CHARACTERIZATION OF REACTANTS, REACTION MECHANISMS, AND REACTION PRODUCTS LEADING TO EXTREME ACID RAIN AND ACID AEROSOL CONDITIONS IN SOUTHERN CALIFORNIA

FINAL REPORT

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ABSTRACT

One daytime and four nighttime aircraft flights were conducted in November 1981 and May 1982 to collect samples of water and aerosol and to measure trace gas concentrations and other air quality parameters in stratus clouds both in the coastal and inland portions of the Los Angeles Basin. Total concentrations of sulfate and nitrate in clouds each exceeded about 100 $\mu g/m^3$. The average cloud water pH was 3.2 and the minimum was 2.4. Data for the relative ionic concentrations in equivalents typically fell in the range: 40-50% nitric acid, 20-30% ammonium sulfate, and 10-20% sodium chloride. It was found that the reaction between sulfur (IV) and hydrogen peroxide was inhibited in the collected water samples, that sulfur (IV) concentrations in the water were hundreds of times those expected from the measured sulfur dioxide gas concentration, Henry's law, water pH, and acid-base equilibria. Sulfur (IV) accounted for an average of 14% of the cloud water sulfur. It is believed that sulfur (IV)-carbonyl compound adducts were largely responsible for these results. The one sampling night in the eastern part of the Basin, sulfate concentrations were much higher in a point source plume, and nitrate concentrations were similar in and out of the plume and averaged about 90 $\mu g/m^3$. These high nitrate concentrations could be due to the prior day's photochemistry, nighttime reaction of nitrogen dioxide and ozone in clouds to produce the nitrate radical and nitrogen pentoxide, and the hydrolysis of PAN. On the average, the dissolved species in the cloud water in May were 50% by weight nitrate and 23% sulfate (after oxidation). It was calculated that the aerosol resulting from the evaporation of the cloud water averaged 24% nitrate and 38% sulfate and had a geometric mean diameter between 0.3 and 0.5 μm. It is suggested that adducts between sulfur (IV) and carbonyl compounds persist in the dry aerosol. Prior data suggesting that sulfur (IV) may account for about 10% of the sulfur (reported as sulfate) in the Los Angeles aerosol are discussed.

ACKNOWLEDGMENTS

The work on this contract was carried out in cooperation with the students and staff of Prof. Michael R. Hoffmann of Caltech, who were working under a parallel contract with the CARB. The assistance of Prof. Hoffmann, J. W. Munger, J. M. Waldman, and D. J. Jacob in this work is greatly appreciated.

T. B. Smith gave valuable help in forecasting suitable times for sampling and in suggesting sampling locations and strategies.

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1. SUMMARY AND CONCLUSIONS

1.1 INTRODUCTION

Meteorology Research, Inc. and Sonoma Technology, Inc. have conducted a study for the California Air Resources Board (CARB) in which an aircraft was used to collect cloudwater samples, filter samples of submicron aerosol, and to make other air quality and meteorological measurements in stratus clouds near the industrial areas of Los Angeles. Caltech conducted a parallel study for the CARB in which fog and rainwater samples were collected on the ground, and chemical analyses were performed for both the ground and airborne sampling.

1.2 OBJECTIVES

The primary objectives of this study were to:

1. Determine the composition of cloud droplets and the interstitial trace gases and aerosol during conditions of extreme acidity in the Los Angeles Basin.

2. Compare the data with one or more of the hypothesized sulfur or nitrogen oxidation mechanisms, and develop mechanisms to explain the observed oxidation rates, pH levels, and sulfate and nitrate concentrations.

3. Demonstrate the occurrence of non-photochemical oxidation processes.

1.3 EXPERIMENTAL

Five aircraft flights were conducted in stratus clouds in the Los Angeles Basin. Two of these flights were at night and early the following day near the coast in November 1981. Three flights were on successive nights in May 1982. Two of the May night flights were near the coast, and one was in the eastern portion of the Los Angeles Basin.

All cloud water analyses and the aerosol filter analyses in November were performed by the students and staff of Prof. M. R. Hoffmann at Caltech. In May, Gregory Kok at the National Center for Atmospheric Research came to Los Angeles and made measurements of hydrogen peroxide in the cloud water samples. In May, the aerosol filter samples were analyzed by Rockwell International.

1.4 RESULTS AND CONCLUSIONS

Extreme conditions of acidity and high sulfate and nitrate concentrations were observed in clouds in the Los Angeles Basin. In November, the average cloud water pH was 3.5 and the low was 3.0. In May, the average cloud water pH was 3.0 and the low was 2.4. The highest observed total sulfate and nitrate concentrations were each in excess of about 100 $\mu g/m^3$.

The sulfate and nitrate concentrations observed at night in clouds were high enough that it is quite unlikely they resulted from the prior day's photochemistry. Evidence was obtained for the formation of significant amounts of nitrate and particulate sulfur by non-photochemical processes at night in clouds.

The ionic composition of the collected cloud water expressed as equivalents typically fell in the following range:

40-50%	Nitric acid
20-30%	Ammonium sulfate
10-20%	Sodium chloride

This simple statement is intended to specify the relative concentrations of the listed cations and anions, but does not imply that ions listed together (for example ammonium and sulfate) have a common origin. The hydrogen ion concentration was typically greater than the equivalent sulfate concentration, and was greater than the concentration of all measured anions other than nitrate in about one-third of the samples. Therefore, it is certain that hydrogen ion from nitrate formation makes a major contribution to the observed cloud water acidity.

1.4.1 Sulfur Chemistry

Significant new results for the in-cloud chemistry of sulfur compounds have been obtained and submitted for rapid publication. They are:

1. The reaction between sulfur in the plus four oxidation state (sulfur (IV), e.g. sulfite) and hydrogen peroxide to form sulfate was strongly inhibited in the collected cloud water samples. Normally this reaction is very fast.

2. Sulfur (IV) concentrations in the cloud water were hundreds of times the concentrations expected from the measured gas phase SO_2 concentrations, the equilibrium dissolution of SO_2 in cloud water, and the acid-base equilibria of the dissolved H_2SO_3 at the measured cloud water pH.

These results can be partially explained by the formation of an adduct between formaldehyde and sulfite in solution. Other laboratory experiments have shown that this adduct is resistant to oxidation by hydrogen peroxide.

It is suggested that adducts between sulfite and formaldehyde or other carbonyl compounds are important in the sulfur budget of the Los Angeles Basin. An average of 14% of the sulfur in the cloud water was in the form of sulfur (IV). It is likely that adducts with carbonyl compounds do not entirely dissociate when the clouds evaporate, so that some organically bound sulfur (IV) persists in the aerosol. Experimental evidence for this suggestion from other studies is discussed.

In the inland portions of the Los Angeles Basin, it was observed that sulfate concentrations were significantly higher in point-source plumes than in other areas. In the Fontana area, two-thirds of the sulfate in excess of

that which would be there in the absence of the plume was in particles smaller than 2 μm diameter. Also about 20% of the plume excess sulfur was in the form of sulfate. These data suggest either unusually large emissions of sulfate or very rapid sulfate formation in the small cloud water droplets in plumes.

Significant interferences were present in the chemical determinations of sulfur (IV), formaldehyde, and in some samples, hydrogen peroxide. The interferences make the reported concentrations uncertain, but are not great enough to weaken the above conclusions.

1.4.2 Nitrogen Chemistry

On the average, 45% of the mass of solutes determined in the cloud water and 48% of the equivalents of anions was nitrate. (If total organic carbon had been determined in the cloud water samples, the mass percentage would have been somewhat lower.) Thus, nitrate was the dominant ionic species in the collected samples.

The average total nitrate concentration observed in the one night flight in the eastern portion of the Los Angeles Basin was 88 $\mu g/m^3$, and the concentration in the Fontana plumes was 94 $\mu g/m^3$. Nitrate concentrations in clouds were generally high in the inland portion of the basin, were much the same in and out of the plumes sampled, and were two to three times the nitrate concentrations typically observed during days with very high ozone concentrations. Thus, nitrate formation at night in clouds is indicated.

An efficient chemical mechanism for the formation of nitrate in clouds at night from ozone and NO_2 is described. This mechanism has the potential to form nitric acid at rates above 10 $\mu g\ m^{-3}\ h^{-1}$ at the observed ozone and NO_2 concentrations, but the actual rates of nitric acid formation by this mechanism are probably smaller than this.

It is possible that the hydrolysis of peroxyacetyl nitrate (PAN) in clouds contributed to the observed nitrate concentrations, and data for this reaction are discussed.

The experimental procedures for the airborne sampling of nitrates in urban clouds are not well developed at this time. Some uncertainty exists in the experimental data, but it is believed these uncertainties do not weaken the conclusions in this summary.

1.4.3 Aerosol Formation

Experimental results for the solute concentrations in the cloud water and cloud droplet size distributions were used to calculate an estimate of the composition and size distribution of the aerosol remaining after the clouds evaporated. In this calculation, it was assumed that nitric and hydrochloric acids evaporated along with the cloud water until either all the hydrogen ion or all the nitrate and chloride were gone. It was also assumed that all cloud droplets had the same chemical composition (even though it is likely that the smaller droplets were more concentrated).

The results of these estimates were in agreement with expectations. It was estimated that on the average, the aerosol particles left behind when the

clouds evaporated had diameters about 0.05 times the cloud droplet diameters, so 10 μm cloud droplets produced 0.5 μm aerosol particles. Sulfate and nitrate particles in the 0.5 to 1 μm size range are typically found in the Los Angeles Basin. Theoretical and experimental data strongly suggest that particles in this size range cannot be produced only by photochemistry during summer days. It is generally believed that the particles in the 0.5 to 1 μm size range are formed in or processed by fog and clouds, and the experimental data in this report provide solid support for that belief. The fact that sulfate and nitrate particles formed in fog and clouds are larger than particles formed purely photochemically is important, because a given mass of the larger particles is more effective at scattering light and in causing haze than is the same mass of smaller particles.

The estimates based on the experimental cloud water compositions showed that an average of 64% of the nitrate and chloride in the cloud water would evaporate along with the water. This corresponds to an average of 35% of the measured solute concentration. The solutes measured in the cloud water averaged 45% nitrate and 20% sulfate, while the composition of the remaining aerosol was estimated to be 23% nitrate and 32% sulfate. These percentages include only chemical species included in the chemical analyses. No measurement was made of total organic carbon, which is known to be a significant component of the cloud water. Including organic compounds in the data would reduce the calculated percentages of sulfate and nitrate.

2. RECOMMENDATIONS

This project was intended to be an exploratory study of the chemistry of clouds in the Los Angeles Basin to provide guidance for further research. The results of this study have led to the initiation in several laboratories of research on the chemistry of adducts between sulfur (IV) and carbonyl compounds and the reactions of these adducts with oxidants such as hydrogen peroxide. Airborne sampling to obtain additional ambient data on the chemistry of these compounds has been proposed. It is recommended that the CARB remain abreast of this work because of its possible relevance to sulfate standards. It is possible that roughly 10% of the reported ambient sulfate concentrations in the Los Angeles Basin may be due to organically stabilized sulfur (IV) compounds in the ambient aerosol.

The rapid formation of nitrate in clouds at night deserves additional study to determine the dominant reaction pathways and their reaction rates.

It is clear that non-photochemical formation of sulfate and nitrate in clouds is important in the Los Angeles Basin, and must be considered when planning air quality control strategies. The detailed information on the dominant reaction pathways and their reaction rates required for air quality modeling is not complete enough at this time that the importance of these processes can be satisfactorily calculated. Rapid progress is being made in understanding this chemistry, so model calculations may be much more reliable in a few years. It is recommended that the CARB remain in contact with this work and continue to support it.

It is believed that the results of this study have applicability in fog and clouds outside the Los Angeles Basin.

3. INTRODUCTION

Acid deposition has long been a source of concern in Scandanavia, and more recently became a source of concern in the northeastern United States and the Maritime Provinces of Canada (Likens 1976). Relatively little attention was given to acid deposition in California beyond the immediate vicinity of industrial operations until the work of Liljestrand and Morgan (1978, 1981), but it is now becoming clear that the likelihood of adverse impacts in California is great enough that the problem deserves study. A survey of acid deposition in California has recently been prepared by Lawson and Wendt (1982).

Acid fog is also a source of concern, and work on the chemical characterization of fog has been rapidly expanding in the last two years (Waldman et al. 1982a and 1982b, Hoffmann and Jacob 1982, and Jacob et al. 1982a, 1982b, and 1983). Higher concentrations of dissolved sulfate and nitrate and lower pH values can typically be found in fog and cloud water than in rain or drizzle.

Studies of the chemistry of fog and clouds in California are of interest for two reasons. First, the conversion of sulfur dioxide and nitrogen oxides to sulfate and nitrate in clouds contributes both to the acidification of the atmosphere and to acid deposition. Second, when the clouds evaporate, the sulfates and nitrates formed in clouds contribute to the aerosol particles which cause haze. Soluble aerosol particles formed in or processed by clouds tend to be larger than photochemically formed particles, and for that reason are more effective at scattering light and causing haze.

Airborne measurements of the chemical composition of clouds in California urban areas were made in a previous study. Parungo et al. (1980a, 1980b) sampled in and out of clouds in oil refinery plumes in the Los Angeles Basin. They found that air pollution levels had a significant influence on cloud droplet size distributions, and observed more rapid nitrate formation in clouds at night than at other times.

This report contains the results of a study conducted by Meteorology Research, Inc. and Sonoma Technology, Inc. for the California Air Resources Board. An instrumented aircraft was used to collect cloudwater samples, filter samples of submicron aerosol, and make other air quality and meteorological measurements in stratus clouds near the industrial areas of Los Angeles. Caltech conducted a parallel study for the CARB in which fog and rainwater samples were collected on the ground, and chemical analyses were performed for both the ground and airborne sampling.

Five sampling flights were made in November 1981 and May 1982. The two November flights were conducted during the night of 23 November and early the following morning near the coastline or over water. The three May flights were on successive nights beginning on 20 May. The first and last flight were near the coast, and the second flight was in the inland portion of the Los Angeles Basin in an area bounded by Pomona, Corona, and Fontana. The highest sulfate and nitrate concentrations were observed during this inland flight.

4. OBJECTIVES

The objectives of the study were to:

1. Determine the composition of cloud droplets and of the ambient submicron aerosol during conditions of extreme acidity in the Los Angeles basin. Specific emphasis was placed on identifying and quantifying the major oxidants and reductants in cloud water and precipitation samples and determining the relative contributions of the various constituents to acidity.

2. Determine the relationship of the pH, strong acid and oxidant concentrations of cloud or precipitation water samples to the composition of the background air and submicron aerosol.

3. Compare the data with one or more of the hypothesized sulfur or nitrogen oxidation mechanisms and to develop mechanisms to explain the oxidation rates, pH levels, and sulfate and nitrate concentrations found during this and previous studies.

4. Demonstrate the occurrence of non-photochemical oxidation processes.

5. EXPERIMENTAL

This chapter contains a brief outline of the instrument system used in the Queen Air to acquire the experimental data, the instrument calibration methods, the chemical analytical methods, and an outline of the data processing procedures used. A complete record of the results of all measurements made in this program is contained in a separate Data Volume. The portion of the data on which this report is based is contained in appendices to this report.

5.1 AIRBORNE SAMPLING SYSTEM

The sampling aircraft used was a Beechcraft Queen Air, an all-weather aircraft modified for use in air quality sampling. It has six sampling ports, manifolds for aerosol and gas sampling, and two inverters each providing 1 Kw of 110 V 60 Hz power for instrument use. An engine-driven vacuum pump plus a DC motor driven vacuum pump provided vacuum for the filter sampling. The flight crew consisted of a pilot, an instrument operator, and an observer.

5.1.1 Continuous Monitoring Instrumentation

The locations of the sample inlet lines and the external probes used during the May 1982 sampling are shown in Figure 5-1. The same configuration was used in the November, 1981 sampling, except that an ASSP-100 was used in place of the FSSP-100 for the cloud droplet concentration and size distribution measurements. Tables 5-1 and 5-2 list the aircraft instruments for both sampling periods.

5.1.2 Filter Sample Collection

Table 5-3 lists the filter samples collected by the Queen Air during the November, 1981 sampling flights. Table 5-4 lists the samples collected during the May, 1982 flights. A cyclone removed cloud water droplets larger than about 2 μm from the sample flow, so that the filters sampled predominantly submicron aerosol. Cloud droplets smaller than about 2 μm could also reach the filters. Backup filters collected gases such as HNO_3 and NH_3. The possibility of adsorption and desorption of these gases from the wet walls of the sample lines is discussed in later sections.

5.1.3 Cloud Water Sample Collection

Cloud water samples were collected during both programs using a sampler designed by a group at the State University of New York at Albany (Mohnen 1980, Winters et al. 1979). The cloud water was collected by impaction on the front of seven 9.5 mm (3/8 in.) diameter rods which projected into the air flow above the aircraft. Grooves in front of these rods conducted the cloud water downward into a collection bottle. Mild suction hastened the flow of

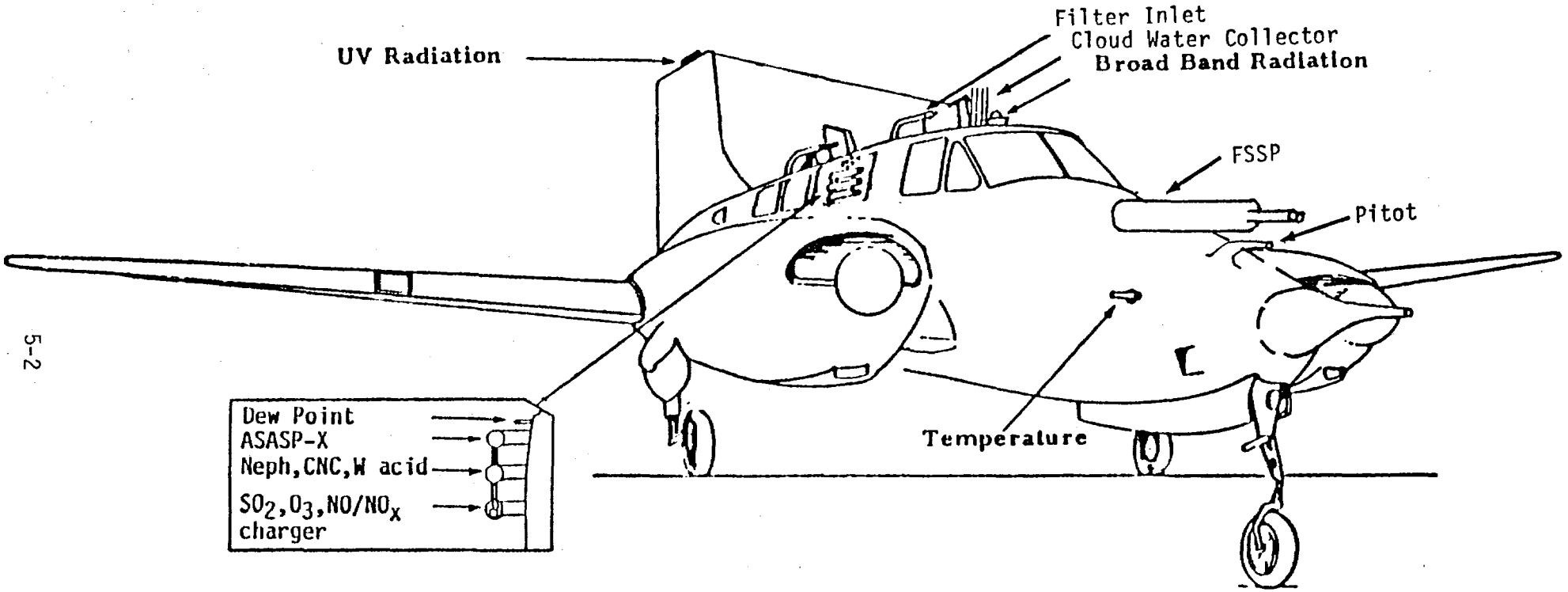

Figure 5-1. Queen Air Sample Inlet Lines and External Probes - May 1982 intensive.

Table 5-1. QUEEN AIR INSTRUMENTATION

PARAMETER	SAMPLER MANUFACTURER AND MODEL	ANALYSIS TECHNIQUE	NORMAL MEASUREMENT RANGES (FULL SCALE)	TIME RESPONSE (TO 90%)	APPROXIMATE RESOLUTION
SO_2	Meloy 285	Flame Photometric	100, 500, 1000 ppb	30 s	1 ppb
NO/NO_x	Monitor Labs 8440	Chemiluminescence	200, 500, 1000 ppb	5 - 10 s	<10 ppb
O_3	Monitor Labs 8410	Chemiluminescence	500 ppb	5 s	5 ppb
b_{scat}	MRI 1569	Integrating Nephelometer	100, 1000 Mm^{-1}	5 s	1 Mm^{-1}
Condensation Nuclei	Environment One Rich 100	Light Attenuation in an Expansion Chamber	10^5 cm^{-3}	3 s	10^3 cm^{-3}
Aerosol Charge Acceptance	Washington University	Aerosol Charge Acceptance	Primarily responds to .01 - .1 μ particles	~ 1 s	
Broad Band Radiation	Eppley PSP	Pyranometer	0 - 1026 w/m^2 Cosine response	1 s	2 w/m^2
Ultraviolet Radiation	Eppley	Barrier-Layer Photocell	295 - 385 mμ 0 - 34.5 w/m^2 Cosine response	1 s	0.1 w/m^2

Table 5-1. QUEEN AIR INSTRUMENTATION (continued)

PARAMETER	SAMPLER MANUFACTURER AND MODEL	ANALYSIS TECHNIQUE	NORMAL MEASUREMENT RANGES (FULL SCALE)	TIME RESPONSE (TO 90%)	APPROXIMATE RESOLUTION
Turbulence	MRI 1120	Pressure Fluctuations	0 - 10 $cm^{2/3}$ s^{-1}	3 s (to 60%)	0.1 $cm^{2/3}$ s^{-1}
Temperature	YSI/MRI	Bead Thermister/ Vortex Housing	-55° to +45° C	5 s	0.5° C
Dew Point	Cambridge Systems 137	Cooled Mirror	-50° to +50° C	0.5 s/° C	0.5° C
Altitude	Validyne	Absolute Pressure Transducer	0 - 3000 m msl	1 s	6 m
Indicated Airspeed	Validyne	Differential Pressure Transducer	23 - 68 m s^{-1}	1 s	0.1 ms^{-1}
Position	King KX170B/ HTI DVOR	Aircraft DME/VOR	0 to 359° and 0 to 150 km from the station	1 s	1° (bearing), 0.2 km (distance)
Data Logger (includes time)	MRI Data System	9-Track Tape - 6 hour capacity in continuous operation	± 9.99 VDC	Records data once per second	0.01 VDC
Stripchart Recorder	Linear Instruments	Dual Channel	0.01, 0.1, 1, 10 VDC	< 1 s	
Printer	Axiom		80 Character lines	Prints out data every 10 seconds and at every event code or data flag change	

Table 5-2. QUEEN AIR AEROSOL INSTRUMENTATION

Instrument	Size Range	Method
PMS ASASP-X		Optical particle counter with illumination in laser cavity and 35 to 120 degree collection
Range 3	0.09 - 0.2 μm	
2	0.15 - 0.3 μm	
1	0.24 - 0.8 μm	
0	0.6 - 3.0 μm	
PMS ASSP-100(1)	3 - 45 μm	Optical particle counter which detects forward scattering
PMS FSSP-100(2)		
Range 3	0.5 - 8 μm	Optical particle counter which detects forward scattering.
2	1 - 16 μm	
1	2 - 32 μm	
0	2 - 47 μm	

(1) Used during the November, 1981 sampling intensive.

