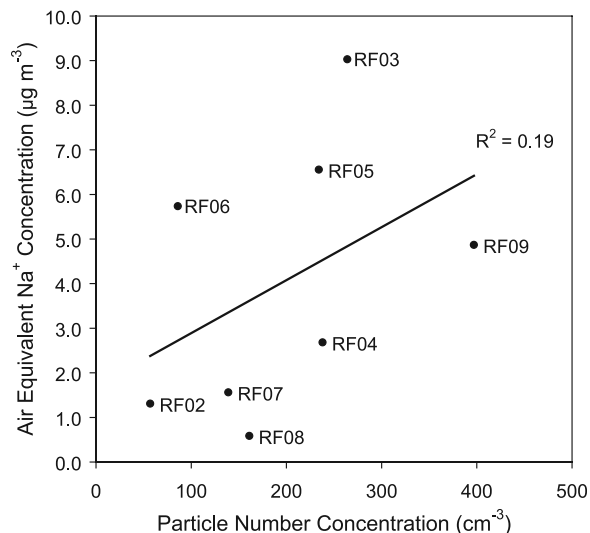


Figure 10. Flight averaged air equivalent concentrations of Na^+ versus below cloud particle number concentration ($D_p > 0.1 \mu\text{m}$) derived from PCASP measurements.

have been masked if the same parcel of air was not sampled at cloud base and cloud top, as was likely the case during DYCOMS-II. In addition, the rapid oxidation of available SO_2 by H_2O_2 may have occurred prior to cloud water sampling at the lowest in-cloud flight level. Further, it has been argued that a significant fraction of sulfur oxidation in the remote marine boundary layer occurs in deliquesced sea salt aerosol particles before they participate as CCN in cloud formation [Sievering *et al.*, 1991, 1999; Gurciullo *et al.*, 1999].

[55] The relative importance of the various SO_2 oxidation pathways was examined using published rate laws for oxidation by H_2O_2 [Hoffmann and Calvert, 1985], O_3 [Hoffmann, 1986], and by O_2 in the presence of Fe and Mn as catalysts [Ibusuki and Takeuchi, 1987]. For the calculation of oxidation rates, the measured cloud water pH was used to determine the H^+ concentration and the equilibrium fractions of $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , and SO_3^{2-} . The concentrations of H_2O_2 , Fe(III), and Mn(II) were taken from the DYCOMS-II cloud water chemical analyses. Fe(III) was assumed to comprise 25% of total measured Fe while Mn(II) was assumed to be 100% of total Mn [Xu *et al.*, 1999], although the relative importance of the trace metal catalyzed O_2 oxidation pathway was found to be insensitive to changes in the fraction of Fe and Mn assumed to exist as Fe(III) and Mn(II). The RF03 average ozone concentration of 27 ppb was used to represent ozone concentrations during all sample periods.

[56] As expected on the basis of the high H_2O_2 concentrations and low pH values of the DYCOMS-II cloud water samples, the H_2O_2 oxidation pathway was predicted to be dominant for each of the DYCOMS-II sample periods. Oxidation rates for the H_2O_2 pathway exceeded those for the trace metal catalyzed O_2 pathway by approximately five orders of magnitude. H_2O_2 oxidation rates exceeded those for the O_3 pathway by a similar margin during sample periods characterized by small mean drop sizes. However, oxidation by O_3 became more important as drop size

increased, mainly because of the increase in drop pH that accompanied increases in mean drop diameter. For sample periods in which the largest mean drop sizes were observed, the H_2O_2 rates were one order of magnitude greater than for O_3 . Any input of SO_2 into the remote marine environment that is absorbed by cloud drops would therefore be expected to be rapidly oxidized by the abundant H_2O_2 . Although complexation of S(IV) and HCHO to form HMS may compete for any additional SO_2 introduced into the cloud drops, the timescale for complexation is two or more orders of magnitude longer than for oxidation by H_2O_2 or O_3 at the conditions encountered during the study [Straub and Collett, 2002]. Most observed concentrations of total S(IV) in the DYCOMS-II cloud water samples were below detection limits, supporting this assessment.

