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CHARACTERIZATION OF REACTANTS, MECHANISMS, AND SPECIES IN SOUTH COAST AIR BASIN CLOUDWATER

Final Report

STI 94120-606-12FR

Prepared for:

California Air Resources Board
Post Office Box 2815
Sacramento, California 95812

Agreement No. A4-032-32

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January 1987

ABSTRACT

Sonoma Technology, Inc. (STI) conducted a study in May and June 1985 for the California Air Resources Board in which an aircraft was used to collect cloud water, aerosol, and gas samples and to make other air quality and meteorological measurements in stratus clouds in the Los Angeles Basin. This study continued the research on Los Angeles Basin stratus begun in 1981. The average composition of the cloud water was in the range found in previous years, and was approximately 42% by equivalents nitric acid, 27% ammonium sulfate, 18% sodium chloride, and 13% other metal nitrates and sulfates. The minimum, mean, and maximum values for the concentration of several cloud water species were: nitrate, 5, 22, and 40 $\mu g/m^3$; sulfate, 4, 10.6, and 16 $\mu g/m^3$; H_2O_2, 12, 57, and 167 μM; and pH, 2.9, 3.35, and 3.8. If sufficient SO_2 were added to the clouds, the measured H_2O_2 would cause the sulfate concentrations to rapidly increase by an average of 5.2 $\mu g/m^3$ or 65%. Five flights were designed to approximately follow air parcels to determine chemical conversion rates in the clouds. The ambient concentrations ($\mu g/m^3$) of most non-volatile dissolved species in the cloud water usually decreased with time, showing that removal processes were important. One flight was made during a drizzle and trace metal concentrations in the cloud water decreased by about a factor of two each hour due to droplet settling. Increases with time in lead and ammonia concentrations in the cloud water showed that vertical mixing was important. There was a slight tendency for nitrate concentrations to increase with time, but sulfate concentrations were relatively constant because of the very small sulfur (IV) concentrations in the clouds. The settling of droplets out of stratus clouds through air below the clouds containing ammonia and then the evaporation of these relatively large droplets is suggested as a significant mechanism for the formation of large, nitrate-containing aerosol particles below the clouds.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the assistance of Eric Fujita of the California Air Resources Board in this work. T. B. Smith has again provided valuable assistance in weather forecasting and advice on the plan of the study and the interpretation of the data. Several consultants provided unique capabilities and helpful advice: P. K. Dasgupta of Texas Tech University, G. L. Kok of NCAR, and D. Grosjean.

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1. SUMMARY AND CONCLUSIONS

1.1 INTRODUCTION

Sonoma Technology, Inc. (STI) conducted a study in May and June 1985 for the California Air Resources Board in which an aircraft was used to collect cloud water, aerosol, and gas samples and to make other air quality and meteorological measurements in stratus clouds in the Los Angeles Basin. This study continued the research on Los Angeles Basin stratus begun in 1981.

1.2 OBJECTIVES

The main objectives of the study were to:

1. Determine the rate of formation of sulfate, nitrate, and acidity in clouds in polluted air masses in the Los Angeles Basin.
2. Characterize the air masses in which these rates were measured to provide information on reaction pathways and on the distribution of reaction products between the cloud water and the interstitial aerosol.
3. Determine the spatial relationship of acidity in clouds to sources in and upwind of the Los Angeles Basin.
4. Compare the results with simple model calculations.
5. Make the results available in a Final Report and a comprehensive Data Volume which can be used by others to evaluate cloud chemistry computer models.

1.3 EXPERIMENTAL

Sampling flights in stratus clouds were made with a Beechcraft Queen Air. Sixty one channels of air quality, meteorological, and navigational data were recorded on magnetic tape once per second. Grab samples of cloud water, interstitial aerosol, and gas species were collected. New methods were used again in this study to collect cloud water directly into solutions which stabilized labile species such as hydrogen peroxide and sulfur (IV) to prevent sample degradation between collection and analysis. A partially successful attempt was made to use an isokinetic sampler to collect sulfate and nitrate in an air sample with 100% sampling efficiency regardless of whether these species were present as a gas, in fine particles, or in cloud droplets. The total ambient sulfate and nitrate concentrations from such measurements are required to determine chemical conversion rates.