(2) Used during the May, 1982 sampling intensive.

Note: The Particle Measuring Systems (PMS) optical particle counters (excluding the ASSP) can be manually set to any range, or can be set to automatically cycle through the ranges with one second in each range.

Table 5-3. QUEEN AIR FILTER SAMPLE COLLECTION SYSTEM
November 1981 Flights

Particle Size Segregation	Typical Flow Rate (1 pm ambient)	Filter Material	Analytical Methods
Cyclone <2μm cut	50	2μm Teflo 47 mm dia	IC: $SO_4^{=}$, NO_3^{-}, Cl^{-} Colorimetry: $NH4^{+}$
"	25	2μm Teflo 25 mm dia	XRF: trace elements (NEA, Inc.)
"	15	0.4μm Nuclepore 25 mm dia	Gravimetric mass then archive
"	30	Pallflex QAST 2500 47 mm Quartz Pre-fired Masked to 0.71 cm2	Volatile and Elemental C (NEA, Inc.)
"	40	2μm Teflo Followed by 47 mm dry Nylon	Teflo: IC: $SO_4^{=}$, NO_3^{-}, Cl^{-} Nylon: IC NO_3 (for HNO_3)
"	1	Tungstic acid denuder tube & packed tube	Desorb into NO-NO_x monitor (R. Braman)

Notes: IC = ion chromatography
Teflo = polyolefin ringed Teflon web filter obtained from Ghia

Table 5-4. QUEEN AIR FILTER SAMPLE COLLECTION SYSTEM
May 1982 Flights

Particle Size Segregation	Typical Flow Rate (1 pm ambient)	Filter Material	Analytical Methods
Cyclone <2μm cut	50	2μm Teflo 47 mm dia	IC: $SO_4^{=}$, NO_3^{-}, Cl^{-} Colorimetry: $NH4^{+}$
"	25	2μm Teflo 25 mm dia	Archived
"	8	0.4μm Nuclepore 25 mm dia	Archived
"	30	Pallflex QAST 2500 47 mm quartz pre-fired masked to 0.71 cm2	Archived
"	40	2μm Teflo Followed by 47 mm Nylon	Teflo: IC: $SO_4^{=}$, NO_3^{-}, Cl^{-} Nylon: IC NO_3 (for HNO_3)
"	20	2μm Zefluor followed by 47 mm oxalic acid impregnated glass	Colorimetry: $NH4^{+}$ (for NH_3)

Notes: IC = ion chromatography
Teflo = polyolefin-ringed Teflon web filter obtained from Ghia
Zefluor - Teflon mat backed Teflon web filter obtained from Ghia

Chemical analyses performed by EMSC, Rockwell International.

the water through small tubes leading from the bottom of the collection rods to the collection bottle inside the aircraft cabin. The bottles could easily be changed during sampling.

The cloud water collector is very inefficient at collecting submicron diameter particles (Winters et al. 1979). Thus, the cloud water samples were relatively uncontaminated by accumulation mode and nuclei mode aerosol. Water collection rates up to 2 ml/min in heavy stratus clouds were observed. When the clouds were very thin (liquid water content less than roughly 0.05 g/m^3), no water would flow into the collection bottle.

When collection bottles were removed from the sampler, they were capped and placed in an insulated box which contained a bottle rack located on top of frozen "Blue Ice." This method of storage provided some cooling for the samples, and isolated them from temperature fluctuations. It is estimated that the storage temperature for the cloud water bottles was between 5° and 10° C.

The methods used for the chemical analysis of these cloud water samples are described in section 5.3.

5.2 INSTRUMENT CALIBRATION

To ensure the accuracy and comparability of the data, the zero and span of the gas instruments were calibrated before and after the flights. The following calibration methods were used.

1. SO_2 - The primary method for calibration of the Meloy 285 SO_2 monitor was dilution of a bottle of high concentration SO_2 span gas (25 ppm in air - Scott Marrin, Inc.) with bottled "zero" air. The relative flow rates of the high concentration SO_2 span gas and the dilution air were controlled with a Columbia Scientific, Inc. (CSI) Model 1700 calibration system whose calibration has been checked with a Hastings HBM-1 bubble flow meter.

2. NO-NO_x - Calibration of the NO-NO_x instrument was performed using the same methods as for the SO_2 instrument. NO from a bottle (100 ppm in nitrogen - Scott Marrin, Inc.) was diluted with bottled "zero" air. The NO_2 readings were calibrated by gas phase titration. When either the SO_2 or NO-NO_x instruments were calibrated using the dilution system, multipoint calibrations were performed.

3. O_3 - A calibrated O_3 source (CSI Model 1700 Calibration System) was used for calibration of the ozone instrument. Multipoint O_3 calibrations (25 to 400 ppb) were achieved by changing the current through the UV lamp in the ozone generator. The accuracy and precision of the O_3 source were checked against a Dasibi Model 1003 PC.

4. b_{scat} - Freon-12 was used to calibrate the Integrating Nephelometer.

5. The optical particle counters were checked with nebulized polystyrene latex particles and with glass beads.

After the flights, the calibration data were reviewed to check the completeness, accuracy, and precision of the results.

5.3 PROCEDURES FOR CHEMICAL ANALYSES

The chemical analysis of the cloud water was performed by students and staff of Prof. M. R. Hoffmann at the California Institute of Technology using procedures described by Munger et al. (1983). The flow diagram of the Caltech analytical procedure appears in Figure 5-2, and the analytical methods used are listed in Table 5-5. Only water-leached bottles were used in the aircraft sampling, and the cation and anion analyses indicated in the diagram were both performed on the contents of each collected bottle when the sample size was adequate.

Immediately after the plane landed, a 2.5 ml aliquot was removed from each sample bottle and stabilized with formaldehyde at pH 4 for the later determination of sulfur (IV). An additional 1.5 ml aliquot was removed from the sample bottle and stabilized for the determination of HCHO according to the methods of Nash (1953) and Rietz (1980). The pH of the remaining cloud water sample was measured with a glass electrode. The samples were then returned to Caltech for further analyses.

In November, 1981, sulfate was determined before and after the oxidation of the sulfur (IV) to sulfate, and the sulfur (IV) concentration was determined by difference. In May, 1982, the sulfur (IV) concentration was determined directly by the method of Humphrey et al. (1970). Sulfate was determined after oxidation of all sulfur to sulfate, and the reported sulfate concentrations were obtained by subtracting the sulfur (IV) concentrations from this total concentration.

In the May flights, an additional small sample of cloud water was collected at each sampling location immediately after the collection of the main sample. This sample was passed through an anion ion exchange resin immediately after collection to remove sulfite and was then stored in the same manner as the other samples. When the plane landed, these aliquots were analyzed for H_2O_2 by Gregory Kok of NCAR using the horseradish peroxidase method described by Kunen et al. (1983). Separate aliquots were treated with catalase to remove H_2O_2, then analyzed by the horseradish peroxidase method to determine the small corrections (less than 3%) for interferences due to organic peroxides and fluorescent organic materials. Known quantities of hydrogen peroxide were passed through the ion exchange resins used in each flight to see if impurities collected in the resin caused interferences. The H_2O_2 values for 21-22 May (Tape 302) are lower limits, because these tests showed that solids in the cloud water retained in the ion exchange resin catalyzed H_2O_2 decomposition. These post-flight tests showed that the ion exchange resin did not pick up materials which decomposed hydrogen peroxide on the other two May flights.

The methods used for the determination of the amounts of materials collected on the filters are listed in Tables 5-3 and 5-4. All of these methods, except those used for the tungstic acid tubes, are standard commercial methods. Brief outlines of these methods appear in Richards et al. (1981).

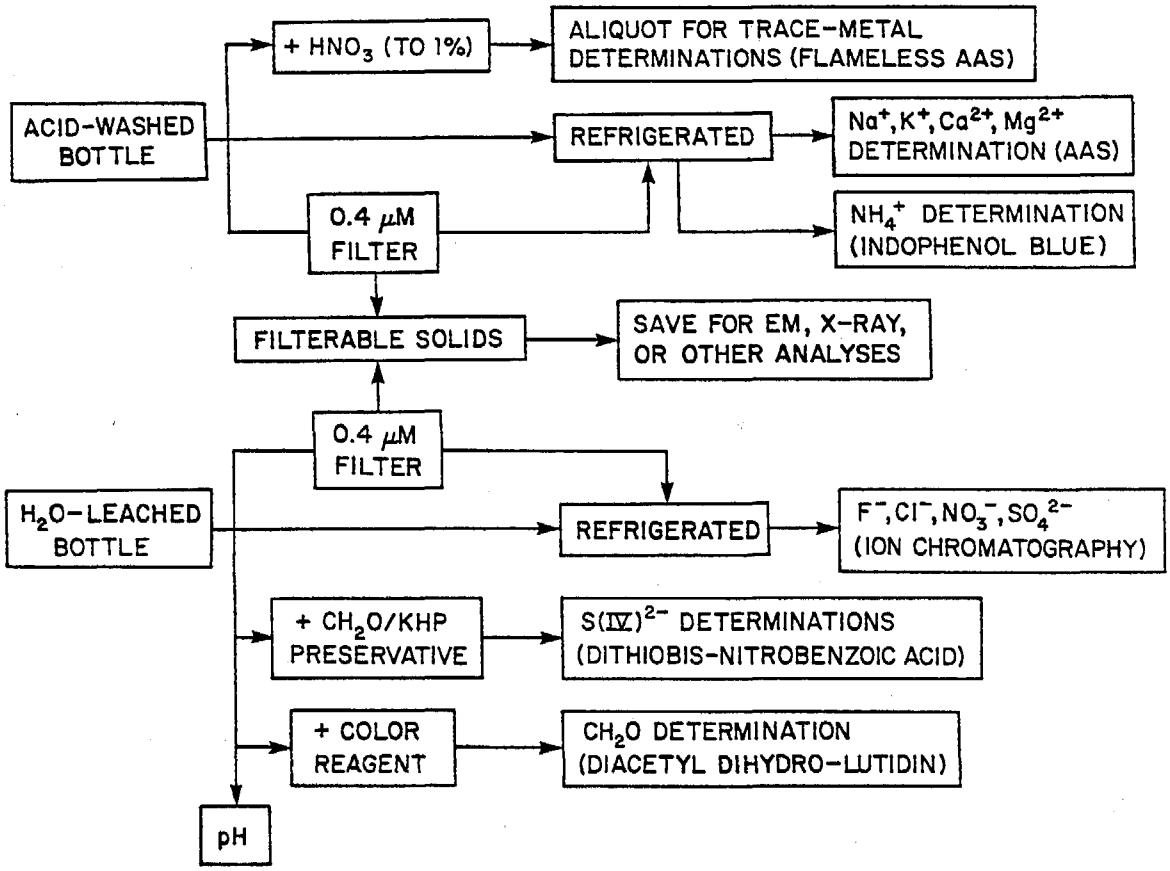

Figure 5-2. Flow diagram for the chemical analysis of cloud water samples (Munger et al. 1983).

Table 5-5. Analytical methods used at Caltech for cloud water samples.

Analyte	Method
pH	Radiometer pHM 82. Calibrated with pH 4.00 and 7.00 buffers.
Na^+, K^+	Atomic Absorption Spectrophotometry (AAS). Varian AA5 with air-acetylene flame. Conditions as described in Varian manual.
Ca^{++}, Mg^{++}	AAS. Same as above except lanthanum added to release interferences.
NH_4^+	Phenol-hypochlorite method (Solorzano 1967).
F^-, Cl^-, NO_3^-, $SO_4^=$	Ion chromatography. Dionex Model 10. Standard conditions described in Dionex manual.
$SO_3^=$	$SO_3^=$ preserved with HCHO at pH 4.00 (1 mM KHP) (Dasgupta et al. 1980). Preserved solution injected into ion chromatograph using 1 mM KHP as eluent. $SO_4^=$ peak compared to $SO_4^=$ from standard IC run on unpreserved sample.
HCHO	Reaction with acetylacetone and ammonium acetate, (Nash 1953; Rietz 1980).
Fe, Mn, Zn, Pb, Cu, Ni, Co, V	AAS using carbon rod atomization. Varian AA6, CRA 90. Conditions given by Varian and Perkin-Elmer.

In November, hollow tubes coated with tungstic acid were used to collect gas phase nitric acid and ammonia. The hollow tubes were followed by packed tubes containing tungstic acid to collect particulate nitrate and ammonium. These tubes were supplied by Prof. R. S. Braman, and returned to him for analysis. The procedures used have been described by Braman et al. (1982) and McClenny et al. (1982).

5.4 DATA PROCESSING

Data from the various monitors aboard the Queen Air were recorded on an MRI data system. The data system uses a Pertec tape recorder to write data at one second intervals on nine-track magnetic tape, and an Axiom printer to make a printed record of selected channels of data at ten second intervals. The printer tape provides both a data system backup and a record for the flight crew to review in the field.

One magnetic tape was used to record the data from each flight. These tapes are numbered sequentially. Time intervals during a flight when data are recorded are called passes, and are numbered sequentially within each tape. Therefore each measurement period is uniquely identified by a tape and pass number, and these identifying numbers are frequently included in tabulations of results.

During the sampling flight performed 21-22 May 1982, the Pertec recorder failed. Data recorded on the printer tape were keypunched and used during data processing. The 1 s records between the data points every 10 s were filled with INOP values. Only analog data are recorded on the printer tape, so the data from the two aerosol optical particle counters are missing for this flight.

The Meloy 285 SO_2 monitor is known to shift its zero as a function of pressure. To document this effect, and to compensate for it during data processing, the zero of the SO_2 monitor was determined between passes at each flight altitude. In addition, the zeros of the NO-NO_x and O_3 monitors were determined at the same time.

After each intensive, the 9-track data tapes were dumped and processed. This consisted of applying the appropriate calibration factors for each instrument and applying any zero corrections necessary to correct for the pressure effects discussed above. The plots have been reviewed, and any results due to instrument malfunctions removed.

The Axially Scattering Spectrometer Probe (ASSP) mounted on the nose of the aircraft during the November sampling measures particles in the size range of cloud droplets. Particles are counted and sized as they pass through the probe, and the results accumulated in nine optical size ranges. At the end of each second, the total counts for the previous 0.9 sec are recorded and the counters are reset.

The counts from the Active Scattering Aerosol Spectrometer Probe (ASASP-X) are similarly recorded, except that this instrument makes measurements in four particle size ranges. The size range of the ASASP-X is

advanced each second, so that four seconds are required to make measurements over the full instrument range. During the May sampling, the ASSP was replaced by the Forward Scattering Spectrometer Probe (FSSP). The counts from the FSSP are recorded and processed in the same manner as the ASASP-X.

To help in the interpretation of the November ASSP data, several continuous parameters were calculated from them and included in the plots of the data. These parameters are:

1. Number concentration of particles within the size range of the probe.

2. Liquid water content of the cloud in particles within the size range of the probe.

3. Volume mean particle diameter for particles within the size range of the probe.

These data were smoothed by replacing each reading with the mean value of the data for a seven second interval that is symmetrical about the data point. It should be noted that each of these parameters was derived from only the data from one instrument, and thus each parameter is a measure only of the aerosol properties in the size range monitored by the counter which obtained the data.

When the results in a particular channel were missing or were invalid, the erroneous values were replaced by the integer 32767 = 2^{15} -1. This is the largest positive integer which can be processed by the computer used to reduce the data. This value indicates that the instrument was inoperative, and is sometimes indicated by the abbreviation INOP. Any user of the magnetic tapes should check all readings to see if they are equal to 32767, and should ignore readings which have this value.

5.5 DATA VOLUME

A Data Volume has been prepared which compiles all the data collected in this study and documents the conditions under which they were collected. The portions of the data on which this Final Report is based are contained in the Appendices, so readers of this report do not need to refer to the Data Volume. A copy of the Data Volume has been given to Caltech and to the CARB.

6. OVERVIEW OF THE RESULTS

The experimental results from the November 1981 and May 1982 sampling flights are reviewed in this chapter and are tabulated in Appendices A and B. More detailed discussions of the observed sulfur and nitrogen chemistry appear in Chapters 7 and 8, and a discussion of aerosol formation is in Chapter 9. Limitations of the data are discussed both in this and in subsequent chapters.

6.1 CLOUD WATER MEASUREMENTS

Data for the liquid water content (LWC) of the clouds and the cloud droplet size distributions are discussed in this section, as well as the sources of error and uncertainties in these results.

6.1.1 Liquid Water Content Measurements

Two methods were used to determine the LWC of the clouds. One was to measure the amount of water collected by the cloud water collector, assume a collection efficiency, and calculate the average liquid water content of the sampled clouds from the volume of air swept out by the collector. The other was to transform the counts recorded by the Particle Measuring Systems, Inc. (PMS) optical particle counter probes into cloud water volumes. Both methods are subject to significant uncertainties.

The PMS probe data for LWC are typically uncertain by a factor of two or more. In part, this uncertainty arises from the fact that an error of 26% in the diameter of a droplet will lead to an error of a factor of two in its volume. Therefore, relatively small errors in the calibration of the particle sizes corresponding to the PMS probe channel boundaries or in assigning the detected particles to channels cause large errors in the calculated LWC. The PMS probe used in May, 1982 was a FSSP-100, which automatically cycled through four overlapping particle size ranges. The LWC data from the different ranges were intercompared, and found to be internally consistent when averaged over a full pass. Even so, these LWC data are believed to be uncertain by a factor of two or more.

The theoretical efficiency of ASRC cloud water collector has been calculated as a function of the particle diameter and air speed (Winters et al. 1979) and is about 85% for the cloud droplet size distributions typically encountered in Los Angeles. Experimental comparisons between amount of water collected by the ASRC collector and measurements of the LWC of clouds by Johnson-Williams probes and PMS probes indicate that the collection efficiency of the ASRC collector is quite variable, and is often in the range of 40% to 50% (R. Schemenauer, Environment Canada, private communication). Thus, the LWC values calculated from the volume of water collected are also uncertain by about a factor of two.

Two values used in this report for efficiency of ASRC collector: 85% for the theoretical efficiency and half that for the experimental efficiency. LWC data based on the volume of the collected water and a cloud water collector efficiency of about 45% are believed to give best LWC estimates. Data calculated using an efficiency of 85% are believed to provide an upper limit to the LWC, because it is difficult to imagine mechanisms which will cause more water to be collected than was in the volume swept out by the collector.

Table 6-1 reports LWC data from both the PMS probe and the volume of water collected. When calculating the LWC from the volume of water collected, an average air speed of 54 m/s and a collection efficiency of 45% were used. These numbers correspond to collecting all the water in 4.5 m^3/min. In all cases on 23 May, the LWC calculated from the PMS probe data is less than half the LWC calculated from the volume of water collected. In these cases, the LWC data from the PMS probe data are probably too small, because it is unlikely that more water would enter the cloud water collected than was in the volume swept out by it. The data in this table emphasize the uncertainties in the LWC measurements.

One of the more interesting continuous plots of the PMS probe data obtained in November, 1981 is shown in Figure 6-1. These data were recorded during the departure to the west from Los Angeles International Airport. The probe which recorded these data was sensitive to particles in the 3 μm to 45 μm diameter range, so the plots do not reflect the properties of particles outside this size range. The bottom panel shows that the cloud layer extended from about 400 ft to 1600 ft altitude, and that the LWC was the greatest at the top of the cloud layer. This gradient in LWC with altitude was almost always observed in this study. The particle number concentration and particle diameter data show that the higher LWC at the top of the cloud was primarily due to the larger droplet size. Below the cloud, the mean particle size increased gradually from about 5 μm at the surface to about 15 μm at the cloud base. Above the cloud, the particle concentrations were so low that the mean particle diameter is often the size of the one particle counted each second.

The theoretical efficiency of the cloud water collector falls to 50% for particles about 3 μm in diameter, and is essentially zero for submicron particles. The cyclone in front of the filters removes particles larger than about 2 μm. Therefore, particles in the 2-3 μm size range are probably not efficiently collected on the filters or in the cloud water. Cloud droplets in this size range are likely to contain higher concentrations of dissolved species than larger droplets (Levine and Schwartz 1982), so this gap in particle collection efficiency may not be negligible.

Another source of uncertainty whose magnitude is unknown is the evaporation of cloud water droplets as they approach the cloud water collector. The air which enters the stagnation region at the water collection grooves is compressed and heated, and this could cause evaporation from the droplets. It was observed in this study and by others (L. Radke, private communication) that no liquid water is collected in light clouds. This suggests that some evaporation does occur.