4. Conclusions

[57] Fifty stratocumulus cloud water samples were collected approximately 400 km off the coast of Southern California and analyzed for pH, major ions, hydrogen peroxide, formaldehyde, S(IV), Fe, Mn, and total organic carbon. The samples were obtained during the DYCOMS-II field project on six nighttime and two daytime flights. These measurements provide a unique record of cloud water composition in the marine boundary layer, an environment for which such measurements are rare.

[58] Sodium and chloride were the two most abundant ions in all DYCOMS-II samples. Using sodium as a sea salt tracer, chloride and potassium were found to be present in proportions similar to those found in seawater. Sulfate, magnesium, and calcium were enriched to varying degrees, suggesting contributions from sources other than sea salt. Concentrations of total sulfate ranged between 15 and 905 μN , of which 58% was nssSO_4^{2-} on average. Other species were observed in a wide range of concentrations as well, such as Na^+ (36–2784 μN), Ca^{2+} (8–188 μN), NO_3^- (3–205 μN), H_2O_2 (37.8–283.1 μM), and HCHO (2.2–8.7 μM). Variability occurred during individual flights as well as from flight to flight. During individual flights, decreases in solute concentrations from cloud base to cloud top were consistent with cloud drop condensational growth and dilution. Differences in solute concentration from one flight to another were partially attributed to changes in cloud drop number concentrations. Flights with higher cloud drop number concentrations were associated with smaller cloud drops and higher solute concentrations.

[59] To evaluate variations in solute concentrations without the strong dependence on LWC, air equivalent concentrations were determined by multiplying cloud drop solute concentrations by sample period averaged LWC. Flight averaged air equivalent concentrations of nssSO_4^{2-} varied from 0.3 $\mu\text{g m}^{-3}$ to 3.4 $\mu\text{g m}^{-3}$. Air equivalent NO_3^- concentrations ranged between 0.2 $\mu\text{g m}^{-3}$ and 1.4 $\mu\text{g m}^{-3}$. Na^+ concentrations ranged between 0.6 and 9.0 $\mu\text{g m}^{-3}$. For species such as nssSO_4^{2-} , NO_3^- , and NH_4^+ , the wide range of observed air equivalent concentrations is, in part, a consequence of variations in below-cloud aerosol number concentration, as indicated by positive correlations between those quantities. On the other hand, air equivalent Na^+ concentrations do not correlate well with below-cloud aerosol concentrations. Fe and Mn were

below detection limits for many sample periods and no correlation was found with aerosol number concentrations for those flights. The spatial inhomogeneity noted by others across individual DYCOMS-II flight legs was also apparent in cloud water air equivalent concentrations. During one flight, samples collected during overlapping flight segments showed good agreement while concentration differences of 60% were observed for separate cloud top locations.

[60] Despite a study location well offshore, air equivalent concentrations of nssSO_4^{2-} and NO_3^- on many flights were found to be higher than some previous studies that sampled background marine air masses. Air mass back trajectories from the north and northwest, often along the coast of North America, suggest some degree of continental influence during DYCOMS-II; however, elevated concentrations of nssSO_4^{2-} and NO_3^- could not be linked to any particular air mass history. Biogenic sources of nssSO_4^{2-} , perhaps associated with regions of upwelling and enhanced biological activity, may also have contributed to higher nssSO_4^{2-} levels. The air equivalent concentrations of NH_4^+ , Fe, Mn, and sea salt species observed during DYCOMS-II appear to be in line with previous measurements in the marine boundary layer. Total concentrations of H_2O_2 and HCHO, determined by adding a calculated equilibrium gas phase concentration to the air equivalent cloud drop concentration, were also similar to previous gas phase measurements made in marine locations.

[61] Comparison of S(IV) oxidation rate laws suggested H_2O_2 as the dominant oxidant for regional in-cloud sulfate production. Given an abundance of H_2O_2 , sulfate production appears to have been limited by the availability of SO_2 during DYCOMS-II.