All flights were made between approximately midnight and 6:00 AM, which is the time interval when stratus clouds were most often present. The flights were made the mornings of 21, 24, 25, 26, and 27 May and 1, 10, and 11 June. Two of these mornings, missed approaches to a series of airports were used to characterize the three-dimensional distribution of pollutants in coastal locations, and six of these mornings orbits were flown at a series of locations approximately in the same air parcel to determine the evolution with time of the composition of the stratus clouds.

The liquid water content of the clouds was greater than in previous studies, so larger samples were collected and there was more opportunity for replication of the analyses. The analytical results returned by the three participating laboratories were of high quality. Measured cation concentrations balanced the measured anion concentrations well, and conductivities calculated from the measured ion concentrations agreed with the measured electrical conductivities. It is believed that valid data were obtained for the cloud water concentrations of the reactive species that were stabilized on collection.

1.4 RESULTS AND CONCLUSIONS

The following summary of results and conclusions describes the more important results obtained in the current study and places these results in the perspective gained in the three studies in this series.

1.4.1 Cloud Water Composition

Most cloud water samples have a composition close to the average composition, and the average compositions have not changed significantly in the 1982-1985 time period. The average composition of the samples collected in May-June 1985 is shown in Figures 1-1 and 1-2. These data fall in the range specified in the Final Report for the 1981-1982 cloud sampling flights, which was

> 40-50% of the equivalents were nitric acid,
> 20-30% ammonium sulfate, and
> 10-20% were sodium chloride.

This recipe is intended to give a simple summary of the cloud water composition and is not intended to imply that the sources of hydrogen and nitrate ions are related nor that the sources of ammonium and sulfate are related.

Table 1-1 summarizes the mean values and the ranges of concentrations of some of the more significant cloud water species observed in the studies in this series. The following statements summarize some of the findings for the composition of the cloud water:

1. By far the dominant ionic species in cloud water is nitrate.
2. The species of second importance is sulfate. On a mass basis, the

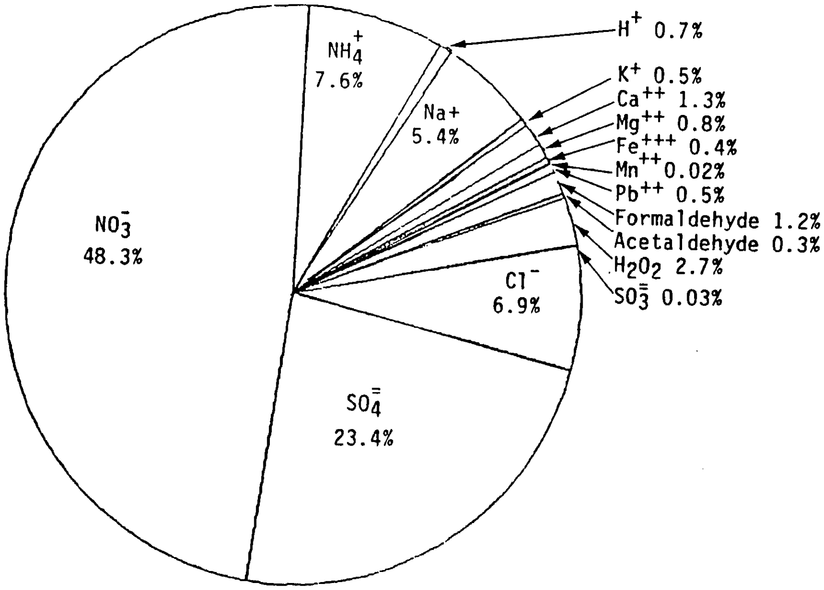

Figure 1-1. May-June 1985 average cloud water composition by mass. Only species determined are included.