Data subject to such errors must be interpreted with caution. We believe that adequate allowance has been made for these uncertainties in the following data analysis.

Table 6-1. Average cloud liquid water contents.

Date	Tape	Pass	Start Time	Location	Liquid water content 10^{-6} = cm^3/m^3 From PMS probe	From collected volume
23 Nov	296	1	2224	depart LAX	0.19	
		2	2244	off Malibu	0.27	
		4	2328	off El Segundo	0.11	
		5	2353	El Seg. to S.Bch	0.03	
24 Nov		6	0025	Seal Beach	0.035	
		7	0047	Seal Beach	0.035	
		8	0122	approach LAX	0.29	
24 Nov	297	2	0732	off Los Alamitos	0.019	
		3	0807	off Los Alamitos	0.022	
		4	0834	ALBAS*	0.013	
		5	0915	ALBAS	0.022	
		6	0957	PEDRO**	0.014	
		November average			0.0875	
20 May	301	2	2235	off Long Beach	0.14	0.20
21 May	302	1	2257	Etiwanda		0.12
		3	2349	Fontana		0.19
22 May		5	0025	Fontana		0.30
		7	0102	Pomona-Corona		0.26
		9	0132	Pomona-Corona		0.17
		11	0206	Fontana		0.4
23 May	303	5	0134	ALBAS*	0.042	0.13
		7	0209	ALBAS	0.077	0.50
		8	0219	ALBAS	0.071	0.60
		9	0228	ALBAS	0.13	1.3
		May average			0.09	0.38

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

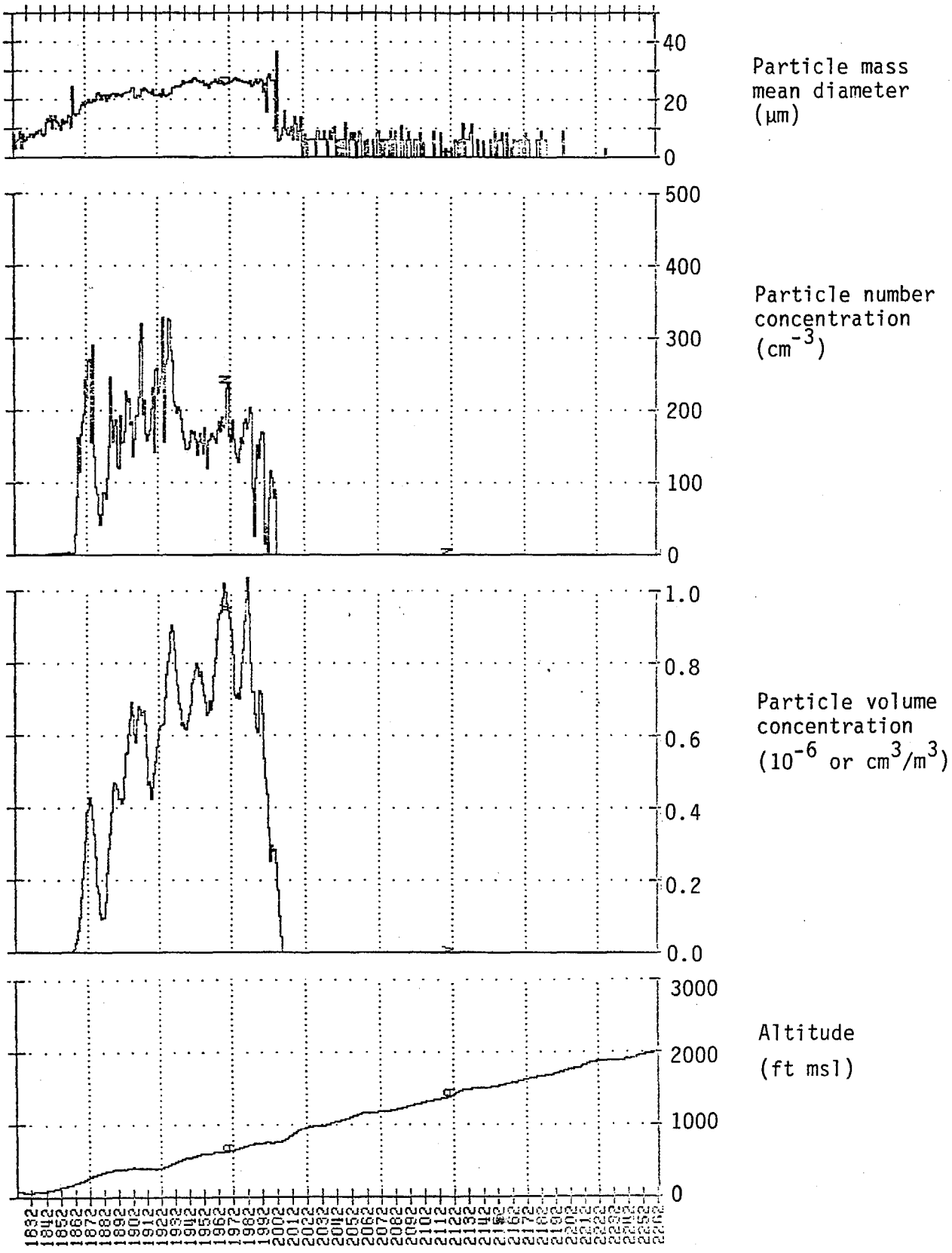

Figure 6-1. Cloud droplet parameters measured during departure from LAX, 22:24 PST, 23 November 1981.

6.1.2 Cloud Droplet Size Distributions

The cloud droplet size distributions measured with the PMS probes are less subject to error than the LWC measurements because they are less sensitive to small errors in determining the droplet size. Sample results from the May, 1982 sampling are shown in Figure 6-2. The data for 23 May show an increase in the droplet size and the cloud LWC with increasing altitude. Additional discussion of these size distributions appears in Chapter 9 on aerosol formation.

6.2 CLOUD WATER CHEMISTRY

An overview of the cloud water chemistry results is presented here. More complete discussions of the observed sulfur chemistry appear in Chapter 7 and nitrogen chemistry in Chapter 8.

6.2.1 Data Tabulations

All of the cloud water analytical data received from Caltech and Gregory Kok are reported in Appendix B. The concentrations of the dominant ionic species are summarized in Table 6-2. On the average, five cations and four anions account for 92% to 96% of the total cations and anions. The dominant ions are H^+ and NO_3^-, and their concentrations are about equal. The ionic concentrations of most cloud water samples fall in the following range:

40-50%	Nitric acid
20-30%	Ammonium sulfate
10-20%	Sodium chloride

These results do not necessarily imply that the ammonium ions are associated with sulfate, or that acidity is associated with nitrate. However, they do clearly show that the number of equivalents of hydrogen ion in the cloud water is typically greater than the number of equivalents of sulfate, so that sulfate formation alone cannot account for the observed acidity.

6.2.2 Ion Balances

One useful test of the quality of ionic analytical data is to evaluate how well the reported concentrations of anions and cations match each other. This is only a test of the analytical results, because this balance must exist in any solution submitted for analysis. Calculating ion balances requires making some assumptions about the ionic form of various species in solution. Here it was assumed that sulfur (IV) was present either as HSO_3^- or as a singly charged anion adduct with carbonyl compounds. The assumed ionic forms of metals other than the alkali or alkaline earth metals were: $FeOH^{++}$, VO_3^-, Pb^{++}, Cu^{++}, Ni^{++}, and Mn^{++}. The results of the ion balance calculations are listed in Table 6-3.

In general, the ion balances are satisfactory. The lack of ion balance is large compared to the concentrations of most species, so the ion balance primarily serves as a check on the general quality of the analytical results and on the measured concentrations of the dominant species, H^+ and NO_3^-.

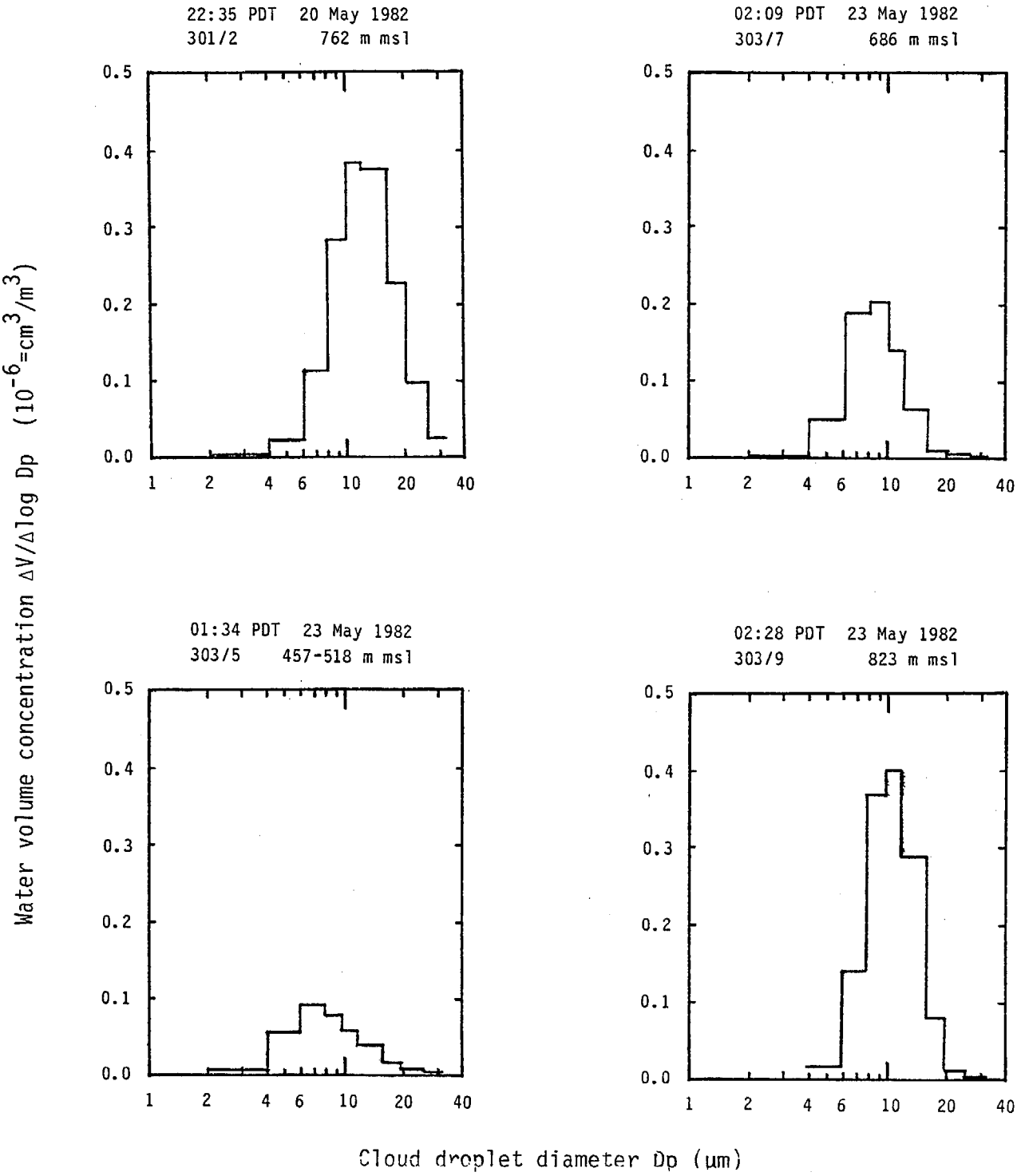

Figure 6-2. Cloud droplet size distributions. The 20 May measurements were made off Long Beach and the 23 May measurements at ALBAS, a navigation point off Huntington Beach. The data Tape/Pass sampling altitude are indicated.

Table 6-2. Dominant species in cloud water.

Date	Tape	Pass	Start Time	Location	Fraction of cations due to each ion					Fraction of anions due to each ion			
					H^+	NH_4^+	Na^+	K^+	Ca^{++}	NO_3^-	$SO_4^=$	Cl^-	HSO_3^-
23 Nov	296	1	2224	depart LAX	0.17	0.08	0.30	0.12	0.20	0.28	0.23	0.46	0.00
		2	2244	off Malibu	0.37	0.16	0.35	0.01	0.04	0.46	0.17	0.30	0.03
		4	2328	off El Segundo	0.34	0.07	0.46	0.01	0.03	0.26	0.21	0.45	0.04
		5	2353	El Seg. to S.Bch	0.58	0.19	0.16	0.01	0.02	0.55	0.21	0.15	0.05
24 Nov		6	0025	Seal Beach	0.50	0.23	0.23	0.00	0.02	0.57	0.22	0.12	0.05
		7	0047	Seal Beach	0.60	0.22	0.13	0.00	0.02	0.56	0.20	0.14	0.04
		8	0122	approach LAX	0.32	0.18	0.25	0.15	0.03	0.26	0.26	0.43	0.00
24 Nov	297	2	0732	off Los Alamitos	0.45	0.25	0.20	0.01	0.04	0.54	0.16	0.27	0.00
		3	0807	off Los Alamitos	0.62	0.24	0.08	0.01	0.02	0.40	0.33	0.12	0.08
		4	0834	ALBAS*	0.39	0.24	0.25	0.01	0.03	0.19	0.22	0.33	0.00
		5	0915	ALBAS	0.53	0.23	0.18	0.01	0.02	0.42	0.30	0.17	0.07
		6	0957	PEDRO**	0.00	0.92	0.07	0.00	0.00	0.46	0.12	0.24	0.02
		November average			0.41	0.25	0.22	0.03	0.04	0.41	0.22	0.26	0.03
20 May	301	2	2235	off Long Beach	0.63	0.11	0.16	0.01	0.02	0.48	0.29	0.19	0.01
21 May	302	1	2257	Etiwanda	0.65	0.19	0.05	0.00	0.04	0.68	0.26	0.03	0.01
		3	2349	Fontana	0.27	0.37	0.04	0.01	0.18	0.56	0.34	0.06	0.02
22 May		5	0025	Fontana	0.06	0.51	0.03	0.01	0.32	0.44	0.41	0.06	0.06
		7	0102	Pomona-Corona	0.59	0.28	0.03	0.00	0.03	0.70	0.24	0.02	0.01
		9	0132	Pomona-Corona	0.53	0.34	0.04	0.01	0.02	0.69	0.25	0.02	0.01
		11	0206	Fontana	0.47	0.42	0.02	0.00	0.05	0.67	0.27	0.02	0.01
23 May	303	5	0134	ALBAS	0.38	0.20	0.19	0.02	0.08	0.44	0.42	0.10	0.01
		7	0209	ALBAS	0.46	0.26	0.14	0.02	0.05	0.45	0.39	0.10	0.01
		8	0219	ALBAS	0.43	0.21	0.16	0.01	0.06	0.48	0.36	0.10	0.01
		9	0228	ALBAS	0.44	0.32	0.11	0.01	0.04	0.42	0.38	0.10	0.02
		May average			0.45	0.29	0.09	0.01	0.08	0.55	0.33	0.07	0.01
		Grand average			0.43	0.27	0.16	0.02	0.06	0.48	0.27	0.17	0.02

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

Table 6-3. Ion balance calculations.

Date	Tape	Pass	Start Time	Location	Caltech sample no.	Total conc. Cations + µeq/l	Total conc. Anions - µeq/l	Ion balance Diff. (+)-(-) µeq/l	Ion balance Ratio +/-	pH from ion balance	pH difference
23 Nov	296	1	2224	depart LAX	23-2	1646	1531	115	1.08	3.80	0.24
		2	2244	off Malibu	23-3	1195	1253	-58	0.95	3.31	-0.05
		4	2328	off El Segundo	23-5	472	536	-64	0.88	3.65	-0.15
		5	2353	El Seg. to S.Bch	23-6	1529	1899	-370	0.81	2.90	-0.15
24 Nov		6	0025	Seal Beach	23-7	2105	2464	-359	0.85	2.85	-0.13
		7	0047	Seal Beach	23-8	1585	1983	-398	0.80	2.87	-0.15
		8	0122	approach LAX	23-9	657	693	-36	0.95	3.61	-0.07
24 Nov	297	2	0732	off Los Alamitos	24-3	1458	1427	31	1.02	3.20	0.02
		3	0807	off Los Alamitos	24-4	307	359	-52	0.85	3.61	-0.11
		4	0834	ALBAS*	24-5	2902	539	2363	5.38	0.00	0.00
		5	0915	ALBAS	24-6&7	410	375	35	1.09	3.74	0.07
		6	0957	PEDRO**	24-8	3879	2732	1147	1.42	0.00	0.00
		November average				1512	1316	196	1.34	3.35	-0.05
20 May	301	2	2235	off Long Beach	20-2	1625	1443	182	1.13	3.08	0.09
21 May	302	1	2257	Etiwanda	21-1	6092	6686	-594	0.91	2.34	-0.06
		3	2349	Fontana	21-2	7065	8280	-1214	0.85	2.51	-0.21
22 May		5	0025	Fontana	21-3	6488	6430	58	1.01	3.46	0.07
		7	0102	Pomona-Corona	21-4	4651	5423	-771	0.86	2.45	-0.11
		9	0132	Pomona-Corona	21-5	4218	5195	-978	0.81	2.49	-0.16
		11	0206	Fontana	21-6	4326	5445	-1119	0.79	2.50	-0.19
23 May	303	5	0134	ALBAS	22-2	2334	2171	163	1.07	3.14	0.09
		7	0209	ALBAS	22-3	910	781	129	1.16	3.54	0.16
		8	0219	ALBAS	22-5	1079	916	163	1.18	3.52	0.19
		9	0228	ALBAS	22-4	581	582	00	1.00	3.59	0.00
		May average				3579	3941	-362	0.98	2.96	-0.01
		Grand average				2501	2571	-71	1.17	3.15	-0.03

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

The last two columns at the right of Table 6-3 illustrate the use of the ion balance calculations to check the measured hydrogen ion concentrations. The next to the last column contains the pH corresponding to the hydrogen ion concentration that would make the measured cation concentration exactly match the measured anion concentration. The last column gives the amount by which this pH derived from the ion balance differs from the measured pH. In nearly all cases, the two pH values agree within 0.2 pH units.

6.2.3 Interferences

It is believed that significant interferences were present in the chemical analyses of the cloud water samples, and that allowance must be made for them in the interpretation of the data. Some known interferences are described in this section. The search for interferences is not complete enough to be assured that this list of interferences is complete.

Interference of hydrogen peroxide in the sulfite determinations. No measures were taken to destroy H_2O_2 in the cloud water samples before they were made basic and the sulfite concentration determined. Due to the stability of the H_2O_2 in the cloud water samples, it is possible that some hydrogen peroxide remained at the time the adduct between sulfur (IV) and the added formaldehyde was broken. If this was the case, the H_2O_2 would react with the liberated sulfur (IV), and the reported sulfur (IV) concentrations would be too small.

Interference of sulfite in the formaldehyde determinations. Klippel and Warneck (1980) have reported that sulfite interferes with the determination of formaldehyde, and suggested a method of avoiding this interference. No measures were taken to eliminate this interference in these analyses, so some reported formaldehyde concentrations may be too small.

Interferences in the hydrogen peroxide determinations. The cloud water aliquots to be analyzed for H_2O_2 were passed through an anion exchange resin immediately after collection to stabilize the solutions. After each flight, known quantities of H_2O_2 were passed through the resin to check for interferences caused by retained impurities. It was typically found that the H_2O_2 passed through the used ion exchange resins with no loss. After the flights in the Pomona-Ontario-Fontana area, these tests showed that the ion exchange resin picked up impurities which catalyzed H_2O_2 decomposition. On this night (Tape 302, 21-22 May 1982), samples collected in the later part of the flight could have lost as much as half the collected H_2O_2 in the ion exchange resin.

Corrections were made for interferences in the H_2O_2 determinations caused by organic peroxides or fluorescent organic materials. This was done by dividing the cloud water sample into two aliquots, and adding catalase to one. This enzyme destroys H_2O_2 but not organic peroxides. Both aliquots were analyzed by the horseradish peroxidase method (Kunen et al. 1983) and the difference between the results taken as a measure of the H_2O_2 concentration. The corrections determined from the catalase treated samples were typically less than 3% of the measured H_2O_2 concentrations.

Means are now known for reducing or eliminating all the above interferences, so these uncertainties should not persist in future work.

6.3 AEROSOL CHEMISTRY

Aerosol filter samples were collected in November as described in Table 5-3, but the data were not satisfactory. The quantities of sulfate and nitrate reported for the blank filters were highly variable, and sometimes were as great as for any of the exposed filters. This problem has not been experienced before or since, so is believed to be associated with the handling and analysis of the filters after they were removed from the airplane. The problem was not associated with the filters, because filters from the same manufacturer's containers were used in May and gave very satisfactory blank values. The November filter data are not included in this report.

Filter chemistry data from the May 1982 sampling appear in Table B-3 of Appendix B. Data from the blank filters collected in May appear in Table B-4, and Table B-5 compares data from replicate filters collected at the same time. The analytical laboratory was not informed which filters were blanks or replicates. The excellent quality of the blank filter and replicate results show that the laboratory analyses of the filters were precise and probably were accurate.

The connection between the amounts of materials collected on the filters and the ambient aerosol concentrations is not straightforward. As described in Section 5.1.2, the air sample passes through a cyclone which removes particles larger than about 2 μm diameter. The walls of the sampling lines become moist in clouds, and heating of the air flow by its deceleration in the sampling line may cause the evaporation of some cloud water. The Teflon filters retain the particulate material in the air flow which has passed through this sampling system. It is likely that some materials initially retained by the Teflon filter evaporate during the sample collection. Some Teflon filters were followed by either a Nylon filter to collect nitric acid or an oxalic acid impregnated filter to collect basic gases, such as ammonia. The material on these backup filters could either be initially in the gas phase, or could be volatilized from the Teflon filters.

Another source of uncertainty whose magnitude is unknown is the evaporation of cloud water droplets which enter the filter sampling manifold. The air flow entering this manifold is decelerated and compressed, and as a result its temperature rises. This will cause some evaporation of the droplets entering the manifold, and will allow some droplets which were larger than about 2 μm in the atmosphere to pass through the cyclone. The magnitude of this possible error has not been determined.