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References

- Ayers, G. P., and J. L. Gras (1980), Ammonia gas concentrations over the Southern Ocean, *Nature*, 284, 539–540.
- Ayers, G. P., and J. L. Gras (1983), The concentration of ammonia in Southern Ocean air, *J. Geophys. Res.*, 88, 10,655–10,659.
- Ayers, G. P., R. W. Gillett, H. Granek, C. de Serves, and R. A. Cox (1997), Formaldehyde production in clean marine air, *Geophys. Res. Lett.*, 24, 401–404.
- Barth, M. C., D. A. Hegg, and P. V. Hobbs (1989), Measurements of atmospheric gas-phase and aqueous phase hydrogen peroxide concentrations in winter on the east coast of the United States, *Tellus, Ser. B*, 41, 61–69.
- Bator, A., and J. L. Collett Jr. (1997), Cloud chemistry varies with drop size, *J. Geophys. Res.*, 102, 28,071–28,078.
- Baumgardner, D. (1989), Airborne measurements for cloud microphysics, *NCAR Res. Aviation Facil. Bull.*, 24, 22 pp., Natl. Cent. for Atmos. Res., Boulder, Colo.
- Baumgardner, D. (1996), Status of in-situ microphysical measurements, paper presented at ETL/CSU Cloud Modeling and Measurement Workshop, Boulder, Colo.
- Birmili, W., B. Yuskiewicz, A. Wiedensohler, F. Stratmann, T. W. Choulaton, and K. N. Bower (1999), Climate-relevant modification of the aerosol size distribution by processes associated with orographic clouds, *Atmos. Res.*, 50, 241–263.