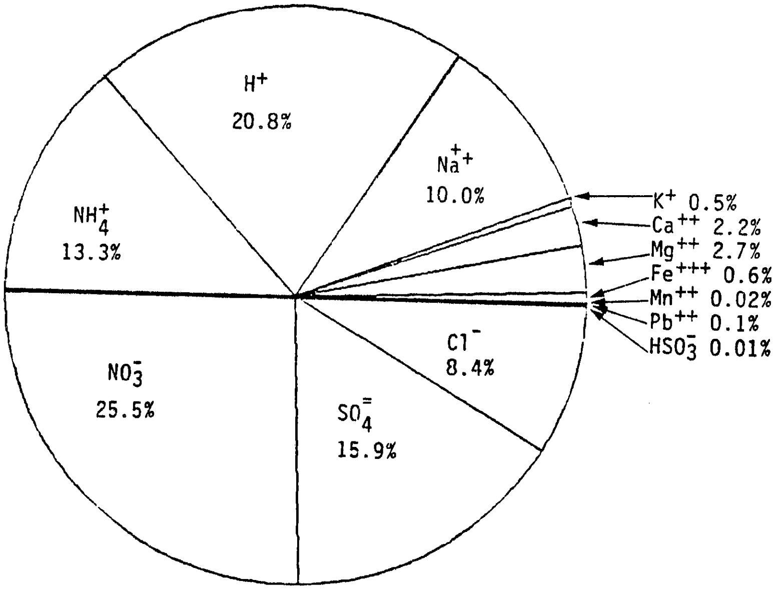

Figure 1-2. May-June 1985 average cloud water composition by equivalents. Only ionic species determined are included.

Table 1-1. Summary of cloud water concentrations

Analyte	Time Period	Mean	Maximum	Minimum
Ambient concentrations of water species in µg/m^3				
Sulfate	May 1982	15.4	38.4	4.0
	Jun 1984	6.5	12.1	3.3
	May-Jun 85	10.6	15.5	3.7
Nitrate	May 1982	35.8	91.0	7.6
	Jun 1984	16.5	24.0	7.3
	May-Jun 85	21.8	40.4	5.2
Ammonium	May 1982	5.8	18.	0.6
	Jun 1984	1.6	2.3	0.8
	May-Jun 85	3.4	7.5	0.6
Water concentrations in µM				
H2O2	May 1982	33	88	1
	Jun 1984	55	127	16
	May-Jun 85	57	167	12
HCHO	May 1982	37	72	6
	Jun 1984	43	73	20
	May-Jun 85	29	53	11
pH	May 1982	2.98	3.59	2.34
	Jun 1984	3.01	3.60	2.83
	May-Jun 85	3.35	3.82	2.90

average sulfate concentration in the cloud water was less than half that of nitrate.

3. In most samples and also on the average, the number of equivalents of hydrogen ion was greater than the number of equivalents of sulfate. Therefore, sulfate alone cannot account for the cloud water acidity.

4. A few cloud samples collected in the fall of 1983 after storms had a composition which was not close to the typical cloud water composition but was very close to the composition of sea salt. Sea salt does contribute to the observed ionic species in the cloud water.

5. All observed cloud water pH values fell in a relatively narrow range close to pH 3.0 and the great majority of the readings were in the range from pH 2.5 to 3.5.

6. The most important cation in the cloud water was ammonium, followed closely by sodium.

7. Sulfur (IV) was found in significant concentrations in the cloud water in 1981 and 1982, but has been essentially absent in the cloud water since that time. This change may be due to recent decreases in the sulfur emissions in the Los Angeles basin.