The filter chemistry data in Table 6-4 suggest that some volatilization from the Teflon filter does occur. When the number of equivalents of ammonium on the Teflon filter is divided by the sum of the number of equivalents of sulfate and nitrate, the ratios are typically very close to unity. Chloride on the filters was determined, and was typically quite small. Other ionic species were not determined, so the complete ion balance on these filters can not be calculated. The cloud water chemistry data in Table 6-2 suggest that sodium may make up much of the difference when the number of equivalents of

Table 6-4. Teflon filter ion balances.

Tape/Pass	Species concentration $\mu g/m^3$			eq NH_4^+
	NO_3^-	$SO_4^=$	NH_4^+	eq(NO_3^- + $SO_4^=$)
301/1	0.44	8.32	2.88	0.89
301/2	1.19	1.78	0.69	0.68
302/1-2	3.99	20.1	8.41	0.97
302/3-4	16.3	31.6	15.9	0.96
302/5-6	31.0	68.1	32.9	0.95
302/7-10	4.34	12.1	5.55	0.96
302/11-12	3.60	14.9	6.48	0.98
303/1	12.8	9.79	7.42	1.00
303/2	15.0	9.56	7.98	1.00
303/3	1.23	8.53	3.30	0.93
303/5-6	1.35	4.10	1.63	0.84
303/7-10	0.08	1.10	0.33	0.76

ammonium was less than the equivalents of sulfate and nitrate. The data in Table 6-4 can be accounted for if nitric acid in excess of that stabilized by ammonium and metal cations evaporates from the filter and is collected by the backup Nylon filter.

The data in Table B-3 show that on the average, about twice as much nitrate was collected by the backup Nylon filter as by the Teflon filter. This is true even in clouds. Levine and Schwartz (1982) have shown that in clouds, nitric acid is very rapidly drawn into the liquid phase. Therefore, it is unlikely that the nitrate on the backup Nylon filters was in the gas phase in the clouds; it is more likely that it volatilized from the liquid phase before or after collection on the Teflon filter. If the volatilization of nitrate from cloud water collected by the cyclone is negligible, the sum of the nitrate on the Teflon and Nylon filters gives the concentration of nitrate in the gas phase and in particles small enough to pass through the sampling line and the cyclone.

6.4 TRACE GAS CHEMISTRY

Continuous data for the concentrations of ozone, sulfur dioxide, and NO-NO_x were recorded by standard instruments. It is believed that the data from these instruments are reliable even in clouds. The absolute water content of the atmosphere in this study was well below that typically encountered in the summer in more humid environments. The sampling manifolds were designed so that the liquid water which accumulates in them would not drain into the instruments. Several data intercomparisons and external quality assurance audits of the trace gas measurements by the Queen Air in recent years have shown that the trace gas data are accurate.

Hollow tubes coated with tungstic acid were used to measure nitric acid and ammonia concentrations in November 1981. This measurement method has been evaluated in less polluted environments and found to be reliable (Braman et al. 1982, McClenny et al. 1982), but has not been evaluated for use in polluted urban clouds. The method can be calibrated in the laboratory by adding solutions containing ammonium or nitrate to the hollow tubes and drying them, so moisture alone does not cause interferences. The hollow tubes were followed by packed tubes, which contained a granular filling coated with tungstic acid. The packed tubes were used to measure the concentrations of particulate ammonium and nitrate. The data from the tungstic acid tubes are reported in Table B-3 in Appendix B.

7. SULFUR CHEMISTRY RESULTS

Significant new information on the chemistry of sulfur compounds in the atmosphere has been obtained in this study, and has been submitted for rapid publication (Richards et al. 1983c). These and other results observed for the chemistry of sulfur compounds are presented in this Chapter.

The experimental data on which this discussion is based are contained in the appendices, and are summarized in Table B-3 of Appendix B. Some interferences in these measurements are discussed in Section 6.2.3.

7.1 THE STABILIZATION OF SULFUR (IV) AGAINST OXIDATION BY H_2O_2

Table 7-1 shows the data from all cases in which measurements were made of both the concentration of sulfur (IV) and H_2O_2 in the collected cloud water. In all cases, measurable concentrations of both species were found. This result requires the modification of current theories for the formation of sulfate in the atmosphere, and is one of the more important findings of this study.

It is well known that sulfur (IV) and H_2O_2 react with each other very rapidly in laboratory solutions which do not contain the variety of species found in the Los Angeles atmosphere (Penkett et al. 1979, Martin and Damschen 1981, McArdle and Hoffmann 1983). This reaction is fast enough in laboratory systems that it is thought to be an important, if not the most important reaction causing the oxidation of sulfur dioxide in cloud water (Penkett et al. 1979). As an example, the rate data of Martin and Damschen (1981) predict that sulfur (IV) would have a lifetime of less than one second when the H_2O_2 concentration is greater than 40 μM, whereas the concentrations in Table 7-1 marked by a dagger were measured after the cloud water had been stored for over one hour. The data of this study clearly show that sulfur (IV) has been stabilized in the collected cloud water samples so it is not rapidly oxidized by H_2O_2. This finding raises questions about the importance of the reaction between H_2O_2 and sulfur (IV) for forming sulfate in the Los Angeles Basin.

It is interesting to note that H_2O_2 was found in the cloud water samples even when appreciable gas phase concentrations of sulfur dioxide were present. In the most extreme case, the H_2O_2 concentration in the cloud water was 9.4 μM when the ambient sulfur dioxide concentration was 58 ppb. Again, existing theory predicts that H_2O_2 in the cloud water droplets would react with gas phase SO_2 at a rate primarily controlled by the gas-to-liquid mass transfer rate (Schwartz and Freiberg 1981, Freiberg and Schwartz 1981), and that this rate is fast enough to consume the H_2O_2 in a few minutes (Jacob and Hoffmann 1982, 1983). These data strongly suggest that the overall process of the transfer of gas phase SO_2 to the liquid phase and its reaction with H_2O_2 proceeds much more slowly than predicted by current theory.

Table 7-1. Inhibition of the reaction of H_2O_2 with S (IV).

Date	Start Time	Location	Measured concentrations SO_2 ppb	S(IV) μM	H_2O_2 μM
24 Nov	0025	Seal Beach	16	129	-
	0047	Seal Beach	8	89	-
20 May	2235	off Long Beach	3	12	34
21 May	2257	Etiwanda	10	52	9.1
	2349	Fontana	48	183	2.8
22 May	0025	Fontana	58	365	9.4
	0102	Pomona-Corona	6	29	13
	0132	Pomona-Corona	4	33	2.8
	0206	Fontana	13	51	0.91
23 May	0134	ALBAS*	0	18	79
	0209	ALBAS	0	5	76
	0219	ALBAS	0	10†	88†
	0228	ALBAS	0	11	51

* Aircraft navigation point off Huntington Beach

† The aliquots to be analyzed for sulfur (IV) and hydrogen peroxide were separated at the same time more than one hour after collection.®

7.2 HIGH CONCENTRATIONS OF SULFUR (IV)

The S(IV) concentrations observed in the cloud water were much higher than expected. This result suggests that the inhibition of the reaction between gas phase SO_2 and dissolved H_2O_2 was not due to the inhibition of the mass transfer.

The expected concentrations of S(IV) were calculated using the Henry's Law and acid dissociation constants for sulfurous acid reported by Maahs (1982), the observed pH, and the observed gas phase concentration of SO_2 to calculate the concentrations of $SO_2 \cdot H_2O$ and HSO_3^-. The $SO_3^=$ concentrations were negligible, and no corrections for the effect of the ionic strength on activity were made. The observed S(IV) concentrations were divided by the expected concentrations, and the ratios appear in Table 7-2. In most cases, the observed S(IV) concentrations were hundreds of times the expected concentrations. Something draws large amounts of sulfur (IV) into the cloud water and stabilizes it against oxidation by H_2O_2.

7.3 ADDUCTS BETWEEN SULFUR (IV) AND CARBONYL COMPOUNDS

The known chemical reactions between sulfur (IV) in solution and carbonyl compounds can at least partially account for the above observations. The adduct between formaldehyde and sulfite is stable in solution in the presence of H_2O_2 (Kok 1983). Also, this adduct ties up the free sulfite in solution (Dasgupta et al. 1980) so that the partial pressure of SO_2 over the solution is reduced and additional SO_2 will dissolve. The data in Tables B-1 through B-3 show that formaldehyde was found in all cloud water samples, so it is expected that the adduct between sulfite and formaldehyde is present in these samples. Other carbonyl compounds (aldehydes and ketones) are known to be present in the Los Angeles atmosphere (Grosjean 1982), and are expected to contribute to these observations.

The adduct between sulfite and formaldehyde is called hydroxymethanesulfonic acid (HMSA), and is a dibasic acid. The monosodium salt of HMSA is a stable solid, and is commercially available. In solution, HMSA is a strong acid. At the pH of Los Angeles cloud water, the first proton would be dissociated and the second would not.

The fact that HMSA is a strong acid is important. If formaldehyde and other carbonyl compounds are present, it is possible for SO_2 to produce acidity in cloud water in the absence of any oxidation of sulfur (IV) to sulfur (VI).

The equilibrium constant for the reaction of formaldehyde and sulfite to form HMSA is known (Dasgupta et al. 1980). This makes it possible to see if the observations reported above can be accounted for by known chemical equilibria. Calculations did not lead to consistent results, and numerical results from them are not reported here. The calculations performed and the results from them can be summarized as follows: The measured temperature and pH data were used to estimate the dissociation constant of HMSA from the data reported by Dasgupta et al. (1980). Then the measured sulfur (IV) and formaldehyde concentrations were used to estimate the fraction of the sulfur (IV) in the form of HMSA under the assumption that no other carbonyl compounds

Table 7-2. Comparison of measured sulfur (IV) concentrations with values calculated from the SO_2 concentration.

Date	Start Time	Location	Measured concentrations SO_2 ppb	pH	S(IV) µM	Measured S(IV) / Calc. S(IV)
24 Nov	0025	Seal Beach	16	2.98	129	230
	0047	Seal Beach	8	3.02	89	280
20 May	2235	off Long Beach	3	2.99	12	120
21 May	2257	Etiwanda	10	2.40	52	520
	2349	Fontana	48	2.72	183	190
22 May	0025	Fontana	58	3.39	365	73
	0102	Pomona-Corona	6	2.56	29	370
	0132	Pomona-Corona	4	2.65	33	500
	0206	Fontana	13	2.69	51	210

were present. Typically, about half or less of the sulfur (IV) was in the adduct. Thus, the measured formaldehyde alone cannot account for the data.

The data of Grosjean (1982) show that a number of other carbonyl compounds are present in the Los Angeles atmosphere, and that the formaldehyde concentration is typically something like one-quarter the total carbonyl compound concentration. To explore a limiting case, the above calculations were repeated with formaldehyde concentrations ten times the measured concentrations. These calculations typically gave the result that about 10% of the sulfur (IV) was free, and in most cases the fraction of the sulfur (IV) that was free fell in the range between 2% and 20%. Thus, these results calculated using ten times the measured formaldehyde concentrations still show too much free sulfur (IV) to account for the inhibition of the reaction between sulfur (IV) and H_2O_2 and the high sulfur (IV) concentrations reported in Table 7-2.

The discussion in Section 6.2.3 makes it clear that there are significant uncertainties in the observed sulfur (IV) and formaldehyde concentrations. Because of these uncertainties, these semi-quantitative calculations were not pursued further. Understanding the chemistry of sulfur (IV) and carbonyl compounds in the Los Angeles atmosphere requires both additional field data on the concentrations of these species and additional laboratory data on the kinetics and equilibria of reactions among them.

7.4 THE PERSISTENCE OF SULFUR (IV) AFTER THE CLOUDS EVAPORATE

The observation in this study of high concentrations of sulfur (IV) in Los Angeles cloud water provides a possible explanation of earlier puzzling observations. It was noted previously (Richards et al., 1977) during attempts to distinguish sulfuric acid from other sulfates in the Los Angeles basin that about 10% of the aerosol sulfur could be volatilized as if it were sulfuric acid, but was not sulfuric acid because it would only partially lose this volatility on exposure to ammonia. The observation of a volatile component in the sulfur aerosol in Los Angeles basin appears to be the rule rather than the exception (Richards et al., 1978a, 1978b, 1979; Fig. 11 in Kittelson et al., 1978). These observations can be explained if some of the S(IV) observed in cloud water in this study persists in the aerosol when the clouds evaporate. S(IV) has previously been detected in the aerosol in Los Angeles (Farber et al., 1982)

The data of this study suggest that sulfur (IV) is important in the Los Angeles sulfur budget. On the average, 14% of the sulfate determined by ion chromatography in the cloud water was S(IV) when the samples were collected, and this ratio ranged from 3% to 47%.

Elevated concentrations of formaldehyde have been seen in the ambient aerosol in Germany (Klippel and Warneck, 1980), and the possible contribution of HMSA to these observations has been suggested (Klippel and Warneck, 1980; Dasgupta, 1981; Dasgupta et al., 1982). Since pure HMSA is unstable and dissociates to HCHO and SO_2, some of this adduct may return to the gas phase when the clouds evaporate. The monosodium salt of HMSA is stable and is a commercial product, so partial neutralization of the HMSA should increase its stability in the aerosol. Laboratory studies of the properties of the ammonium salt of HMSA would be useful in understanding the fate of HMSA.

The possible presence of sulfur (IV) in the Los Angeles aerosol is not inconsistent with prior data showing the correspondence between aerosol sulfur measured by x-ray fluorescence and sulfate measured by water extraction and wet chemical analytical methods. Most wet analytical methods oxidize any sulfur (IV) present so this component of the aerosol is reported as sulfate.

7.5 SULFATE IN PLUMES

The highest observed sulfate concentrations were associated with plumes. This was especially true in the flight in the inland basin as shown in the data in Table 7-3. The first two rows show data from two sampling orbits in plumes. Sulfur dioxide and NO_x gas concentrations were elevated, and the ozone concentration was depressed by the NO emissions. The third row shows data from an orbit in Fontana in which the plume concentrations were much smaller, and the ozone concentration was close to that generally found in the inland basin that night. All other orbits in the inland basin that night were in air with lower concentrations of sulfur dioxide. The mean value of all data collected in the inland basin the night of 21-22 May, except for the in-plume data in the first two lines of Table 7-3, is shown in the fourth line of the table.

The total sulfate concentrations in the plumes are two to three times the concentrations out of the plumes. The available data do not make it possible to say how much of this plume excess sulfate is directly emitted primary sulfate, and how much is secondary sulfate rapidly formed in the plume. However, two-thirds of the increased sulfate in the plumes is in particles small enough to pass the 2 μm cut cyclone and be collected on the Teflon filters, and only one-third of it is in cloud droplets large enough to be collected by the cloud water collector. Therefore, if most of the plume excess sulfate is secondary, these data show that the majority of it must be formed in particles smaller than about 2 μm.

The fraction of the plume excess sulfur which is sulfate suggests that some of the plume excess sulfate was formed in the atmosphere. The mean sulfate concentration in the plume samples was 82 $\mu g/m^3$, which is 51 $\mu g/m^3$ greater than out of the plume. The sulfur dioxide concentrations in the plume were 45 ppb (175 $\mu g/m^3$ as sulfate) greater than out of the plume. Thus, 23% of the plume excess sulfur was sulfate. The lower sulfate concentration in the plume samples was 57 $\mu g/m^3$, which is 26 $\mu g/m^3$ greater than out of the plume. This value corresponds to 13% of the plume excess sulfur being sulfate. Not many sources emit such a large fraction of the sulfur as sulfate. Thus, rapid sulfate formation in the plumes is a likely explanation of the data.

The nitrate data in and out of plumes show less variability, and are discussed in Chapter 8.

7.6 MECHANISMS FOR THE FORMATION OF SULFATE

The data in this report clearly show that adducts between carbonyl compounds and sulfite are significant in the sulfur budget of the Los Angeles

Table 7-3. Concentrations in and out of plumes in the eastern Los Angeles Basin. Tape 302, 21-22 May 1982.

Pass	Location	Trace gas concentrations			Sulfate concentrations			Total nitrate conc.
		SO_2	NO_x	O_3	Filter	Cloud water	Total	
		ppb	ppb	ppb	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$
In concentrated plume								
3	Fontana	48	73	27	32	25	57	94
5	Fontana	58	78	28	68	38	106	94
Not in concentrated plume								
11	Fontana	13	37	60	15	28	43	115
Mean for passes 1, 7, 9, and 11		8	37	66	15	16	31	88

basin. Additional laboratory and field data on these compounds must be obtained before further modeling of their roles in the formation of sulfate in the Los Angeles Basin can proceed.

The role of H_2O_2 is now less certain than it was before this study. The finding that the reaction between H_2O_2 and sulfur (IV) in solution is strongly inhibited raises questions about the importance of H_2O_2 in the formation of sulfate. Finding H_2O_2 in cloud water collected in the presence of appreciable concentrations of sulfur dioxide adds to these questions. Again, additional experimental data are required before these questions can be resolved and the importance of H_2O_2 in sulfate formation in the Los Angeles Basin estimated.

8. NITROGEN CHEMISTRY RESULTS

Nitrate is the dominant anion in the cloud water. In many samples, nitrate formation must be a significant source of acidity because the hydrogen ion concentration is larger than the combined concentration of all anions other than nitrate. Therefore, nitrogen chemistry makes a significant contribution to the chemical properties of clouds in the Los Angeles Basin.

There are known chemical pathways by which the nitrate found in the cloud water could be formed. This chapter contains a discussion of the nitrogen chemistry data and its uncertainties, and compares the experimental results with possible nitrate formation mechanisms.

8.1 UNCERTAINTIES IN THE ANALYTICAL RESULTS

There are significant uncertainties in the relationship between the amounts of nitrate collected in the cloud water and filter samples and the concentrations of these species in the atmosphere. These uncertainties arise primarily from the fact that the art of airborne sampling of nitrogen species in clouds is not well developed. Improved sampling methods are being developed, but in the meantime, it is necessary to work with the best methods available and to be careful in the interpretation of the data.

Some of the sources of uncertainty in the data were discussed in Section 6. The following points should be kept in mind when interpreting the data.

1. The cloud water collector has about half the collection efficiency expected from theoretical calculations, and experimental results discussed in Section 6.1.1 suggest that some water is lost through evaporation. Nitric acid is volatile, so if evaporation does occur during the collection of the cloud water, some evaporation of nitric acid may also occur.

2. The filter samples are collected behind a cyclone and wet sampling lines. Nitric acid can be adsorbed in or desorbed from the water on the walls of the filter sampling system, causing the amounts of nitric acid collected on the filters to be either too large or too small.

3. The discussion in Section 6.3 of the data in Table 6-4 presents good evidence that nitric acid evaporates from the Teflon filters during sampling, and is collected on the backup Nylon filters. Thus, much of the nitrate collected on the backup Nylon filters may have been in particles rather than in the gas phase in the atmosphere.

4. Nitric acid may evaporate from the Teflon filters after the end of the sampling, causing low results.

5. Ammonia may be adsorbed by the (acid) aerosol deposit on the Teflon filter during storage before analysis.

Tests of the efficiency of collection of nitric acid by Nylon filters show that they are close to 100% efficient and will hold appreciably larger amounts of nitric acid than collected in these experiments (Appel et al. 1981). Therefore, incomplete collection of nitric acid by the Nylon filters is believed not to be a source of error.

8.2 NIGHTTIME NITRATE FORMATION BY OZONE AND NITROGEN DIOXIDE

One of the reasons for sampling at night in this study was to see if the rapid formation of nitric acid in clouds from ozone and nitrogen dioxide could be observed. The possible importance of this reaction pathway has been suggested by Heikes and Thompson (1981) and by Richards (1983a). A brief summary follows.

The following elementary reaction steps participate in the chemistry of the nitrogen oxides at night:

	Rate constant k or equilibrium constant 0 °C	25 °C	Units
1. $NO + O_3 = NO_2 + O_2$	$1.8\ 10^{-2}$	$2.4\ 10^{-2}$	$(ppb\ min)^{-1}$
2. $NO_2 + O_3 = NO_3 + O_2$	$2.6\ 10^{-5}$	$5.0\ 10^{-5}$	$(ppb\ min)^{-1}$
3. $NO_3 + NO_2 + M = N_2O_5 + M$	5.6	3.9	$(ppb\ min)^{-1}$
4. $N_2O_5 + M = NO_3 + NO_2 + M$	0.29	6.9	min^{-1}
Equilibrium constant	0.052	1.8	ppb
5. $N_2O_5 + H_2O = 2\ HNO_3$		$<1.9\ 10^{-8}$	$(ppb\ min)^{-1}$
6. $N_2O_5 + H_2O = 2\ HNO_3$ (surface)	-	-	
7. $NO_2 + NO_3 = NO_2 + NO + O_2$	$6.5\ 10^{-4}$	$8.4\ 10^{-4}$	$(ppb\ min)^{-1}$
8. $2\ NO_3 = 2\ NO_2 + O_2$	$1.7\ 10^{-4}$	$3.4\ 10^{-4}$	$(ppb\ min)^{-1}$
9. $NO_3 + NO = 2\ NO_2$	30.	28.	$(ppb\ min)^{-1}$
10. $NH_4NO_3 = HNO_3 + NH_3$	-	-	
Equilibrium constant	0.09	50.	ppb^2

Except for reactions 1, 5, and 10, the above reaction rate constants and equilibrium constants were obtained from Graham and Johnston (1978). They report that reactions 1 through 9 are capable of explaining the laboratory reactions of the NO_x-O_3 system in the dark. The rate constant for reaction 1

was obtained from Hampson and Garvin (1978), for reaction 5 from Morris and Niki (1973), and the equilibrium constant for reaction 10 from Stelson, Friedlander, and Seinfeld (1979).