- Borys, R. D., D. H. Lowenthal, M. A. Wetzel, F. Herrera, A. Gonzalez, and J. Harris (1998), Chemical and microphysical properties of marine stratiform cloud in the North Atlantic, *J. Geophys. Res.*, *103*, 22,073–22,085.
- Bower, K. N., and T. W. Choulaton (1993), Cloud processing of the cloud condensation nucleus spectrum and its climatological consequences, *Q. J. R. Meteorol. Soc.*, *119*, 655–679.
- Clarke, A. D., N. C. Ahlquist, and D. S. Covert (1987), The Pacific marine aerosol: Evidence for natural and acid sulfates, *J. Geophys. Res.*, *92*, 4179–4190.
- Collett, J. L., Jr., A. Bator, D. E. Sherman, K. F. Moore, K. J. Hoag, B. B. Demoz, X. Rao, and J. E. Reilly (2002), The chemical composition of fogs and intercepted clouds in the United States, *Atmos. Res.*, *64*, 29–40.
- Corbett, J. J., P. S. Fischbeck, and S. N. Pandis (1999), Global nitrogen and sulfur inventories for oceangoing ships, *J. Geophys. Res.*, *104*, 3457–3470.
- Covert, D. S. (1988), North Pacific Marine background aerosol: average ammonium to sulfate molar ratio equals 1, *J. Geophys. Res.*, *93*(D7), 8455–8458.
- Dasgupta, P. K., K. DeCesare, and J. C. Ullrey (1980), Determination of atmospheric sulfur dioxide without tetrachloromercurate (II) and the mechanism of the Schiff reaction, *Anal. Chem.*, *52*, 1912–1922.
- Daum, P. H., S. E. Schwartz, and L. Newman (1984a), Acidic and related constituents in liquid water stratiform clouds, *J. Geophys. Res.*, *89*, 1447–1458.
- Daum, P. H., T. J. Kelly, S. E. Schwartz, and L. Newman (1984b), Measurements of the chemical composition of stratiform clouds, *Atmos. Environ.*, *18*, 2671–2684.
- Dong, S., and P. K. Dasgupta (1987), Fast fluorometric flow injection analysis of formaldehyde in atmospheric water, *Environ. Sci. Technol.*, *21*, 581–588.
- Feingold, G., S. M. Kreidenweis, and Y. Zhang (1998), Stratocumulus processing of gases and cloud condensation nuclei: 1. Trajectory ensemble model, *J. Geophys. Res.*, *103*, 19,527–19,542.
- Fitzgerald, J. W. (1991), Marine aerosols: A review, *Atmos. Environ., Part A*, *25*, 533–545.
- Gerber, H., B. G. Arends, and A. S. Ackerman (1994), New microphysics sensor for aircraft use, *Atmos. Res.*, *31*, 235–252.
- Gurciullo, C., B. Lerner, H. Sievering, and S. N. Pandis (1999), Heterogeneous sulfate production in the remote marine environment: Cloud processing and sea-salt particle contributions, *J. Geophys. Res.*, *104*, 21,719–21,731.
- Hegg, D. A., and P. V. Hobbs (1981), Cloud water chemistry and the production of sulfate in clouds, *Atmos. Environ.*, *15*, 1597–1604.
- Hegg, D. A., and P. V. Hobbs (1986), Sulfate and nitrate chemistry in cumulus clouds, *Atmos. Environ.*, *20*, 901–909.
- Hegg, D. A., and P. V. Hobbs (1988), Comparisons of sulfate and nitrate production in clouds on the mid-Atlantic and Pacific Northwest coasts of the United States, *J. Atmos. Chem.*, *7*, 325–333.
- Hegg, D. A., P. V. Hobbs, and L. F. Radke (1984a), Measurements of the scavenging of sulfate and nitrate in clouds, *Atmos. Environ.*, *18*, 1939–1946.
- Hegg, D. A., L. F. Radke, and P. V. Hobbs (1984b), Measurements of transformations in the physical and chemical properties of clouds associated with onshore flow in Washington State, *J. Clim. Appl. Meteorol.*, *23*, 979–984.