8. In May-June 1985 and in all prior studies in this series, hydrogen peroxide has been found in all cloud water samples which have been analyzed for this species. Hydrogen peroxide is known to oxidize sulfur (IV) to sulfate very rapidly.

1.4.2 Spatial Distributions

The composition of the atmosphere above Los Angeles when stratus clouds are present shows strong vertical gradients, but at cloud level the composition is fairly uniform throughout the basin.

The stratus clouds which can be sampled by aircraft occupy an altitude range only a few hundred feet deep approximately 2000 ft above ground level. Below the clouds, ozone concentrations at night show large changes with the height above ground level. Ozone concentrations are typically at or close to zero at ground level but are in the range of 50 to 100 ppb in the clouds. Ozone concentrations just above cloud tops are typically 10 to 60 ppb greater than in the top of the clouds.

When flying at a constant altitude in and out of clouds, it is usually observed that the ozone concentrations are higher out of the cloud than in. Data from a series of horizontal flights in June 1984 were averaged and ozone concentrations were 7.6 ppb greater out of the clouds than in. Decreased ozone concentrations in the clouds may be due to a combination of meteorological and chemical processes.

Data from the May-June 1985 and prior studies show no significant horizontal spatial gradients for the concentration of sulfate and nitrate in the cloud water in the Los Angeles Basin. The sulfate and nitrate concentrations in the cloud water in coastal areas were similar to those found in the inland portions of the Basin. The cloud water pH also shows little variation within the Basin. This generalization even holds for cloud water samples collected just offshore. Lead, soot, and other pollutants in the water samples collected offshore show that the clouds sampled there contained urban emissions.

High sulfate and nitrate concentrations in clouds in the vicinity of sources were observed in only one case. This was in the clouds near Fontana the night of 21-22 May 1982, when the emissions in that area were greater than they are now. The sulfate and nitrate concentrations observed that night were roughly double the highest concentrations observed in recent years.

The only measured species in the cloud water to show a significant horizontal spatial gradient was hydrogen peroxide. In May-June 1985, hydrogen peroxide concentrations were highest just offshore and along the coast and became smaller with increasing distance inland. The average hydrogen peroxide concentrations in the Fontana area were roughly 30% of the average concentrations measured offshore.

1.4.3 Removal Processes

A significant effort was made in May-June 1985 to obtain cloud water composition data in such a manner that changes in composition with time could be observed and chemical formation rates could be estimated. When samples were collected at roughly one hour intervals in approximately the same air parcel, it was found that the ambient concentrations of most species in the clouds changed little with time. Figure 1-3 shows the average time evolution of the composition of the clouds observed in the May-June 1985 flights which followed air parcels. The data in this figure are ambient concentrations ($\mu g/m^3$), so they are unaffected by cloud evaporation and cloud condensation. Note the logarithmic scale and the small distance in the plot for factor of ten concentration change.

Except for lead, the average concentrations of trace metals tended to decrease, the sulfate concentration tended to remain constant, and the nitrate concentration tended to increase with time. Ammonium showed the greatest increases in concentration. None of these trends in concentrations were statistically significant. The processes for removing acid species from the clouds were more evident in the data than the formation processes, so removal is discussed first in this summary.

The one time in May-June 1985 when a significant concentration trend was observed during a flight was the morning of 26 May, when there was enough drizzle where the aircraft was sampling to cause some runoff from paved areas. Figure 1-4 shows on a logarithmic scale the ambient concentrations ($\mu g/m^3$) of species in the cloud water during this event. The average concentration of sodium, potassium, calcium, and magnesium in the cloud water decreased by about a factor of 2 each hour. The concentrations of nitrate and sulfate decreased less than that, and the ammonium and lead concentrations changed little. These data show that the settling of large droplets out of the clouds can be a significant removal process.