One important property of the above reactions is that N_2O_5 and NO_3 are in rapid equilibrium with each other. The lifetime of N_2O_5 with respect to thermal dissociation (reaction 4) is only 3 min at 0 °C, and is shorter at higher temperatures. If the NO_2 concentration is greater than 1 ppb, the lifetime of a NO_3 radical with respect to reaction 3 is less than one minute. Because of this rapid exchange between NO_3 and N_2O_5, these species can usually be considered together, and are referred to as NO_3-N_2O_5 in the following text.

Reaction 1 in the forward direction is fast and at night consumes essentially all of either the NO or the ozone. Near the surface in urban areas, NO emissions are great enough to consume the ozone at night. The NO also destroys NO_3 by reaction 9, and hence N_2O_5 by reactions 4 and 9, so that the concentration of all these species is small in the presence of NO. This is the usual nighttime condition on the ground in urban areas. However, ozone is known to persist aloft at night (see, for example, Blumenthal et al., 1980; Swinford, 1980), with the result that the ambient NO concentration aloft becomes very small when the sun goes down. This permits reaction steps 2 through 8 to build up significant concentrations of NO_3, N_2O_5, and HNO_3.

These reactions do not build up significant concentrations of NO_3, N_2O_5, and HNO_3 during the daytime for two reasons: First, the photolysis of NO_2 causes a small concentration of NO to always be present, and this NO reacts with NO_3 very rapidly and converts it back to NO_2. Second, NO_3 is rapidly photolyzed; it has a lifetime of only 7 s when the sun is high in the sky. Thus, it must be dark and ozone must be present for significant concentrations of NO_3-N_2O_5 to be formed.

The application of the above rate constants to ambient data indicates that NO_2 is rapidly oxidized at night to NO_3-N_2O_5 whenever ozone is present. This process occurs in the stratosphere, where it is estimated that 25% of the NO_2 is converted to N_2O_5 each night, then converted back to NO_2 in the daytime (Connell and Johnston, 1979). Direct determinations of the importance of these reactions at the surface have been made by long-path optical absorption measurements of NO_3 concentrations. Data have been obtained at night in urban areas by Platt, Perner, Winer, Harris, and Pitts (1980) and in relatively clean areas by Noxon, Norton, and Marovich (1980) and by Winer et al. (1983). These studies confirm that the above reactions do take place. The concentrations of NO_3 observed in these studies were smaller than predicted by the above mechanism and rate constants. The most likely explanation is that some atmospheric sink exists for NO_3-N_2O_5 other than the ones listed above.

The data of Winer et al. (1983) taken in the desert areas of Southern California show that the nighttime concentrations of NO_3 are much smaller when the humidity is above about 50%. These data imply that NO_3 is rapidly removed from the atmosphere at the higher humidities. At present, there is no proof this rapid removal is due to the rapid hydrolysis of NO_3-N_2O_5 to nitric acid.

There is even uncertainty about the stoichiometery of the conversion of NO_3 to nitric acid. It is possible for one NO_3 radical to produce two molecules of nitric acid if the NO_3 reacts with NO_2 to form N_2O_5, which is

then hydrolyzed. In clouds, NO_3 can react directly with cloud droplets to produce only one molecule of nitric acid. In urban areas, it appears that the atmosphere contains other sinks for NO_3 (Platt et al. 1980), so that NO_3 radicals may be converted into species other than nitric acid.

One thing that can be calculated is the relative probability that an NO_3 radical formed in a cloud will react with a cloud droplet to form nitric acid or with an NO_2 molecule to form N_2O_5. Chameides and Davis (1982) calculated radical lifetimes in clouds, and obtained numbers of the order of 100 s. For NO_3 to have a lifetime this long with respect to the reaction with NO_2, the NO_2 concentration must be below about 0.1 ppb. Thus, NO_3 formed in clouds in the Los Angeles Basin will react with NO_2 rapidly enough that the NO_3 and N_2O_5 concentrations will be approximately equal to their equilibrium values. NO_3 and N_2O_5 will both be present in clouds, and each will combine with cloud droplets to produce nitric acid.

A comparison of a rough estimate of the rate at which nitric acid could be formed via NO_3 in clouds at night with the experimental data obtained in this study appears in Table 8-1. The first column of the table gives the rate at which NO_3 is formed from the reaction between ozone and NO_2 at the average ozone and NO_2 concentrations observed in each pass. The second column of the table gives the rate at which nitric acid would be formed if each NO_3 is converted into one nitric acid molecule. The third column in the table gives the observed total nitrate concentration. For the November flights, the total nitrate concentrations were determined from the hollow and packed tungstic acid tubes, which were not behind a cyclone to remove cloud water. Tungstic acid tube data were not available for all November sampling flights. For the May flights, the total nitrate concentrations were determined from the nitrate collected in the cloud water, on the Teflon filters, and the backup Nylon filters. There are many pathways by which this nitrate is formed, including:

1. Photochemical reactions during the prior day,

2. Hydrolysis of PAN,

3. The reaction of NO_2 with ozone at night in clouds to produce NO_3.

The fourth column in the table shows how long it would take the third pathway, nitric acid formation via NO_3, acting alone to produce all of the observed nitrate. The numbers in this column are based on the assumption that each NO_3 radical produces one molecule of nitric acid.

The results in Table 8-1 are consistent with the possibility that nitric acid is rapidly formed in clouds at night from NO_2 and ozone, but do not prove that this is the case. In May, this reaction alone could account for the observed nitrate concentrations because the sampling flights were made about six hours after dark. In fact, it is believed that each of the three mechanisms listed above contribute to the formation of nitrate in clouds.

The data of Grosjean (1983) suggest that nitrate formed during the prior day's photochemical reactions are not the dominant source of the high nitrate concentrations observed in the eastern portion of the Basin the night of 21-22 May. He measured gas and particulate nitrate concentrations in Claremont on two days when the ozone concentration exceeded 400 ppb, five additional days

Table 8-1. Calculated rate of HNO_3 formation in clouds from NO_2 and O_3.

Date	Tape	Pass	Start Time	Location	NO_3 formation rate	Nitric acid form. rate	Total nitrate conc.	Ratio conc./rate
					ppb/h	$\mu g/m^3 \cdot h$	$\mu g/m^3$	h
23 Nov	296	1	2224	depart LAX	0.14	0.37		
		2	2244	off Malibu	0.73	1.91	19.06	10.00
		4	2328	off El Segundo	0.07	0.19	6.04	31.43
		5	2353	El Seg. to S.Bch	0.20	0.53		
24 Nov		6	0025	Seal Beach	1.50	3.90	3.45	0.88
		7	0047	Seal Beach	2.23	5.79	3.45	0.60
		8	0122	approach LAX	0.76	1.97		
24 Nov	297	2	0732	off Los Alamitos	0.70	1.83	2.11	1.15
		3	0807	off Los Alamitos	0.79	2.06	2.11	1.02
		4	0834	ALBAS*	0.83	2.16	3.80	1.76
		5	0915	ALBAS	0.79	2.04	3.80	1.86
		6	0957	PEDRO**	0.58	1.51		
		November average			0.78	2.02	5.48	6.09
20 May	301	2	2235	off Long Beach	1.21	3.15	12.59	4.00
21 May	302	1	2257	Etiwanda	5.61	14.57	76.58	5.25
		3	2349	Fontana	4.16	10.81	93.98	8.69
22 May		5	0025	Fontana	4.56	11.85	94.35	7.96
		7	0102	Pomona-Corona	4.49	11.67	92.11	7.89
		9	0132	Pomona-Corona	5.54	14.41	68.86	4.78
		11	0206	Fontana	4.88	12.70	115.22	9.07
23 May	303	5	0134	ALBAS	1.11	2.88	16.28	5.65
		7	0209	ALBAS	0.72	1.87	15.85	8.46
		8	0219	ALBAS	0.72	1.87	21.45	11.45
		9	0228	ALBAS	0.69	1.80	25.10	13.93
		May average			3.06	7.96	57.49	7.92
		Grand average			1.87	4.86	35.59	7.15

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

when ozone exceeded 300 ppb, and additional days with lower ozone maxima. The highest total nitrate concentrations reported by Grosjean were observed at night, and were as large as 47 $\mu g/m^3$. The highest daytime total nitrate concentration was 39 $\mu g/m^3$, and most afternoons the total nitrate concentration ranged between 20 and 35 $\mu g/m^3$. Thus, total nitrate concentrations observed during days with very strong photochemcial activity were about one-third those observed in the clouds the night of 21-22 May.

The 23 November sampling off El Segundo beginning at 23:28 PST was in clean air with low ozone concentrations (20 ppb) and almost no NO_2. Therefore, NO_3 was formed very slowly in this case, and it would take a long time for this mechanism to produce the observed nitrate concentrations. The sampling over Seal Beach just after midnight on 24 November was in fresh plumes, so that little time was available for the NO_2 to react with ozone.

8.3 NITRATE FORMATION BY PAN HYDROLYSIS

Laboratory experiments have been performed by Holdren et al. (1970) to measure the rate of hydrolysis of peroxyacetyl nitrate (PAN) dissolved in distilled water, rain water, and distilled water whose pH was adjusted to 4.0 with sulfuric acid. It was found that in this pH range, the rate of hydrolysis was independent of pH, and nitrate was a hydrolysis product. For the temperature range of the Los Angeles cloud sampling reported here, the lifetime of PAN was 60 to 90 min in the laboratory experiments. PAN is known to be present in the Los Angeles atmosphere, and its hydrolysis could contribute to the nitrate concentrations reported above. (We are indebted to J. Bottenheim for reminding us of this.) PAN measurements were not made during this study, so the contribution of PAN hydrolysis to the observed nitrate concentrations is not known.

It would not be difficult to obtain information on the relative importance of the reaction pathways listed above in the formation of nitrate in clouds at night in the Los Angeles Basin. The onset of cloud formation is reasonably predictable, so that airborne measurements can be made just before and during cloud formation. The addition of PAN and total nitrate measurements to those made in this program would provide enough information to determine the role of each of the above reaction pathways in forming nitrate.

9. IMPLICATIONS FOR AEROSOL FORMATION

The results in this report can be used to derive information on the origins and properties of visibility reducing aerosol in the Los Angeles basin. The airborne measurements include the determination of the cloud droplet size distribution and the chemical composition of the collected cloud water. This information can be used to make a rough estimate of the size distribution and composition of the aerosol remaining after the clouds in which these samples were collected evaporate.

Several assumptions are required for this rough calculation. They are listed here in decreasing order of their estimated importance. It is assumed that:

1. All cloud droplets have the composition equal to the composition of the collected water. (In fact, it is expected that the smaller droplets are more concentrated. See for example, Levine and Schwartz (1982).)

2. All species have been determined, and the dry aerosol has a density of 1 g/cm^3. This assumption contains compensating errors, which are discussed below.

3. Neither nitric nor hydrochloric acid remain in the dry aerosol.

These assumptions are admittedly a source of some uncertainty. However, the cube root in the conversion of volumes to diameters makes it possible to obtain reasonably good estimates of the aerosol particle diameter from somewhat uncertain estimates of the aerosol particle mass. An error of a factor of two in the cloud water solute concentration or the density of the aerosol results in only a 26% error in the aerosol particle diameter.

The assumption of unit density for the dry aerosol is intended to partially compensate for the fact that not all components of the cloud water were determined. For example, it is known that the cloud water contains significant amounts of organic species in addition to formaldehyde (Pankow et al. 1982). Depending on the relative humidity, the "dry" aerosol also includes significant amounts of water. If the water, organic materials, and other substances not included in the analytical scheme were to make the actual mass of each aerosol particle 80% larger than in these calculations, and the aerosol density was 1.8 g/cm^3 rather than 1 g/cm^3, the final results would be exactly the same as calculated here. Since the actual aerosol density is certainly greater than 1 g/cm^3, the assumption of unit density for the dry aerosol partially offsets the neglect of the undetermined species.

The cloud water contains large concentrations of nitric acid, and most of this will evaporate when the clouds evaporate. The water also contains chloride, which will volatilize as hydrochloric acid. For purposes of this

approximate calculation, it is assumed that nitric acid and hydrochloric acid evaporate in equal proportions. Thus, if 60% of the nitrate is lost through evaporation, 60% of the chloride will also be lost. Furthermore, it is assumed that this evaporation will continue until either all the hydrogen ions are gone or until all the nitrate and chloride are gone. This is equivalent to assuming that neither nitric acid nor hydrochloric acid remains in the aerosol after the clouds evaporate. In all but three cases, nitrate plus chloride were in excess of the hydrogen ions, so that some nitrate and chloride usually remained in the aerosol.

The first step in the calculation of the composition and the size distribution of the aerosol remaining after the clouds evaporate is the determination of the solids content of the cloud water. These data are shown in the first column of Table 9-1. The percentages of these weights which are sulfate and nitrate are shown in the next two columns for later comparison with the percentages in the dry aerosol. The next column gives the fraction of the nitrate and chloride lost when the cloud evaporates. This fraction is equal to ratio (equivalents hydrogen ion)/(equivalents nitrate plus chloride). In the three cases where this ratio was greater than unity, it was set equal to one. The weight of nitric acid and hydrochloric acid lost during the evaporation of the cloud is then subtracted from the total solute concentration to obtain the total non-volatile solute concentration in the fifth column. The percentage of the solute lost is also reported in the next column. On the average, about one-third of the solutes included in the analytical scheme evaporate when the cloud evaporates.

It is interesting to look at the change in composition of the solutes during the evaporation process. In the cloud water, an average of 45% of the solute is nitrate and 20% is sulfate. After evaporation of the cloud, these percentages change to 24% nitrate and 33% sulfate. Ammonium nitrate is known to be volatile (Stelson et al. 1979), and evaporation of this species as the ambient temperature increases will reduce the aerosol nitrate concentrations to lower levels than reported in these calculations.

The right hand column of Table 9-1 gives the ratio of the diameter of the dry aerosol particle to the cloud droplet from which it was formed. Because the aerosol is assumed to have unit density, this ratio is the cube root of the weight fraction of non-volatile solids in the cloud water. These ratios can be used to convert cloud drop size distributions into aerosol size distributions, and examples are given in Figure 9-1. The average particle size ratio is about 0.05 which corresponds to a 10 μm cloud droplet yielding an 0.5 μm aerosol particle.

These results are significant for several reasons. It has long been known that aerosol in the 0.5 to 1 μm size range cannot be grown in photochemical smog chambers and that theoretical calculations strongly suggest that aerosol in this size range will not form in typical photochemical smog conditions (see, for example, McMurry 1977, McMurry and Friedlander 1979). On the other hand, sulfate is commonly found in the 0.5 to 1 μm size range in the Los Angles Basin (see, for example, Hering and Friedlander 1982). It has been speculated that the larger sulfate aerosol particles are formed in or processed by clouds and fog, but these data provide direct evidence in support of that idea. In addition, the high sulfate concentrations observed in the cloud water remove the concern expressed by Hering and Friedlander (1982) that

Table 9-1. Particle composition change during cloud evaporation.

Date	Tape	Pass	Start Time	Location	Cloud water: Total solute conc. mg/l	Cloud water: Wt. % NO_3^-	Cloud water: Wt. % $SO_4^=$	Fraction NO_3^- & Cl^- lost	Non-volatile solutes: Total conc. mg/l	Non-volatile solutes: % of solutes lost	Non-volatile solutes: Wt. % NO_3^-	Non-volatile solutes: Wt. % $SO_4^=$	Diameter ratio
23 Nov	296	1	2224	depart LAX	100	26	17	0.24	88	13	23	20	0.046
		2	2244	off Malibu	80	45	13	0.46	57	29	34	18	0.043
		4	2328	off El Segundo	32	28	17	0.42	24	23	21	22	0.032
		5	2353	El Seg. to S.Bch	117	55	16	0.68	66	44	32	29	0.049
24 Nov		6	0025	Seal Beach	159	54	16	0.62	98	38	33	27	0.054
		7	0047	Seal Beach	121	57	16	0.69	66	46	32	29	0.049
		8	0122	approach LAX	42	26	21	0.44	32	23	19	27	0.035
24 Nov	297	2	0732	off Los Alamitos	90	53	12	0.58	54	40	37	21	0.045
		3	0807	off Los Alamitos	22	41	26	1.00	11	48	0	51	0.028
		4	0834	ALBAS*	57	11	10	1.00	44	22	0	13	0.038
		5	0915	ALBAS	24	40	22	0.97	12	49	2	44	0.029
		6	0957	PEDRO**	202	39	8	0.01	201	1	39	8	0.059
		November average			87	40	16	0.59	63	31	23	26	0.042
20 May	301	2	2235	off Long Beach	90	47	22	1.00	37	59	0	54	0.045
21 May	302	1	2257	Etiwanda	429	65	19	0.84	183	57	24	45	0.075
		3	2349	Fontana	568	50	24	0.38	453	20	40	30	0.083
22 May		5	0025	Fontana	469	37	27	0.13	444	5	34	29	0.078
		7	0102	Pomona-Corona	353	67	18	0.70	182	49	39	35	0.071
	"	9	0132	Pomona-Corona	339	65	19	0.61	200	41	43	31	0.070
		11	0206	Fontana	357	64	19	0.54	230	36	45	30	0.071
23 May	303	5	0134	ALBAS	149	39	29	0.76	97	35	15	45	0.053
		7	0209	ALBAS	54	40	27	0.97	30	45	2	49	0.038
		8	0219	ALBAS	66	42	24	0.87	38	42	9	41	0.040
		9	0228	ALBAS	39	39	28	0.84	24	38	10	45	0.034
		May average			265	51	23	0.69	174	39	24	39	0.060
		Grand average			172	45	20	0.64	116	35	23	32	0.051

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

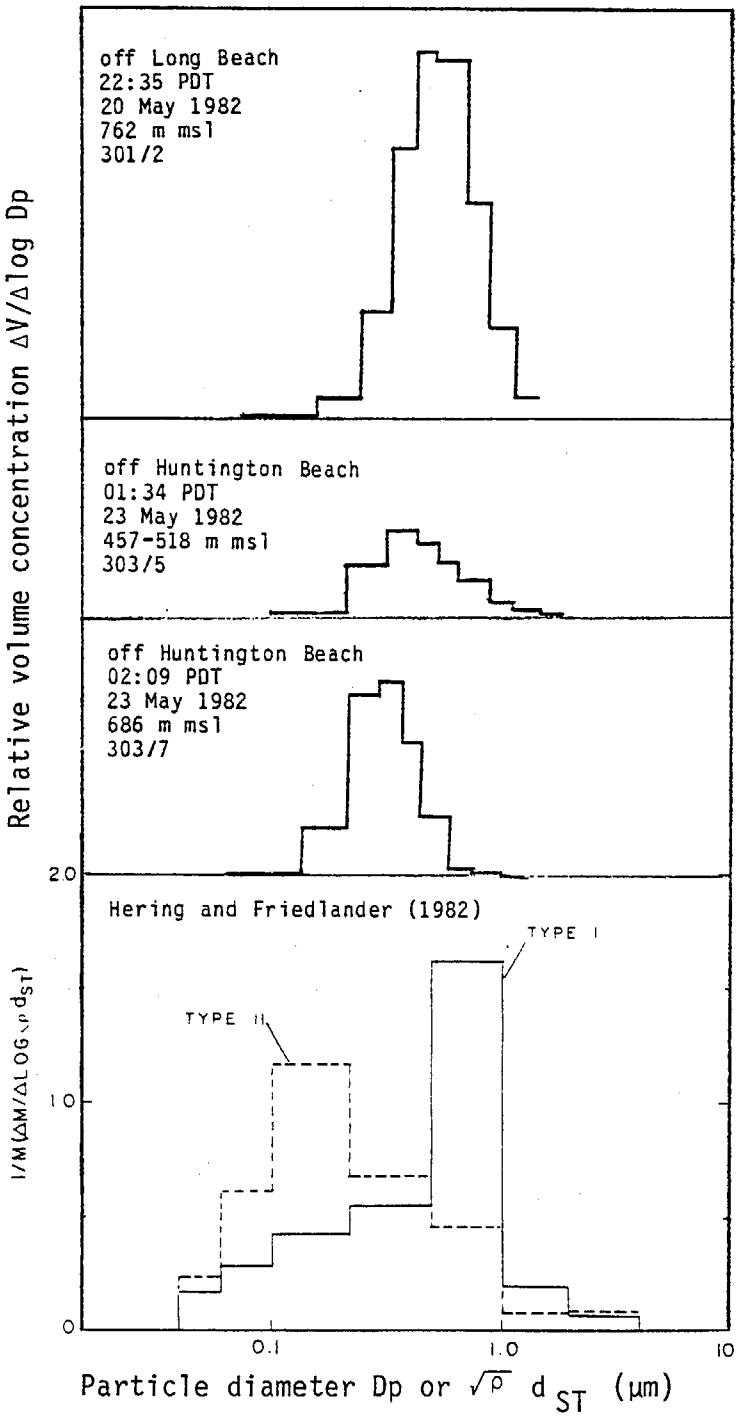

Figure 9-1. Comparison of calculated aerosol particle size distributions (top three curves) with experimentally measured average size distributions (bottom pair of curves).

the number concentration of droplets in clouds and fogs may not be high enough to account for the observed sulfate concentrations.

The data are of further significance because aerosol particles near 0.5 μm in size are more effective on a mass basis in causing haze than are the smaller particles which can be grown in photochemical smog. Thus, sulfate formed in or processed by fogs and clouds is more effective in causing haze than the same amount of sulfate formed purely photochemically. If particles in the 0.5 to 1 μm size range formed in clouds or fog are present in the atmosphere, then photochemically formed small particles can coagulate with them and add to the concentration of these large particles.

Additional data for the composition of the aerosol formed when the clouds evaporate are reported in Table 9-2. Because only the species included in the analytical scheme were included in the calculation, these results should be used with caution. The omission of all carbon species except formaldehyde in these data is expected to be a significant source of error. Formaldehyde is included in this table of non-volatile species to partially offset the omission of the other organic species. If all species in the cloud water had been determined, the addition of their concentrations to this calculation would equally decrease all composition percentages, so the species reported in Table 9-2 would remain in the same proportion to each other.

The approximate calculations in this chapter show that aerosol formed in clouds and fog can account for the relatively large particles observed in Los Angeles aerosol. The large particles are of importance because they are more effective at scattering light and causing haze than are the smaller, photochemically-formed aerosol particles.