- Heikes, B. G. (1992), Formaldehyde and hydroperoxides at Mauna Loa Observatory, *J. Geophys. Res.*, *97*, 18,001–18,013.
- Heikes, B. G., M. Lee, D. Jacob, R. Talbot, J. Bradshaw, H. Singh, D. Blake, B. Anderson, H. Fuelberg, and A. M. Thompson (1996a), Ozone, hydroperoxides, oxides of nitrogen, and hydrocarbon budgets in the marine boundary layer over the South Atlantic, *J. Geophys. Res.*, *101*, 24,221–24,234.
- Heikes, B. G., et al. (1996b), Hydrogen peroxide and methylhydroperoxide distributions related to ozone and odd hydrogen over the North Pacific in the fall of 1991, *J. Geophys. Res.*, *101*, 1891–1905.
- Heikes, B., J. Snow, P. Egli, D. O'Sullivan, J. Crawford, J. Olson, G. Chen, D. Davis, N. Blake, and D. Blake (2001), Formaldehyde over the central Pacific during PEM-Tropics B, *J. Geophys. Res.*, *106*, 32,717–32,731.
- Heintzenberg, J., D. C. Covert, and R. Van Dingenen (2000), Size distribution and chemical composition of marine aerosols: A compilation and review, *Tellus, Ser. B*, *52*, 1104–1122.
- Hoffmann, M. R. (1986), On the kinetics and mechanism of oxidation of aquated sulfur dioxide by ozone, *Atmos. Environ.*, *20*, 1145–1154.
- Hoffmann, M. R. and J. G. Calvert (1985), *Chemical Transformation Modules for Eulerian Acid Deposition Models*, vol. II, *The Aqueous-Phase Chemistry*, Natl. Cent. for Atmos. Res., Boulder, Colo.
- Hoppel, W. A., G. M. Frick, and J. W. Fitzgerald (1994), A cloud chamber study of the effect that nonprecipitating water clouds have on the aerosol size distribution, *Aerosol Sci. Technol.*, *20*, 1–30.
- Hudson, J. G., and P. R. Frisbie (1991), Cloud condensation nuclei near marine stratus, *J. Geophys. Res.*, *96*, 20,795–20,808.
- Hudson, J. G., and G. Svensson (1995), Cloud microphysical relationships in California marine stratus, *J. Appl. Meteorol.*, *34*, 2655–2666.
- Huebert, B. J., S. Vanbramer, and K. L. Tschudy (1988), Liquid cloudwater collection using modified Mohnen slotted rods, *J. Atmos. Chem.*, *6*, 251–263.
- Husain, L., O. V. Rattigan, V. Dutkiewicz, M. Das, C. D. Judd, A. R. Khan, R. Richter, R. Balasubramanian, K. Swami, and C. J. Walcek (2000), Case studies of the SO₂ + H₂O₂ reaction in clouds, *J. Geophys. Res.*, *105*, 9831–9841.
- Ibusuki, T., and K. Takeuchi (1987), Sulfur dioxide oxidation by oxygen catalyzed by mixtures of manganese (II) and iron (III) in aqueous solutions at environmental reaction conditions, *Atmos. Environ.*, *21*, 1555–1560.
- Jaeschke, W., and A. Gunther (2002), An airborne two-stage impactor for chemical analysis of size-segregated cloud drops, *Atmos. Res.*, *64*, 121–132.
- Katoshevski, D., A. Nenes, and J. H. Seinfeld (1999), A study of processes that govern the maintenance of aerosols in the marine boundary layer, *J. Aerosol Sci.*, *30*, 503–532.
- Keene, W. C., A. A. P. Pszenny, J. N. Galloway, and M. E. Hawley (1986), Sea-salt corrections and interpretation of constituent ratios in marine precipitation, *J. Geophys. Res.*, *91*, 6647–6658.
- Kelly, T. J., P. H. Daum, and S. E. Schwartz (1985), Measurements of peroxides in cloudwater and rain, *J. Geophys. Res.*, *90*, 7861–7871.
- King, W. D., J. E. Dye, J. W. Strapp, D. Baumgardner, and D. Huffman (1985), Icing wind tunnel tests on the CSIRO liquid water probe, *J. Atmos. Oceanic Technol.*, *2*, 340–352.