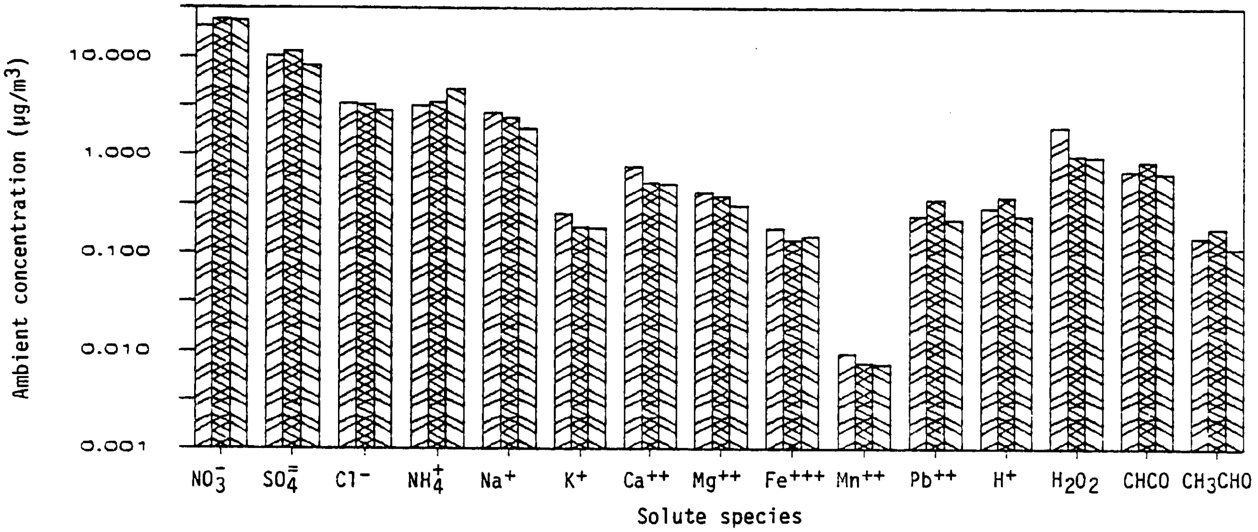

Figure 1-3. Trends with time in the average ambient concentrations of cloud water species measured in flights in which air parcels were approximately followed. Note the logarithmic concentration scale. The three bars for each species show average concentrations measured at approximately one hour intervals.