Table 9-2. Calculated aerosol composition.

Date	Tape	Pass	Start Time	Location	Percent composition of the non-volatile solids								
					NO_3^-	$SO_4^=$	$SO_3^=$	NH_4^+	Na^+	Cl^-	Ca^{++}	Fe	HCHO
23 Nov	296	1	2224	depart LAX	23	20	1.92	2.59	13.13	28.54	7.56	0.00	0.00
		2	2244	off Malibu	34	18	2.58	6.05	16.66	22.99	1.65	0.33	0.95
		4	2328	off El Segundo	21	22	2.64	2.54	20.41	35.01	1.34	0.06	0.55
		5	2353	El Seg. to S.Bch	32	29	4.50	7.88	8.67	14.90	1.11	0.17	1.40
24 Nov		6	0025	Seal Beach	33	27	3.63	8.75	11.21	10.71	0.77	0.17	1.59
		7	0047	Seal Beach	32	29	5.41	9.63	7.09	14.45	0.77	0.31	1.97
		8	0122	approach LAX	19	27	4.60	6.65	11.96	32.63	1.39	0.00	0.00
24 Nov	297	2	0732	off Los Alamitos	37	21	3.64	12.33	12.22	25.25	1.90	0.00	0.00
		3	0807	off Los Alamitos	0	51	7.48	11.69	5.16	13.27	1.07	0.41	3.59
		4	0834	ALBAS*	0	13	4.80	28.98	37.60	14.23	4.57	2.85	0.00
		5	0915	ALBAS	2	44	1.61	13.63	13.34	18.30	1.32	0.42	3.29
		6	0957	PEDRO**	39	8	8.39	32.05	2.92	11.51	0.00	0.10	0.23
		November average			23	26	4.27	11.90	13.36	20.15	1.95	0.40	1.13
20 May	301	2	2235	off Long Beach	0	54	5.41	8.71	16.54	26.98	2.13	1.62	2.13
21 May	302	1	2257	Etiwanda	24	45	4.27	11.57	3.69	3.77	2.66	2.91	1.85
		3	2349	Fontana	40	30	1.79	10.51	1.34	3.58	5.72	2.95	0.94
22 May		5	0025	Fontana	34	29	1.92	13.37	0.98	2.92	9.44	0.63	0.47
		7	0102	Pomona-Corona	39	35	3.58	12.83	1.49	2.17	1.42	2.99	1.89
		9	0132	Pomona-Corona	43	31	3.26	12.95	1.71	1.97	0.98	2.28	1.62
		11	0206	Fontana	45	30	2.83	14.08	0.98	1.71	1.81	1.09	1.56
23 May	303	5	0134	ALBAS	15	45	3.05	8.84	10.67	8.31	4.06	3.59	1.04
		7	0209	ALBAS	2	49	5.76	14.16	9.81	9.11	2.94	2.37	2.27
		8	0219	ALBAS	9	41	4.39	10.45	10.48	8.60	3.37	5.73	2.19
		9	0228	ALBAS	10	45	7.07	14.14	6.28	9.09	1.74	2.67	1.43
		May average			24	39	3.94	11.96	5.82	7.11	3.30	2.62	1.58
		Grand average			23	32	4.11	11.93	9.75	13.91	2.60	1.46	1.35

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

10. LIST OF PUBLICATIONS

The following publications and meeting presentations have been prepared during the work under this contract and are included in this section.

Richards, L. W., J. A. Anderson, D. L. Blumenthal, J. A. McDonald, G. L. Kok, and A. L. Lazrus, Hydrogen Peroxide and Sulfur (IV) in Los Angeles Cloud Water. Atmos. Environ. 17, 911-914 (1983).

Richards, L. W., D. L. Blumenthal, J. A. Anderson, and J. A. McDonald, Sulfate and Nitrate in Los Angeles Cloud Water and Aerosol. Presented at the 185th National Meeting of the American Chemical Society, Seattle, Washington, March, 1983.

Also, a brief post deadline presentation of the work in the Preliminary Communication was made to the Fourth International Conference on Precipitation Scavenging, Dry Deposition, and Resuspension, Santa Monica, CA, 28 November - 3 December, 1982.

An article with the tentative title, Chemical Measurements in Los Angeles Clouds, is being prepared for submission to a journal such as Atmospheric Environment.

Atmospheric Environment 17, 911-914 (1983).

Preliminary Communication

HYDROGEN PEROXIDE AND SULFUR (IV) IN LOS ANGELES CLOUD WATER

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Abstract—Airborne collection and chemical analysis of cloud water samples in the Los Angeles Basin showed that the reaction between hydrogen peroxide and sulfur (IV) was inhibited in the collected samples, so these species reacted to form sulfate more slowly in these samples than would be expected from published laboratory data. The cloud water contained formaldehyde, which can react with sulfite to form hydroxymethanesulfonic acid (HMSA). This adduct contributed to measured S(IV) concentrations in the cloud water, which were more than 100 times greater than those calculated from ambient sulfur dioxide concentrations, water pH, and the Henry's Law and acid-base equilibrium constants. The average S(IV) concentration constituted 14% of the sulfate determined in the cloud water after oxidation. It is likely that a salt formed from HMSA contributed to prior observations of S(IV) and volatile sulfur in the Los Angeles aerosol.

EXPERIMENTAL

Five aircraft flights were conducted (a daytime and a nighttime flight in November 1981 and three nighttime flights in May 1982) to collect samples of water and aerosol in stratus clouds in the Los Angeles Basin using equipment previously described by Richards *et al.* (1981). A cloud water collector that does not collect significant amounts of submicron particles was provided by the Atmospheric Sciences Research Center of the State University of New York at Albany (Mohnen, 1980). The collected water was stored in linear-polyethylene bottles at a temperature between 5 and 10°C until the aircraft landed.

The chemical analysis of the cloud water was performed by students and staff of M. R. Hoffmann at California Institute of Technology using methods described by Waldman *et al.* (1982). Immediately after the plane landed, a 2.5 mℓ aliquot was removed and stabilized with formaldehyde at pH 4 as described by Dasgupta *et al.* (1980). In May, colorimetric determination of sulfur (IV) was performed as described by Humphrey *et al.* (1970). No measures were taken to destroy any hydrogen peroxide in this aliquot. In November, S(IV) was calculated from the difference in sulfate concentrations, measured by ion chromatography, determined before and after oxidation. In May the measured S(IV) concentrations were subtracted from the measured total sulfate concentrations, after oxidation, to obtain the $SO_4^=$ data reported here. A 1.5 mℓ aliquot was also removed and stabilized for the determination of HCHO according to the methods of Nash (1953) and Rietz (1980). No steps were taken in this analysis to minimize the negative interference by S(IV) which has been described by Klippel and Warneck (1980). The pH of the remaining cloud water was measured with a glass electrode.

In the May flights, the collection of each cloud water sample for the above determinations was followed by the collection of a few milliliters of cloud water for the determination of H_2O_2. This sample was passed through an anion ion exchange resin immediately after collection to remove sulfite and was stored in the same manner as the other samples. Immediately after the plane landed, these aliquots were analyzed for H_2O_2 by the horseradish peroxidase method as described by Kunen *et al.* (1982). Separate aliquots were treated with catalase to remove H_2O_2, then analyzed by the

*The National Center for Atmospheric Research is sponsored by the National Science Foundation.

horseradish peroxidase method to determine the small corrections (less than 3%) for interferences due to organic peroxides and fluorescent organic materials. The H_2O_2 values for 21-22 May are lower limits, because solids in the cloud water retained in the ion exchange resin catalyzed H_2O_2 decomposition.

RESULTS AND DISCUSSION

Table 1 reports values for selected parameters for all sampling periods in which either the sulfur dioxide mixing ratio was greater than 1 ppb or H_2O_2 was measured in the cloud water. Because of interferences, the reported S(IV) and HCHO concentrations for all samples and the H_2O_2 concentrations for 21-22 May may be smaller than the true values.

Both H_2O_2 and S(IV) were found in all samples examined for both species. In most cases, the stability of the H_2O_2–S(IV) mixture was not conclusively demonstrated because the water samples to be analyzed for H_2O_2 were passed through an ion exchange resin to remove sulfite soon after the samples were collected. However, for the sample with a collection start time of 0219 on 23 May, the H_2O_2 concentration of 88 μM was determined in an aliquot removed approximately one hour after sample collection, at the same time aliquots were removed and stabilized for the S(IV) and HCHO analyses. The rate data of Martin and Damschen (1981) predict that when the H_2O_2 concentration is greater than 40 μM, the lifetime of S(IV) is less than one second at the pH observed for this sample, so the presence of 10 μM of S(IV) after the cloud water stood for one hour confirms that the reaction between H_2O_2 and S(IV) had been inhibited.

The S(IV) concentrations observed in the cloud water were much higher than expected—hundreds of times higher in most cases. The expected concentrations of S(IV) ($SO_2 \cdot H_2O$ plus HSO_3^-) were calculated using the Henry's Law and acid dissociation constants of sulfurous acid reported by Maahs (1982) and the observed pH and SO_2 mixing ratio. No corrections for the effect of the ionic strength on activity were made, and $SO_3^=$ concentrations were negligible. The observed S(IV) concentrations were divided by the expected concentrations, and the ratios appear in Table 1.

Laboratory experiments have confirmed that S(IV) and H_2O_2 can coexist for hours in the presence of HCHO (Kok *et al.*, 1982), even when the HCHO and S(IV) concentrations were as low as 10 μM each. Therefore, the results reported here for ambient samples can be duplicated in the laboratory.

HCHO was present in the cloud water, and it and other carbonyl compounds are known to form adducts with sulfite in solution. Measurements in the Los Angeles Basin have shown that the concentration of HCHO constitutes roughly a third to a half of the total concentration of gaseous aldehydes (Grosjean, 1982). Data on the dissociation of hydroxymethanesulfonic acid (HMSA), which is the adduct with HCHO, have been reported by Dasgupta *et al.* (1980), and data on the kinetics of formation of this adduct are summarized by

Table 1. Measured data and calculated S(IV) concentration ratios

Date	Start time	Location	Temp. °C	SO_2 ppb	pH	Cloud water concentration S(IV) μM	$SO_4^=$ μM	HCHO μM	H_2O_2 μM	Measured/ calculated S(IV) ratio
24 Nov	0025	Seal Beach	12.6	16	2.98	129	143	52	—	230
	0047	Seal Beach	12.2	8	3.02	89	111	43	—	280
20 May	2235	off Long Beach	12.2	3	2.99	12	195	26	34	120
21 May	2257	Etiwanda	13.0	10	2.40	52	811	113	9.1	520
	2349	Fontana	12.8	48	2.72	183	1226	142	2.8	190
22 May	0025	Fontana	12.7	58	3.39	365	968	70	9.4	73
	0102	Pomona-Corona	13.3	6	2.56	29	628	111	13	370
	0132	Pomona-Corona	13.0	4	2.65	33	624	108	2.8	500
	0206	Fontana	12.7	13	2.69	51	674	120	0.91	210
23 May	0134	ALBAS*	12.9	0	3.05	18	435	34	79	–
	0209	ALBAS	12.2	0	3.38	5	148	23	76	–
	0219	ALBAS	12.1	0	3.33	10	154	28	88	–
	0228	ALBAS	11.5	0	3.59	11	100	11	51	–

*Aircraft navigation point off Huntington Beach.

Kok *et al.* (1982). When the concentrations of S(IV) and HCHO reported in Table 1 were combined with data on the dissociation of HMSA reported by Dasgupta *et al.* (1980), it was calculated that on the average one-third of the total S(IV) was in HMSA. The calculations were repeated for HCHO concentrations ten times larger than reported, with the result that an average of 90% of the S(IV) was in the adduct. Thus, the chemical equilibrium among the species reported does not account for the observed S(IV) concentration. The concentrations of common metals were measured and were found to be high enough that they could influence the S(IV) chemistry.

On the average, 14% of the sulfate determined by ion chromatography in the cloud water was S(IV) when the samples were collected (this ratio ranged from 3% to 47%). Therefore, S(IV) is important in the sulfur budget of the Los Angeles Basin. S(IV) has previously been detected in the aerosol in Los Angeles (Farber *et al.*, 1982), elevated concentrations of HCHO have been seen in the ambient aerosol in Germany (Klippel and Warneck, 1980), and the possible contribution of HMSA to these observations has been suggested (Klippel and Warneck, 1980; Dasgupta, 1981; Dasgupta *et al.*, 1982). Since pure HMSA is unstable and dissociates into HCHO and SO_2, some of this adduct may return to the gas phase when the clouds evaporate. The monosodium salt of HMSA is stable and is a commercial product, so partial neutralization of the HMSA should increase stability in the aerosol. It was noted previously (Richards *et al.*, 1977) during attempts to distinguish sulfuric acid from other sulfates in the Los Angeles Basin that about 10% of the aerosol sulfur could be volatilized as if it were sulfuric acid, but was not sulfuric acid because it would not lose this volatility on exposure to ammonia. The observation of a volatile component in the sulfur aerosol in the Los Angeles Basin appears to be the rule rather than the exception (Richards *et al.*, 1978, 1979; Fig. 11 in Kittelson *et al.*, 1978). Thus, it appears likely that some of the S(IV) observed in cloud water in this study persists in the aerosol when the clouds evaporate. Most filter extraction and wet chemical analytical methods oxidize S(IV) so this component of the aerosol is reported as sulfate.

In summary, it has been shown that the liquid phase oxidation of S(IV) by H_2O_2 was inhibited in the collected samples. The samples contained enough HCHO that adducts with carbonyl compounds could contribute to the incorporation of significant amounts of S(IV) in the condensed phase. Evidence is presented that these S(IV) adducts provide a pathway for the formation of a significant fraction of the sulfur-containing aerosol in the Los Angeles Basin.

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SULFATE AND NITRATE IN LOS ANGELES CLOUD WATER AND AEROSOL

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INTRODUCTION

It has been known for some time that high sulfate concentrations in the Los Angeles basin are associated with periods of fog or drizzle (Cass, 1975), and hence that liquid-phase reactions may play an important role in the conversion of sulfur dioxide to sulfate. One daytime and four nighttime aircraft flights were conducted in November 1981 and May 1982 in stratus clouds in the Los Angeles basin to measure the composition of the trace gases, aerosol, and cloud water to obtain ambient data related to the liquid-phase chemical processes. A preliminary communication describing some of the observed properties of the chemistry of hydrogen peroxide and sulfur (IV) has been prepared (Richards et al., 1983).

EXPERIMENTAL

The cloud sampling was performed with a Queen Air aircraft and sampling equipment that has been described by Richards et al. (1981). Cloud droplet size distributions were measured with a Particle Measuring Systems ASSP-100 in November 1981 and a FSSP in May 1982. The cloud water collector was provided by the Atmospheric Sciences Research Center of the State University of New York at Albany, and has been described by Mohnen (1980). This collector is designed to be very inefficient at capturing submicron particles and to collect droplets larger than about 3 μm to 5 μm. The collected water was stored in linear polyethylene bottles at a temperature between 5° and about 10°C until the aircraft landed.

Cyclones with a cut point between 1 μm and 2 μm were used to remove cloud water from some sample flows entering the aircraft. A nephelometer on one of these flows showed that cloud droplets were efficiently removed. Filter samples were collected behind a cyclone on Teflon, quartz, and Nuclepore substrates. In one case a Teflon filter was followed by a Nylon backup filter and in another case by an oxalic acid impregnated filter. The errors in these filter samples caused by the wet sampling line and the cyclone are not known. Filter analyses for only the May flights were performed by the EMSC, Rockwell International. Anions were determined by ion chromatography and ammonium by the indophenol colorimetric method.

The chemical analysis of the cloud water was performed by students and staff of M. R. Hoffmann at Caltech using methods described by Waldman et al. (1982) and Munger et al. (1983). Immediately on landing, a 2.5 ml aliquot of the cloud water was removed and stabilized with formaldehyde at pH 4 as described by Dasgupta et al. (1980) for the later determination of sulfite as described by Humphrey et al. (1970). No measures were taken to destroy H_2O_2 in this aliquot. A 1.5 ml aliquot was also removed from each bottle and stabilized for the determination of formaldehyde according to the methods of Nash (1953) and Rietz (1980). No steps were taken in this analysis to minimize the interference by sulfite which has been described by Klippel and Warnek (1980). The pH of the remaining cloud water was measured with a glass electrode. Anions were determined by ion chromatography (after oxidation so that any sulfite is converted to sulfate). Ammonium was determined by the phenol-hypochlorite method (Solorzano, 1967) and metals by atomic absorption spectroscopy.

RESULTS

It has previously been reported (Richards et al., 1983) that (a) H_2O_2 and S(IV) were found in all cloud water samples indicating the inhibition of the fast reaction between these species; (b) S(IV) concentrations in the cloud water were great enough to account for an average of 14% of the sulfate found after the sample had been oxidized; and (c) the water samples contained enough formaldehyde to form significant amounts of the adduct, hydroxymethanesulfonic acid (HMSA). Evidence that sulfite-carbonyl compound adducts persist in the aerosol when the clouds evaporate was also presented.

This report focuses on the combined concentrations observed in the filter and cloud water measurements. The data are summarized in Table 1. Ditto marks indicate when one filter sample was obtained while more than one cloud water sample was collected. No results from the November flights are included because the filter data were unsatisfacory. Ammonium concentrations on the oxalic acid impregnated after-filter were always near the detection limit, indicating that ammonia and ammonium that passed the cyclone were retained by the Teflon filter.

The Teflon filter concentrations are for particles small enough to pass through the (wet) sampling line and 2 μm cut cyclone and be retained by an inert filter. The Nylon after-filter collected nitrate that penetrated the Teflon filter. Many processes can contribute to this penetration; for example, particles small enough to be passed by the cyclone and containing appreciable water content could dry out on the Teflon filter and release nitric acid. The drying could occur during moments out of the clouds or could be caused by the heating that occurs when the sample flow is decelerated.

The concentrations in the cloud water were obtained by multiplying the species concentration in the collected water by the liquid water content (LWC) of the cloud. The LWC was estimated from the rate of water collection using the assumption that the efficiency of the cloud water collector was 40% (R. Schemenauer, private communication). This efficiency is variable, so the cloud water concentrations in Table 1 are uncertain by about a factor of 2.

The total concentrations in Table 1 are the sums of the other measurements and are estimates of the total ambient concentrations. There are

Table 1. Nominal concentrations in clouds in $\mu g/m^3$

Date May 1982	Start time (PDT)	Sampling location	Teflon filter NH_4^+	Teflon filter NO_3^-	Teflon filter $SO_4^=$	Nylon filter NO_3^-	Cloud water NH_4^+	Cloud water NO_3^-	Cloud water $SO_4^=$	Cloud water $SO_3^=$	Total concentration NH_4^+	Total concentration NO_3^-	Total concentration $SO_4^=$
20	2235	off Long Beach	0.7	1.2	1.78	2.8	0.6	8.6	4.0	0.18	1	13	6
21	2257	Etiwanda	8.4	4.0	20.1	38.4	2.6	34.	10.	0.50	11	76	30
	2349	Fontana	15.9	16.3	31.6	24.4	8.8	53.	25.	2.8	25	94	57
22	0025	Fontana	32.9	31.0	68.1	10.9	18.	52.	38.	8.8	51	94	106
	0102	(Pomona-Corona)	5.6	4.3	12.1	26.4	6.1	61.	16.	0.60	12	92	28
	0132		"	"	"	"	4.4	38.	11.	0.46	10	69	23
	0206	Fontana	6.5	3.6	14.9	20.6	13.	91.	28.	1.6	19	115	43
23	0134	ALBAS*	1.6	1.4	4.1	7.3	1.1	7.6	5.6	0.18	3	16	10
	0209	ALBAS*	0.3	0.1	1.1	4.9	2.2	11.	7.4	0.20	3	15	9
	0219	ALBAS*	"	"	"	"	2.4	16.	9.4	0.48	3	21	11
	0228	ALBAS*	"	"	"	"	4.4	20.	14.	1.1	5	25	15

*Aircraft navigation point off Huntington Beach

many sources of error; for example, particles a few microns in diameter are small enough to be inefficiently captured by the cloud water collecter yet large enough to be mostly removed by the cyclone. Even allowing for the many uncertainties, it is clear that high concentrations of sulfate, nitrate, and ammonium were encountered in stratus clouds at night.

On 21 and 22 May, the ratio of equivalents of ammonium to sulfate plus nitrate on the Teflon filter varied from 0.95 to 0.98, suggesting that nitrate not balanced by ammonium evaporated and passed through the filter. All these samples were collected in the eastern part of the Los Angeles basin. On the other days, this ratio was 0.68, 0.84, and 0.76 in chronological order. These three samples were collected over the ocean where the ammonium concentrations were low, so other cations balance sulfate and nitrate.

Due to the limited flight time, it was not possible to follow air parcels during cloud formation and thereby directly determine the relative importance of chemical conversion processes in clouds and in the prior day's photochemistry. The high concentrations observed and the distribution of species between the sample collectors suggest the importance of liquid-phase reactions. The high sulfite concentrations are very likely due to liquid-phase reactions, and appear to play a significant role in the formation of sulfur aerosol in the Los Angeles basin (Richards et al., 1983). The observed nitrate concentrations are compatible with efficient nighttime production of nitrate from NO_2 and O_3 via NO_3 (Richards, 1982). Calculations based on measured O_3 and NO_2 concentrations showed that usually three or more hours would be required for this reaction to produce the observed nitrate concentrations.

The species determined in the cloud water included $SO_4^{=}$, $SO_3^{=}$, NO_3^{-}, F^{-}, Cl^{-}, H^{+} (pH), NH_4^{+}, Na, K, Ca, Mg, Fe, Mn, Pb, Cu, Ni, and CH_2O. These data were used to estimate the solids content of the water and the composition of the aerosol resulting from the evaporation of the clouds. It was assumed that an equal fraction of the Cl^{-} and NO_3^{-} would evaporate along with all the H^{+}. The density of the resulting solid aerosol was assumed to be unity to roughly compensate for water remaining in the aerosol and the lack of data for nonvolatile organic materials. In the water after oxidation, an average of 50% of the weight of the above species was NO_3^{-} and 23% $SO_4^{=}$. The average calculated dry aerosol composition was 24% nitrate and 38% sulfate. When the measured cloud droplet size distributions were combined with the (doubtful) assumption that all droplets in a given sample had the same composition, the calculated geometric mean diameter of the aerosol size distributions fell between 0.3 μm and 0.5 μm.