- Lawrence, M. G., and P. J. Crutzen (1999), Influence of NO_x emissions from ships on tropospheric photochemistry and climate, *Nature*, *402*, 167–170.
- Lazrus, A. L., H. W. Baynton, and J. P. Lodge (1970), Trace constituents in oceanic cloud water and their origin, *Tellus*, *22*, 106–113.
- Lazrus, A., G. L. Kok, S. N. Gitlin, J. A. Lind, and S. E. McLaren (1985), Automated fluorometric method for hydrogen peroxide in atmospheric precipitation, *Anal. Chem.*, *57*, 917–922.
- Leaith, W. R., J. W. Strapp, and G. A. Isaac (1986), Cloud droplet nucleation and cloud scavenging of aerosol sulphate in polluted atmospheres, *Tellus, Ser. B*, *38*, 328–344.
- Leaith, W. R., G. A. Isaac, J. W. Strapp, C. M. Banic, and H. A. Wiebe (1992), The relationship between cloud droplet number concentrations and anthropogenic pollution: Observations and climatic implications, *J. Geophys. Res.*, *97*, 2463–2474.
- Leaith, W. R., C. M. Banic, G. A. Isaac, M. D. Couture, P. S. K. Liu, I. Gultepe, S.-M. Li, L. Kleinman, P. H. Daum, and J. I. MacPherson (1996), Physical and chemical observations in marine stratus during the 1993 North Atlantic Regional Experiment: Factors controlling cloud drop number concentrations, *J. Geophys. Res.*, *101*, 29,123–29,135.
- Lee, M., B. G. Heikes, and D. W. O'Sullivan (2000), Hydrogen peroxide and organic hydroperoxide in the troposphere: A review, *Atmos. Environ.*, *34*, 3475–3494.
- Lenschow, D. H., I. R. Paluch, A. R. Bandy, R. Pearson Jr., S. R. Kawa, C. J. Weaver, B. J. Huebert, J. G. Kay, D. C. Thornton, and A. R. Driedger III (1988), Dynamics and chemistry of marine stratocumulus (DYCOMS) experiment, *Bull. Am. Meteorol. Soc.*, *69*, 1058–1066.
- Liu, P. S. K., W. R. Leaith, A. M. Macdonald, G. A. Isaac, J. W. Strapp, and H. A. Wiebe (1993), Sulphate production in summer cloud over Ontario, Canada, *Tellus, Ser. B*, *45*, 368–389.
- Macdonald, A. M., K. G. Anlauf, C. M. Banic, W. R. Leaith, and H. A. Wiebe (1995), Airborne measurements of aqueous and gaseous hydrogen peroxide during spring and summer in Ontario, Canada, *J. Geophys. Res.*, *100*, 7253–7262.
- Martin, D., M. Tsviou, B. Bonsang, C. Abonnel, T. Carsey, M. Springer-Young, A. Pszenny, and K. Suhre (1997), Hydrogen peroxide in the marine atmospheric boundary layer during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange experiment in the eastern subtropical North Atlantic, *J. Geophys. Res.*, *102*, 6003–6015.
- Martin, G. M., D. W. Johnson, and A. Spice (1994), The measurement and parameterization of effective drop radius of droplets in warm stratocumulus clouds, *J. Atmos. Sci.*, *51*, 1823–1842.
- Menon, S., V. K. Saxena, and B. D. Logie (2000), Chemical heterogeneity across cloud drop size spectra in continental and marine air masses, *J. Appl. Meteorol.*, *39*, 887–903.
- Moore, K. F. (2001), Drop size-dependent chemical composition in clouds and fogs, *Rep. 713*, Dep. of Atmos. Sci., Colo. State Univ., Fort Collins.
- Munger, J. W., J. L. Collett Jr., B. Daube Jr., and M. R. Hoffmann (1989), Chemical composition of coastal stratus clouds: Dependence on droplet size and distance from the coast, *Atmos. Environ.*, *23*, 2305–2320.