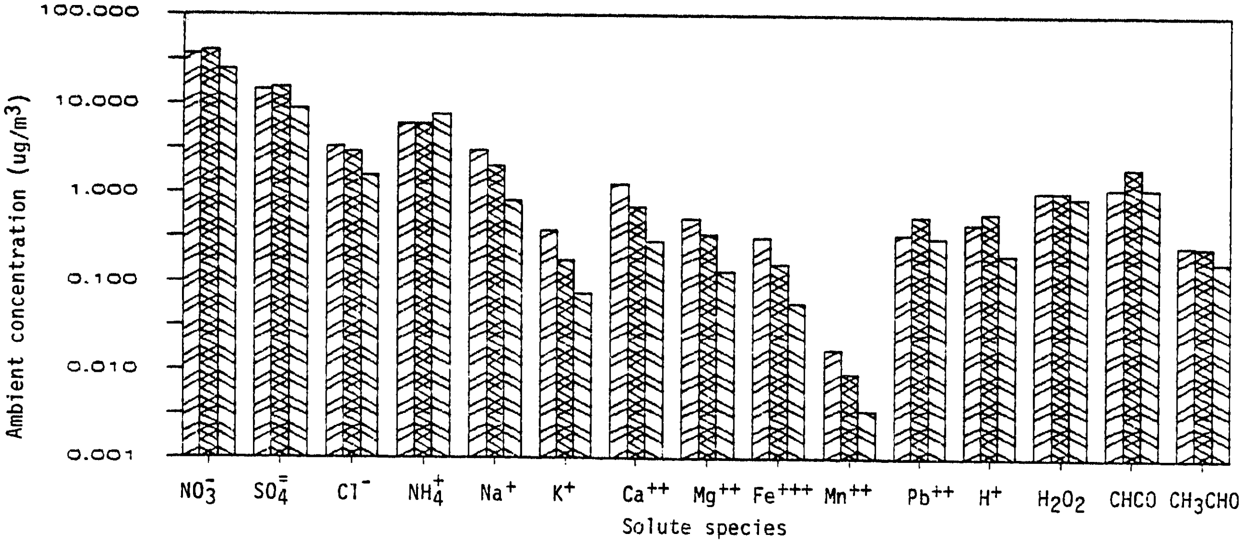

Figure 1-4. Ambient concentration by mass of species in the cloud water on a night when there was significant drizzle. The three bars for each species show concentrations measured at one hour intervals.

The increase with time of the concentration of ammonia and the relative constancy of the concentration of lead in the cloud water indicate that vertical mixing is also a significant processes. The relative importance of vertical mixing and droplet settling in removing species from the clouds can not be determined from the data obtained in this study. The average cloud water concentration trends observed in this study do show that removal processes are typically taking place and have a significant effect on the cloud water composition.

It is suggested that the settling of large droplets and their evaporation before reaching the ground provide a significant pathway for depositing large aerosol particles in the atmosphere below the clouds. Droplet settling has been found in other studies to be an important removal process in California fogs, and large particles containing nitrate have been observed at ground level in the morning in other studies in the Los Angeles Basin.

Rough calculations have been performed to estimate the composition and size distribution of the aerosol left behind when the sampled clouds evaporate the following day. It is assumed that all of the volatile acids, such as nitric and hydrochloric acid, evaporate until either all the nitrate and chloride or all the hydrogen ion are gone. The average composition of the aerosol remaining after the clouds sampled in May-June 1985 have evaporated is shown in Figure 1-5. Only species for which analyses were performed are included in the figure, and no effort has been made to estimate the importance of undetermined species, such as organic compounds. The fraction of nitrate in the aerosol is much smaller than the fraction of nitrate in the cloud water before evaporation shown in Figure 1-1.

1.4.4 Formation Processes

The data discussed in the previous section suggest that competing processes were taking place: removal of dissolved species in the cloud water by drizzle and additions of emissions to the clouds by vertical mixing. Since sulfate and nitrate are not emitted in significant amounts, these species are formed in the atmosphere. This section discusses the information about these formation processes in stratus clouds in the Los Angeles Basin obtained from this series of studies.

High nitrate concentrations are typically observed in the cloud water and the May-June 1985 data show a tendency for the nitrate concentration in the cloud water to increase with time in relation to the concentration of other species. These observations suggest that nitrate is formed in the clouds at night. Mechanisms which could be very effective at forming nitrate in the clouds at night are known, and it is likely that a significant portion of the observed increase in the ratio of the concentration of nitrate to the concentration of other species observed in the cloud water in May-June 1985 is due to the conversion of NO_x to nitrate in the clouds at night.

Sulfate concentrations showed less increase with time than nitrate. Because hydrogen peroxide has been found in every cloud water sample analyzed for this species, it is believed that the rate of formation of sulfate is limited by the availability of sulfur (IV) in clouds. Direct measurements support this belief by showing that sulfur dioxide concentrations in clouds