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APPENDIX A
FLIGHT MAPS AND FLIGHT SUMMARIES

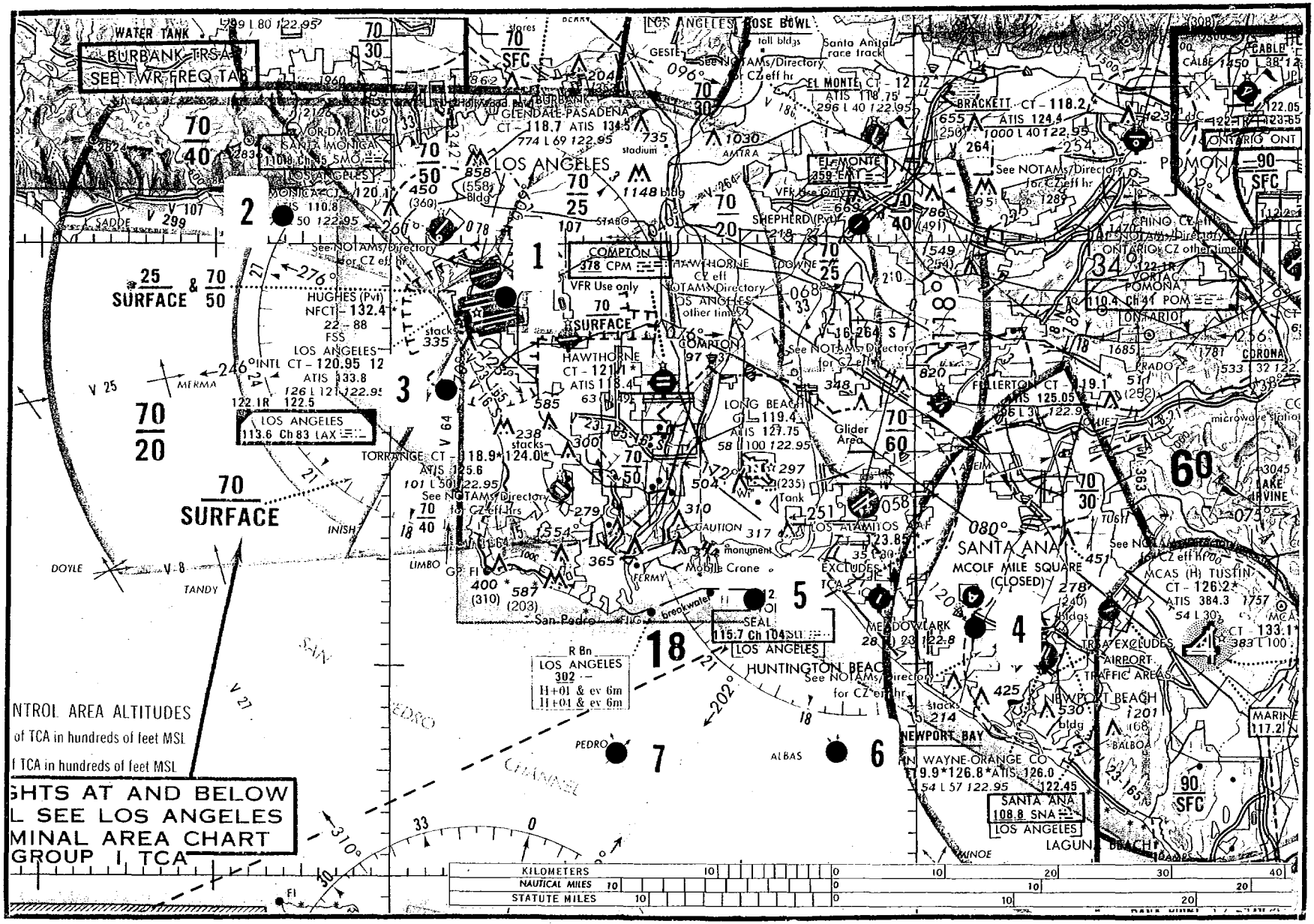

Figure A-1. End Point and Orbit Locations for 23-24 November 1981 Flights

FLIGHT OUTLINE

Date: 11/23-24/81 CLOUD SAMPLING 1981 Tape #296

Pass No.	Sampling Times (PST) Start	End	Flight Type	End Points	Sampling Altitude m MSL Start	End	Traverse Length or Orbit Time	Teflon 47mm H	Nylon 47mm N	Teflon 25mm X	Quartz 47mm Q	Nuclepore 25mm W	Tungstic Acid Tube	Cloud Water Bottle	Comments
1	2224	2232	Spiral	1	38-1219		N.A.							2	
2	2244	2309	Orbit	2	427		25.5 Min.	H4	N4	X4	Q4	W4	TA6 after 2300	3	
3	2318	2324	Traverse	2 - 3	914		22.0 Km.	-	-	-	-	-	-	4	
4	2328	2347	Orbit	3	457		19.2 Min.	H5	N5	X6	Q6	W6	TA7	5	Background orbit
5	2353	0005	Traverse	3 - 4	610		49.8 Km.	-	-	-	-	-	-	6	
6	0025	0045	Orbit	4	457		30.1 Min.	H6	N6	X7	Q7	W7	TA8	7	
7	0047	0107	Orbit	4	549		22.9 Min.	↓	↓	↓	↓	↓	↓	8	
8	0122	0127	Spiral	1	914-	38	N.A.	-	-	-	-	-	-	9	
								H3 H7	N3 N7	X3	Q3	W3	TA9		Very short exposure BLANKS

FLIGHT OUTLINE

Date: 11/24/81 CLOUD SAMPLING 1981 Tape #297

Pass No.	Sampling Times (PST) Start	End	Flight Type	End Points	Sampling Altitude m MSL Start	End	Traverse Length or Orbit Time	Teflon 47mm H	Nylon 47mm N	Teflon 25mm X	Quartz 47mm Q	Nuclepore 25mm W	Tungstic Acid Tube	Cloud Water Bottle	Comments
1	714	719	Spiral	1	38-	914	N.A.							R2	
2	732	802	Orbit	5	457		30.0 Min.	H11	N11	X11	Q11	W14	TA22	R3	7:43 SO_2 flame on
3	807	826	Orbit	5	762		29.4 Min.	↓	↓	↓	↓	↓	↓	R4	
4	834	904	Orbit	6	457		30.1 Min.	H12	N12	X12	Q12	W15	TA11	R5	
5	915	945	Orbit	6	762		29.8 Min.	H13	N13	↓	↓	↓	↓	R6 to 9:27 R7 to end	
6	957	1028	Orbit	7	640		30.1 Min.	H10	N10	X10	-	W13	TA24	R8	TA24 denuder tube broken
7	1043	1055	Spiral	1	1219-	38	N.A.	-	-	-	-	-	-	R9	
								H8 H9	N8 N9	X8 X9		W11 W12	TA9		BLANKS

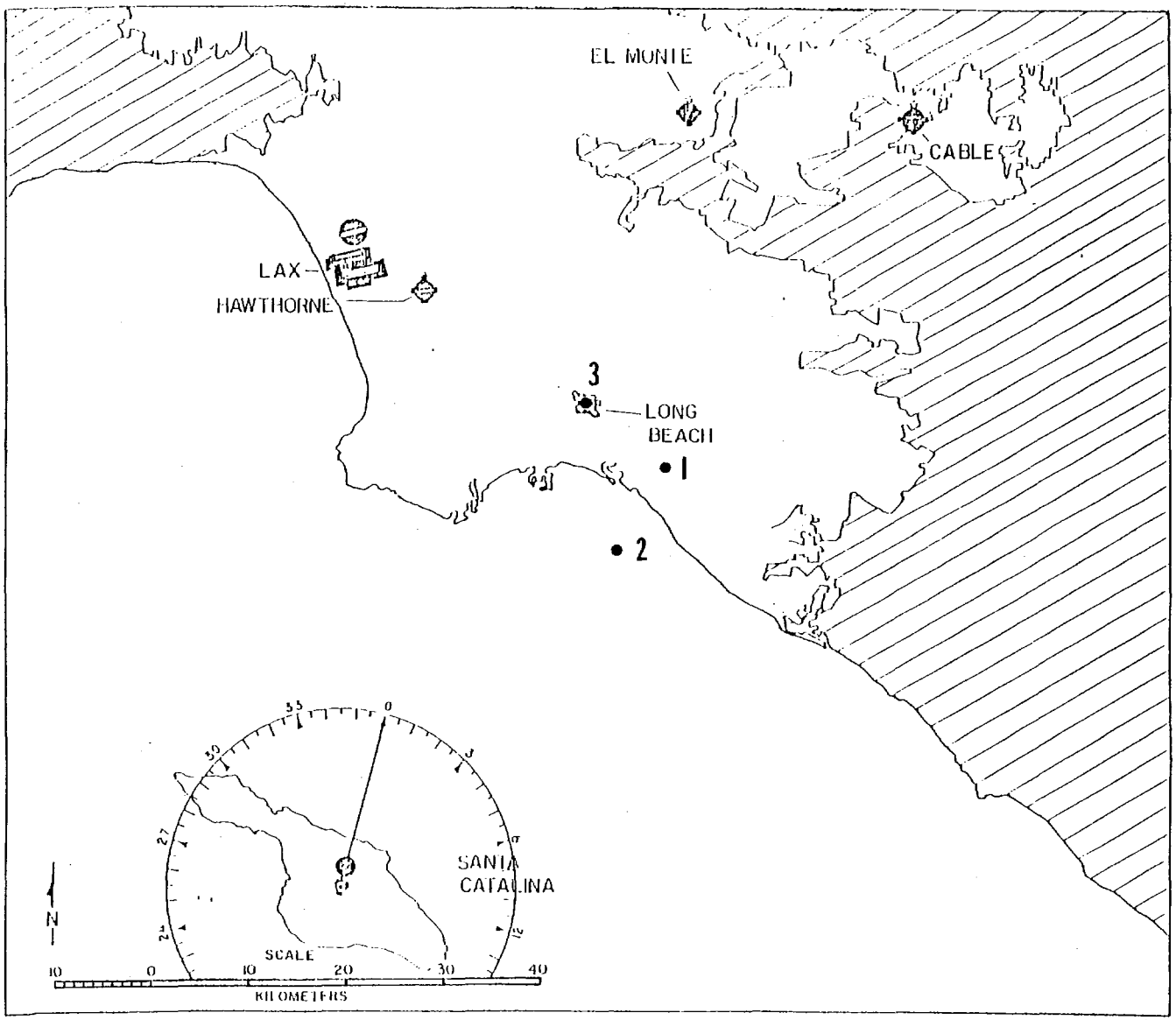

Figure A-2. Queen Air sampling locations for the 20 May 1982 sampling flight.

MRI FLIGHT OUTLINE
CARB CLOUD SAMPLING 1982

Date: 20 May 1982

Tape 301

Pass No.	Sampling Time (PDT) Start	End	Flight Type	End Points	Sampling Altitude m msl	Orbit Time (min)	Teflon 47 mm H	Nylon 47 mm N	Teflon 25 mm X	Quartz 47 mm Q	Nuclepore 25 mm W	Oxalic Acid 47 mm A	Cloud Water Bottle
1	2136	2219	Orbit	1	518	43.50	H1	N1	X1	Q1	W1	A1	C1
2	2235	2308	Orbit	2	762	41.40	H2	N2	X2	"	"	"	C2
3	2314	2321	Spiral	3	1219	-	-	-	-	-	-	-	C13
	Blank filters						H3	N3	X3	Q2	W2,W3	A2	

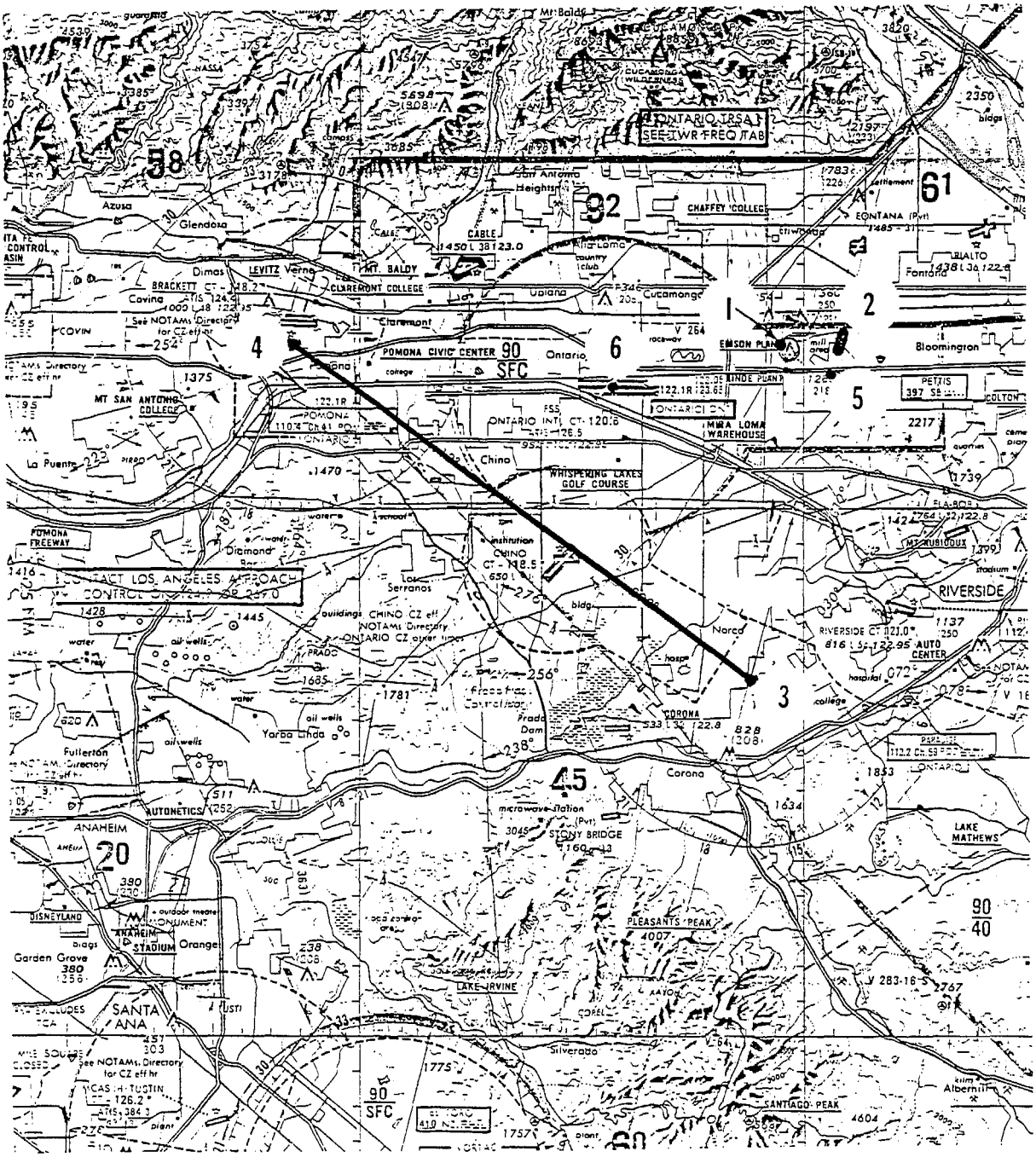

Figure A-3. End point and orbit locations for the 21-22 May 1982 Queen Air flight.

Date: 21-22 May 1982

MRI FLIGHT OUTLINE
CARB CLOUD SAMPLING 1982

Tape 302

Pass No.	Sampling Time (PDT) Start	End	Flight Type	End Points	Sampling Altitude m msl	Orbit Time (min)	Teflon 47 mm H	Nylon 47 mm N	Teflon 25 mm X	Quartz 47 mm Q	Nuclepore 25 mm W	Oxalic Acid 47 mm A	Cloud Water Bottle
1	2257	2335	Orbit	1	853	37.60	H7	N7	X7	Q4	W8	A4	C4
2	2336	2345		1	853	9.72	"	"	"				C14-K4
3	2349	0015		2	853	26.03	H8	N8	X8				C5
4	0016	0021		2	853	5.00	"	"	"				C15-K5
5	0025	0048		2	975	23.07	H9	N9	X9				C6
6	0048	0053		2	975	3.87	"	"	"				C16-K6
7	0102	0124		3-4	975	22.15	H4	N4	X4		W4		C7
8	0125	0131		3-4	975	5.62							C18-K7
9	0132	0154		3-4	1067	22.63							C8
10	0154	0200		3-4	1067	5.73							C19-K8
11	0206	0221		5	975	14.67	H5	N5	X5		W5		C9
12	0221	0225		5	975	3.80	"	"	"		"		C22-K9
13	0234	0240	Spiral	6	1372-305	-	-	-	-	-	-	-	-
14	0254	0307	Zero	7	1219-26	-	-	-	-	-	-	-	-
	Blank filters									Q3,Q5	W9	A3,A5	

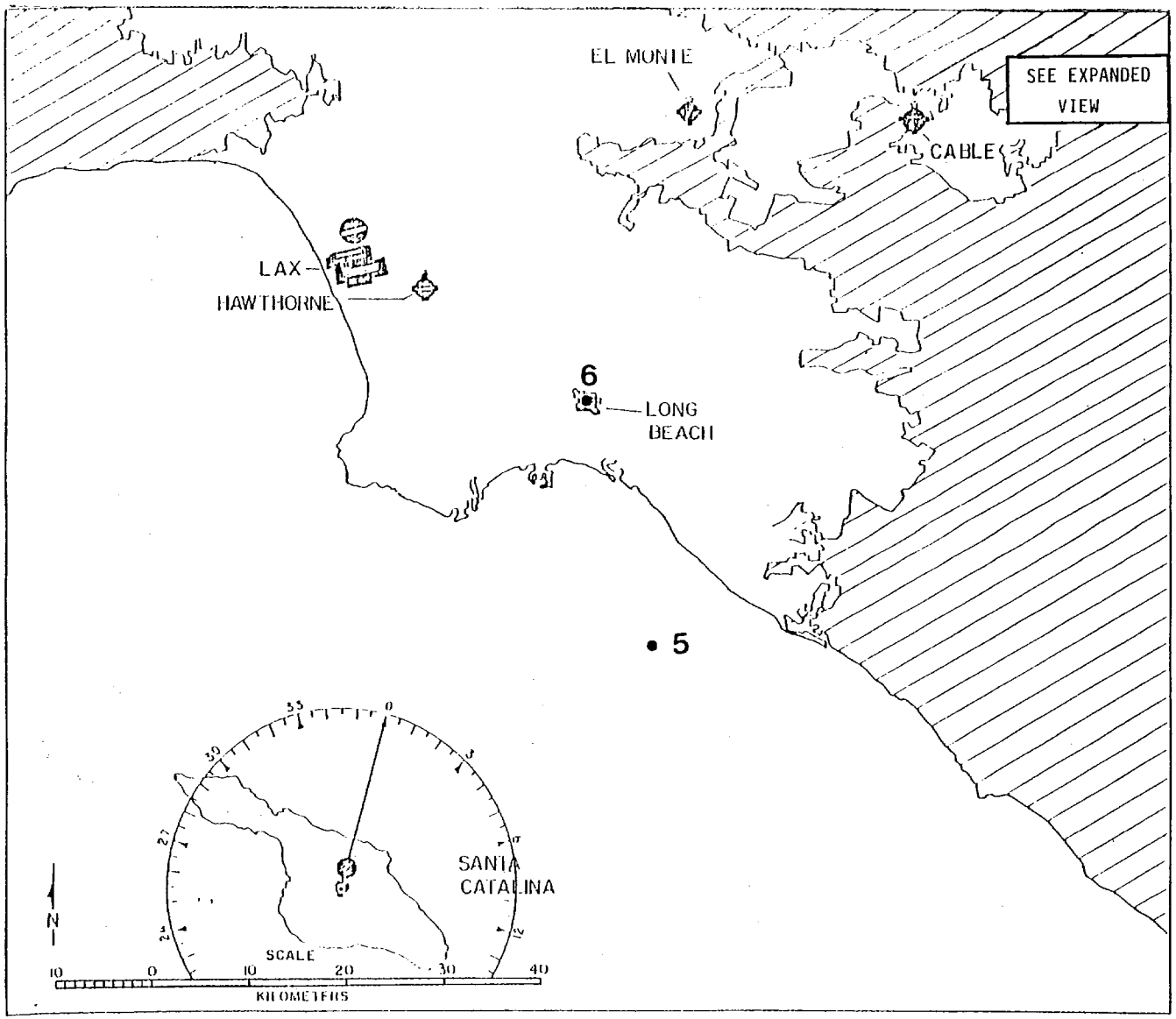

Figure A-4. Sampling locations for the 22-23 May 1982 flight.