- Olszyna, K. J., J. F. Meagher, and E. M. Baily (1988), Gas-phase, cloud and rain-water measurements of hydrogen peroxide at a high-elevation site, *Atmos. Environ.*, *22*, 1699–1706.
- Ooki, A., K. Miura, and M. Uematsu (2003), The increase of biogenic sulfate aerosol and particle number in marine atmosphere over the northwestern North Pacific, *J. Oceanogr.*, *59*, 799–807.
- Parungo, F., C. Nagamoto, I. Nolt, M. Dias, and E. Nickerson (1982), Chemical analysis of cloud water collected over Hawaii, *J. Geophys. Res.*, *87*, 8805–8810.
- Parungo, F. P., C. T. Nagamoto, J. Rosinski, and P. L. Haagenson (1986), A study of marine aerosols over the Pacific Ocean, *J. Atmos. Chem.*, *4*, 199–226.
- Parungo, F. P., C. T. Nagamoto, R. Madel, J. Rosinski, and P. L. Haagenson (1987), Marine aerosols in Pacific upwelling regions, *J. Aerosol Sci.*, *18*, 277–290.
- Prospero, J. M., and D. L. Savoie (1989), Effect of continental sources on nitrate concentrations over the Pacific Ocean, *Nature*, *339*, 687–689.
- Raemdonck, H., W. Maenhaut, and M. O. Andreae (1986), Chemistry of marine aerosol over the tropical and equatorial Pacific, *J. Geophys. Res.*, *91*, 8623–8636.
- Rao, X., and J. L. Collett Jr. (1995), Behavior of S (IV) and formaldehyde in a chemically heterogeneous cloud, *Environ. Sci. Technol.*, *29*, 1023–1031.
- Rao, X., and J. L. Collett Jr. (1998), The drop size-dependence of iron and manganese concentrations in clouds and fogs: Implications for sulfate production, *J. Atmos. Chem.*, *30*, 273–289.
- Rattigan, O. V., J. Reilly, C. D. Judd, K. F. Moore, M. Das, D. E. Sherman, V. A. Dutkiewicz, J. L. Collett Jr., and L. Husain (2001), Sulfur dioxide oxidation in clouds at Whiteface Mountain as a function of drop size, *J. Geophys. Res.*, *106*, 17,347–17,358.
- Reilly, J. E., O. V. Rattigan, K. F. Moore, C. Judd, D. E. Sherman, V. A. Dutkiewicz, S. M. Kreidenweis, L. Husain, and J. L. Collett Jr. (2001), Drop size-dependent S(IV) oxidation in chemically heterogeneous radiation fogs, *Atmos. Environ.*, *35*, 5717–5728.
- Richards, L. W. (1995), Airborne chemical measurements in nighttime stratus clouds in the Los Angeles Basin, *Atmos. Environ.*, *29*, 27–46.
- Richards, L. W., J. A. Anderson, D. L. Blumenthal, J. A. McDonald, G. L. Kok, and A. L. Lazrus (1983), Hydrogen peroxide and sulfur (IV) in Los Angeles cloud water, *Atmos. Environ.*, *17*, 911–914.
- Savoie, D. L., J. M. Prospero, J. T. Merrill, and M. Uematsu (1989), Nitrate in the atmospheric boundary layer of the tropical South Pacific: Implications regarding sources and transport, *J. Atmos. Chem.*, *8*, 391–415.
- Scott, W. D. (1978), The pH of cloud water and the production of sulfate, *Atmos. Environ.*, *12*, 917–921.
- Sievering, H., J. Boatman, J. Galloway, W. Keene, Y. Kim, and M. Laria (1991), Heterogeneous sulfur conversion in sea-salt aerosol particles: The role of aerosol water content and size distribution, *Atmos. Environ., Part A*, *25*, 1479–1487.
- Sievering, H., B. Lerner, J. Slavich, J. Anderson, M. Posfai, and J. Caine (1999), O₃ oxidation of SO₂ in sea-salt water: Size distribution of non-sea-salt sulfate during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, *104*, 21,707–21,717.
- Stevens, B., et al. (2003), Dynamics and Chemistry of Marine Stratocumulus—DYCOMS-II, *Bull. Am. Meteorol. Soc.*, *84*, 579–593.
- Stevens, B., G. Vali, K. Comstock, R. Wood, M. C. van Zanten, P. H. Austin, C. S. Bretherton, and D. H. Lenschow (2005), Pockets of open cells and drizzle in marine stratocumulus, *Bull. Am. Meteorol. Soc.*, *86*, 51–57.
- Straub, D. J. and J. L. Collett Jr. (2002), Design and testing of a new aircraft-based cloud water sampling system, *Rep. 729*, Dep. of Atmos. Sci., Colo. State Univ., Fort Collins.
- Straub, D. J., and J. L. Collett Jr. (2004), An axial-flow cyclone for aircraft-based cloud water sampling, *J. Atmos. Oceanic Technol.*, *21*, 1825–1839.
- Twohy, C. H., P. A. Durkee, B. J. Huebert, and R. J. Charlson (1995), Effects of aerosol particles on the microphysics of coastal stratiform clouds, *J. Clim.*, *8*, 773–783.
- Twohy, C. H., M. D. Petters, J. R. Snider, B. Stevens, W. Tahnk, M. Wetzel, L. Russell, and F. Burnet (2005), Evaluation of the aerosol indirect effect in marine stratocumulus clouds: Droplet number, size, liquid path, and radiative impact, *J. Geophys. Res.*, *110*, D08203, doi:10.1029/2004JD005116.
- Van Dingenen, R., F. Raes, and N. R. Jensen (1995), Evidence for anthropogenic impact on number concentration and sulfate content of cloud-processed aerosol particles over the North Atlantic, *J. Geophys. Res.*, *100*, 21,057–21,067.
- van Zanten, M. C., B. Stevens, G. Vali, and D. H. Lenschow (2005), Observations of drizzle in nocturnal marine stratocumulus, *J. Atmos. Sci.*, *62*, 88–106.
- von Glasow, R., and R. Sander (2001), Variations of sea salt aerosol pH with relative humidity, *Geophys. Res. Lett.*, *28*, 247–250.
- Vong, R. J., B. M. Baker, F. J. Brechtel, R. T. Collier, J. M. Harris, A. S. Kowalski, N. C. McDonald, and L. M. McInnes (1997), Ionic and trace element composition of cloud water collected on the Olympic Peninsula of Washington State, *Atmos. Environ.*, *31*, 1991–2001.
- Waldman, J. M., J. W. Munger, D. J. Jacob, and M. R. Hoffmann (1985), Chemical characterization of stratus cloudwater and its role as a vector for pollutant deposition in a Los Angeles pine forest, *Tellus, Ser. B*, *37*, 91–108.
- Watanabe, K., Y. Ishizaka, and C. Takenaka (2001), Chemical characteristics of cloud water over the Japan Sea and the northwestern Pacific Ocean near the central part of Japan: Airborne measurements, *Atmos. Environ.*, *35*, 645–655.
- Weathers, K. C., et al. (1988), Cloudwater chemistry from ten sites in North America, *Environ. Sci. Technol.*, *22*, 1018–1026.
- Weller, R., O. Schrems, A. Boddenberg, S. Gab, and M. Gautrois (2000), Meridional distribution of hydroperoxides and formaldehyde in the marine boundary layer of the Atlantic (48°N–35°S) measured during the Albatross campaign, *J. Geophys. Res.*, *105*, 14,401–14,412.
- Xu, G., D. E. Sherman, E. Andrews, K. Moore, D. J. Straub, K. Hoag, and J. Collett Jr. (1999), The influence of chemical heterogeneity among cloud drop populations on processing of chemical species in winter clouds, *Atmos. Res.*, *51*, 119–140.

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