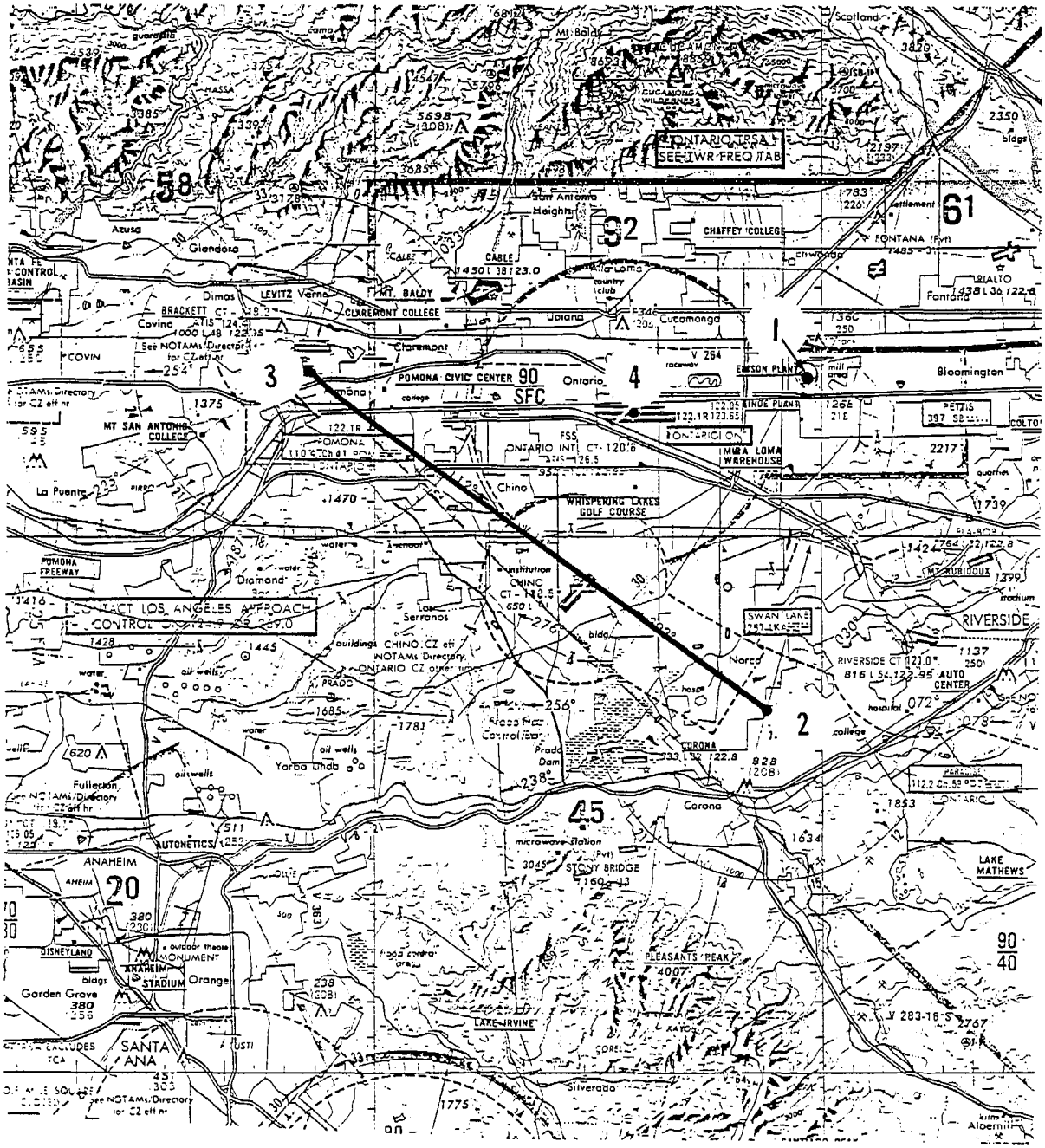

Figure A-5. Expanded view - sampling locations for the 22-23 May 1982 flight.

MRI FLIGHT OUTLINE

Date: 22-23 May 1982 — CARB CLOUD SAMPLING 1982 — Tape 303

Pass No.	Sampling Time (PDT) Start	End	Flight Type	End Points	Sampling Altitude m msl	Orbit Time (min)	Teflon 47 mm H	Nylon 47 mm N	Teflon 25 mm X	Quartz 47 mm Q	Nuclepore 25 mm W	Oxalic Acid 47 mm A	Cloud Water Bottle
1	2327	2347	Orbit	1	853	20.00	H10	N10	X10	Q6	W10	A6	C30(dry)
2	2354	0015		1	853	20.00	H11	N11	X11	"	W11	"	C31(dry)
3	0023	0043		2-3	732	19.2	H12	N12	X12	Q7	W12	A8	C32(dry)
4	0056	0103	Spiral	4	1311-518	-	-	-	-	-	-	-	C33(dry)
5	0134	0201	Orbit	5	457-518	26.83	H13	N13	X13	Q7	W13	A6	C34
6	0201	0207		5	518	5.35	"	"	"	"	"	"	C44-K4
7	0209	0218		5	686	8.87	H14	N14	X14	Q7	W14	A7	C35
8	0219	0226		5	686	7.68							C45-K5
9	0228	0234		5	823	5.6							C36
10	0235	0237		5	823	5.93							C43-K6
11	0238	0247	Zero	6	823-18	-	-	-	-	-	-	-	-
	Blank filters		20-23 May				H6		X6				
			not flown					N15,N16					

APPENDIX B
TABULATIONS OF ANALYTICAL CHEMISTRY RESULTS

Table B-1. Caltech cloud water chemistry data for November 1981.

Sample ID	Time	m elev.	Site	pH	$\mu eq\ell^{-1}$										$\mu g\ell^{-1}$					$mg\ell^{-1}$	$\mu eq/\ell$	
					H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	Fe	Mn	Cu	Ni	V	Cl_2O	SO_3^{2-}	$\Sigma-/\Sigma+$
C1123-2	2224-2232		1	3.56	275	500	192.4	126	331	222	42	704	429	356			--	--	--	NA	NA	--
C1123-3	2244-2309	427	2	3.36	437	416	12.3	193	47.3	77.6	37	372	579	219	190	10.3	94	45	5	.543	82	1.02
C1123-4	2318-2324	919	2-3	3.36	437	337	56.5	180	88.7	103	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--
C1123-5	2328-2347	457	3	3.80	159	215	5.6	34.2	16.2	40.2	16	239	141	113	14	1.5	28	17.3	6	134	42	1.08
C1123-6	2353-0005	610	3-4	3.05	891	248	7.9	288	36.5	43.9	74	276	1043	400	109	8.6	192	80	17	921	178	--
C1123-7	0025-0045	457	4	2.98	1047	478	8.2	477	37.6	47.3	89	296	1393	544	169	8.2	62.3	23.2	13	1.560	258	1.11
C1123-8	0047-0107	549	4	3.02	955	203	6.1	352	25.3	30.2	89	268	1107	400	202	9.3	125	55	30	1.300	178	1.19
C1123-9	0122-0127		1	3.68	209	167.5	95.4	119	22.3	44.0	37	296	179	181	NA	NA	NA	NA	NA	NA	NA	1.05
C1123-11				3.59	257	242	9	77.0	18.5	28.7	NA	NA	NA	--	657	2.9	25.3	12	5	2.410	NA	--
C1124-2	0714-0719		1	3.73	186	133	37.6	200	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--	NA
C1124-3	0732-0802	457	5	3.18	661	286	14.5	369	51.1	66.3	49	383	764	231	--	20	137	109	--	NA	--	1.10
C1124-4	0807-0826	762	5	3.72	191	25.2	2.3	73	6	5.9	21	42	143	119	46	1.6	23	10	4	.403	60	1.07
C1124-5	0834-0904	457	6	2.95	1122	722	30.7	711	101	154	53	177	100	119	1260	59	273	202	90	NA	--	(.38)
C1124-6	0915-0927	762	6	3.73	186	33.1	1.3	71.2	9.7	10.5	5	51	136	113	48	2.8	27	9.4	5.0	.353	54	.98
C1124-7	0927-0945	762	6	3.61	246	110	8.2	117	6.7	11	--	76	179	--	55	2.6	37	11.3	10	.463	--	--
C1124-8	0957-1028	640	7	4.72	19.1	255	12.6	3574	NA	NA	421	651	1260	331	202	59	136	125	8	.463	121	--
C1124-9	1043-1055		1	3.35	447	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--
C1124-10				3.60	251	220	46.3	143	33.8	25.3	74	211	307	256	190	11.2	218	25.3	8	.483	93	1.18

Table B-2. Caltech cloud water chemistry data for May 1982.

		Concentration in μeq/l											Conc. in μg/l					
Sample ID	pH	H^+	Na^+	K^+	NH_4^+	Ca^{++}	Mg^{++}	F^-	Cl^-	NO_3^-	$SO_4^=$	$SO_3^=$	HCHO	Fe	Mn	Pb	Cu	Ni
C0520-1	2.34	4570	14575	435	1875	655	2291	347	3500	10370	5740	--	--	--	--	--	---	---
C0520-2	2.99	1023	263	11.6	177	38.9	59.8	49.5	278	690	414	23	780	592	31	120	418	490
C0521-1	2.40	3980	293	--	1175	243	107	195	194	4520	1725	104	3380	5320	377	1200	1510	1297
-2	2.72	1905	264	72.8	2643	1296	263	203	456	4620	2818	365	4270	13360	672	2014	1142	2822
-3	3.39	407.	190	68.5	3300	2096	288	213	366	2820	2666	730	2110	2820	316	1076	359	343
-4	2.56	2754	118	21.1	1297	129	92	163	111	3807	1313	57.7	3440	5450	197	798	603	730
-5	2.65	2239	149	27.9	1440	98.4	70.5	163	111	3575	1313	66.9	3240	4570	161	587	306	569
-6	2.69	2042	98.3	16.8	1802	208	57.7	163	111	3670	1450	102	3600	2520	64	296	98.7	254.
-7	2.82	1514	232	61.8	2132	818	184.	147	254	3760	1994	--	--	--	--	--	--	--
-8	2.57	2692	320	--	1192	204	98.3	147	138	3300	1225	--	--	--	--	--	--	--
-9	2.61	2455	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
C0522-1	--		1720		2712	4070	920	216	315	7336	2719	--	--	--	--	--	--	--
-2	3.05	891.3	450	37.9	476	197	109	74	227	946	906	36	1010	3480	921	192	420.	230.
-3	3.38	416.9	128	18.6	236	44.1	34.2	43.2	77	351	305	10	680	710	43	79	99.5	85.7
-4	3.59	257.0	65	6.8	187	20.7	18.2	42.1	61	246	222	21	340	636	20	56	60.6	66.5
-5	3.33	467.7	175	15.9	223	64.8	40.6	42.1	93	443	328	20	840	2200	69	115	186	277

Table B-3. Part 1 - Summary of aircraft data.

Date	Tape	Pass	Start Time	Location	CIT No.	pH	H^+ µeq/l	Na^+ µeq/l	K^+ µeq/l	NH_4^+ µeq/l	Ca^{++} µeq/l	Mg^{++} µeq/l	F^- µeq/l
23 Nov	296	1	2224	depart LAX	23-2	3.56	275	500	192.4	126	331	222	42
		2	2244	off Malibu	23-3	3.36	437	416	12.3	193	47.3	77.6	37
		4	2328	off El Segundo	23-5	3.80	159	215	5.6	34.2	16.2	40.2	16
		5	2353	El Seg. to S.Bch	23-6	3.05	891	248	7.9	288	36.5	43.9	74
24 Nov		6	0025	Seal Beach	23-7	2.98	1047	478	8.2	477	37.6	47.3	89
		7	0047	Seal Beach	23-8	3.02	955	203	6.1	352	25.3	30.2	89
		8	0122	approach LAX	23-9	3.68	209	167.5	95.4	119	22.3	44	37
24 Nov	297	2	0732	off Los Alamitos	24-3	3.18	661	286	14.5	369	51.1	66.3	49
		3	0807	off Los Alamitos	24-4	3.72	191	25.2	2.3	73	6	5.9	21
		4	0834	ALBAS*	24-5	2.95	1122	722	30.7	711	101	154	53
		5	0915	ALBAS	24-6&7	3.67	216	72	4.8	94	8.2	10.8	5
		6	0957	PEDRO**	24-8	4.72	19	255	12.6	3574			421
		November average				3.47	515.17	298.98	32.73	534.18	62.05	67.47	77.75
20 May	301	2	2235	off Long Beach	20-2	2.99	1023	263	11.6	177	38.9	59.8	49.5
21 May	302	1	2257	Etiwanda	21-1	2.4	3980	293	0	1175	243	107	195
		3	2349	Fontana	21-2	2.72	1905	264	72.8	2643	1296	263	203
22 May		5	0025	Fontana	21-3	3.39	407	190	68.5	3300	2096	288	213
		7	0102	Pomona-Corona	21-4	2.56	2754	118	21.1	1297	129	92	163
		9	0132	Pomona-Corona	21-5	2.65	2239	149	27.9	1440	98.4	70.5	163
		11	0206	Fontana	21-6	2.69	2042	98.3	16.8	1802	208	57.7	163
23 May	303	5	0134	ALBAS	22-2	3.05	891.3	450	37.9	476	197	109	74
		7	0209	ALBAS	22-3	3.38	416.9	128	18.6	236	44.1	34.2	43.2
		8	0219	ALBAS	22-5	3.33	467.7	175	15.9	223	64.8	40.6	42.1
		9	0228	ALBAS	22-4	3.59	257	65	6.8	187	20.7	18.2	42.1
		May average				2.98	1489	199	27.08	1178	403.26	103.64	123
		Grand average				3.24	981	251	30.03	842	233	86	99

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

Table B-3. Part 2 - Summary of aircraft data.

Date	Tape	Pass	Start Time	Location	Cl^- µeq/l	NO_3^- µeq/l	$SO_4^=$ µeq/l	$SO_3^=$ µeq/l	HCHO µg/l	Fe µg/l	Mn µg/l	Pb µg/l	Cu µg/l
23 Nov	296	1	2224	depart LAX	704	429	356						
		2	2244	off Malibu	372	579	219	82	543	190	10.3	104	94
		4	2328	off El Segundo	239	141	113	42	134	14	1.5	9.7	28
		5	2353	El Seg. to S.Bch	276	1043	400	178	921	109	8.6	80	192
24 Nov		6	0025	Seal Beach	296	1393	544	258	1560	169	8.2	84	62.3
		7	0047	Seal Beach	268	1107	400	178	1300	202	9.3	96	125
		8	0122	approach LAX	296	179	181						
24 Nov	297	2	0732	off Los Alamitos	383	764	231				20	109	137
		3	0807	off Los Alamitos	42	143	119	60	403	46	1.6	54	23
		4	0834	ALBAS*	177	100	119			1260	59	197	273
		5	0915	ALBAS	64	158	113	54	408	52	2.7	64	32
		6	0957	PEDRO**	651	1260	331	121	463	202	59	82	136
		November average			314.00	608.00	260.50	121.63	716.50	249.33	18.02	87.97	110.23
20 May	301	2	2235	off Long Beach	278	690	414	23	780	592	31	120	418
21 May	302	1	2257	Etiwanda	194	4520	1725	104	3380	5320	377	1200	1510
		3	2349	Fontana	456	4620	2818	365	4270	13360	672	2014	1142
22 May		5	0025	Fontana	366	2820	2666	730	2110	2820	316	1076	359
		7	0102	Pomona-Corona	111	3807	1313	57.7	3440	5450	197	798	603
		9	0132	Pomona-Corona	111	3575	1313	66.9	3240	4570	161	587	306
		11	0206	Fontana	111	3670	1450	102	3600	2520	64	296	98.7
23 May	303	5	0134	ALBAS	227	946	906	36	1010	3480	921	192	420
		7	0209	ALBAS	77	351	305	10	680	710	43	79	99.5
		8	0219	ALBAS	93	443	328	20	840	2200	69	115	186
		9	0228	ALBAS	61	246	222	21	340	636	20	56	60.6
		May average			190	2335	1224	139.6	2154	3787	261	594	473
		Grand average			254	1434	721	132.03	1549	2195	145	353	300

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

Table B-3. Part 3 - Summary of aircraft data.

Date	Tape	Pass	Start Time	Location	Ni µg/l	V µg/l	H_2O_2 µM	T °C	Alt. m msl	b_{scat} Mm^{-1}	O_3 ppb	SO_2 ppb	NO_x ppb
23 Nov	296	1	2224	depart LAX				15.9		39	21	.8	7
		2	2244	off Malibu	45	5		13.1	429	89	33	0	13.7
		4	2328	off El Segundo	17.3	6		13.5	457	19	21	0	5.2
	*	5	2353	El Seg. to S.Bch	80	17		16.1	676	32	27	.3	6.5
24 Nov		6	0025	Seal Beach	23.2	13		12.6	457	46	11	16	72
		7	0047	Seal Beach	55	30		12.2	557	60	25	8	46
		8	0122	approach LAX				15.3		32	20	.6	20
24 Nov	297	2	0732	off Los Alamitos	109			12.4	449	56	16	1.1	27
		3	0807	off Los Alamitos	10	4		10.9	796	25	18	.3	28
		4	0834	ALBAS*	202	90		12.4	455	79	13	7.4	37
		5	0915	ALBAS	10.4	8		11	766	18	21	0	26
		6	0957	PEDRO**	125	8		11.7	625	32	22	0	16
		November average			67.69	20.11		13.09	566.70	43.92	20.67	2.88	25.37
20 May	301	2	2235	off Long Beach	490		34	12.2	743	22	55	2.7	10
21 May	302	1	2257	Etiwanda	1297		9.1	13	855	221	52	9.6	49
		3	2349	Fontana	2822		2.8	12.8	855	255	27	48	73
22 May		5	0025	Fontana	343		9.4	12.7	976	366	28	58	78
		7	0102	Pomona-Corona	730		13	13.3	975	204	68	5.6	30
		9	0132	Pomona-Corona	569		2.8	13	985	189	84	3.9	30
		11	0206	Fontana	254		.91	12.7	976	121	60	13	37
23 May	303	5	0134	ALBAS	230		79	12.9	496	68	63	0	8
		7	0209	ALBAS	85.7		76	12.2	674	14	63	0	5.2
		8	0219	ALBAS	277		88	12.1	698	15	63	0	5.2
		9	0228	ALBAS	66.5		51	11.5	794	15	63	0	5
		May average			651		33.27	12.58	821	135	57	12.80	30.04
		Grand average			373	20.11	33	12.85	700	88	38	7.62	27.60

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro

Table B-3. Part 4 - Summary of aircraft data.

Date	Tape	Pass	Start Time	Location	NO ppb	NO_2 ppb	Cloud water (probe) 10^{-6}	Cloud water (bottle) 10^{-6}	NO_3^- § $\mu g/m^3$	$SO_4^=$ Teflon filter $\mu g/m^3$	NH_4^+ § $\mu g/m^3$	HNO_3 §§ $\mu g/m^3$	NH_3 † $\mu g/m^3$
23 Nov	296	1	2224	depart LAX	3.9	3.1	.19						
		2	2244	off Malibu	3.6	10.1	.27		9.02		1.56	10.04	2.02
		4	2328	off El Segundo	3.6	1.6	.11		5.39		1.81	0.65	0.59
		5	2353	El Seg. to S.Bch	3.1	3.4	.03						
24 Nov		6	0025	Seal Beach	10	62	.035		2.14		0.25	1.31	0.77
		7	0047	Seal Beach	5.5	40.5	.035		2.14		0.25	1.31	0.77
		8	0122	approach LAX	2.8	17.2	.29						
24 Nov	297	2	0732	off Los Alamitos	7	20	.019		0.62		0.12	1.49	0.83
		3	0807	off Los Alamitos	8	20	.022		0.62		0.12	1.49	0.83
		4	0834	ALBAS*	8	29	.013		2.68		0.10	1.12	0.26
		5	0915	ALBAS	9	17	.022		2.68		0.10	1.12	0.26
		6	0957	PEDRO**	4	12	.014						
		November average			5.71	19.66	.0875		3.16		0.54	2.32	0.79
20 May	301	2	2235	off Long Beach	0	10	.14	.1 ††	1.19	1.78	.69	2.84	
21 May	302	1	2257	Etiwanda	0	49		.061	3.99	20.1	8.41	38.4	.3
		3	2349	Fontana	3	70		.093	16.3	31.6	15.9	24.4	.3
22 May		5	0025	Fontana	4	74		.15	31	68.1	32.9	10.9	.3
		7	0102	Pomona-Corona	0	30		.13	4.34	12.1	5.55	26.4	.3
		9	0132	Pomona-Corona	0	30		.086	4.34	12.1	5.55	26.4	.3
		11	0206	Fontana	0	37		.2	3.6	14.9	6.48	20.6	.3
23 May	303	5	0134	ALBAS	0	8	.042	.065	1.35	4.1	1.63	7.31	1.9
		7	0209	ALBAS	0	5.2	.077	.25	.08	1.1	.33	4.89	0
		8	0219	ALBAS	0	5.2	.071	.3	.08	1.1	.33	4.89	0
		9	0228	ALBAS	0	5	.13	.66	.08	1.1	.33	4.89	0
		May average			0.64	29.40	0.09	0.19	6.03	15.28	7.10	15.63	0.37
		Grand average			3.28	24.32	0.09	0.19	4.82	15.28	4.34	10.02	0.56

* Aircraft navigation point off Huntington Beach
** Aircraft navigation point south of San Pedro
§ NO_3 and NH_4^+ from packed tungstic acid tube in November and H Teflon filter in May
§§ HNO_3 (as NO_3^-) from hollow tungstic acid tube in November and Nylon filter in May
† NH_3 (as NH_4^+) from hollow tungstic acid tube in November and oxalic acid impregnated filter in May
†† Based on 85% cloud water collector efficiency. Data for 45% efficiency appear in Table 6-1.

Table B-4. Analytical results for blank filters.
May 1982

Filter No.	Analyte μg/filter			
	NO_3^-	$SO_4^=$	NH_4^+	Cl^-
NT-3	0.56	<0.37	<0.37	0.21
NT-15	0.55	<0.37	<0.37	0.20
NT-16	0.96	<0.37	<0.37	0.18
H-3	0.55	<0.37	<0.37	0.15
H-6	<0.37	<0.37	<0.37	<0.15
Mean	0.56	Below det. lim.		0.15

Table B-5. Comparison of replicate filter data.

Tape/Pass	Filter Code	Species concentration $\mu g/m^3$		
		NO_3^-	$SO_4^=$	NH_4^+
301/1	NT	0.43	9.7	3.2
	H	0.44	8.3	2.9
302/3-4	NT	11.5	30.	12.2
	H	16.3	32.	15.9
303/1	NT	10.0	9.2	6.7
	H	12.8	9.8	7.4
303/2	NT	13.8	8.9	7.3
	H	15.0	9.6	8.0
303/3	NT	0.54	7.5	2.8
	H	1.23	8.5	3.3