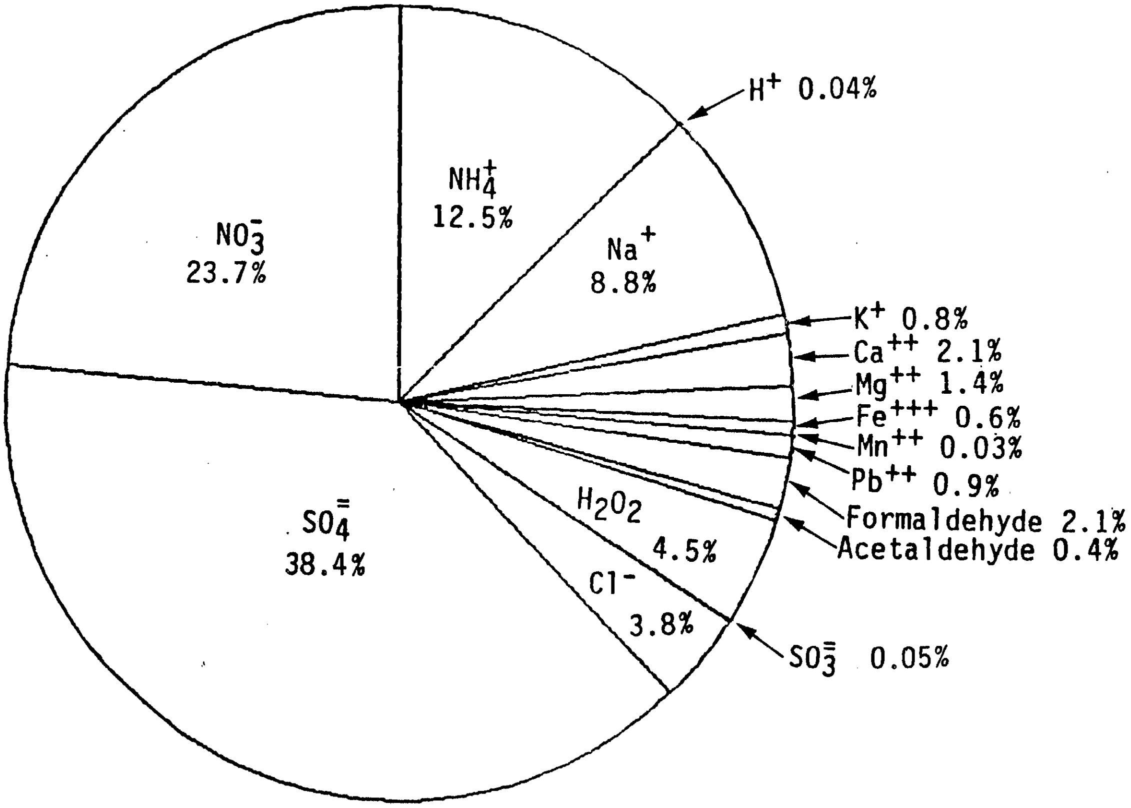

Figure 1-5. Calculated May-June 1985 average composition by mass of the aerosol remaining after cloud evaporation. Only species determined are included. Compare with Figure 1-1.

are above the detection limit (about 1 ppb) only in isolated plumes, and that sulfur (IV) concentrations in the cloud water are usually more than 1000 times smaller than the sulfate concentrations.

The observed hydrogen peroxide concentrations provide the potential for the formation of significant amounts of sulfate in the stratus clouds if sulfur dioxide were to be mixed into the clouds. In 1985, the ratio of hydrogen peroxide to sulfate was such that sulfate concentrations would immediately increase by an average of 65% to an average concentration of 15 $\mu g/m^3$ if enough more sulfur dioxide was mixed into the clouds to react with all the hydrogen peroxide. In three cases out of the total of 18 examined, this additional sulfate would have caused the sulfate concentration in the cloud water to have exceeded the California standard of 25 $\mu g/m^3$.

The data from the airborne cloud sampling reported here combined with the current understanding of the chemistry of hydrogen peroxide and sulfur (IV) show that hydrogen peroxide is the most important oxidant for converting sulfur dioxide into sulfate in the stratus clouds which were sampled in these studies.

The fact that only limited formation of nitrate and sulfate was observed during the time of the sampling flights reported here does not imply that these rates are always small in clouds. For example, no data were obtained while clouds were forming in a polluted air mass, and rapid chemical processes could take place at that time. Also, because of the logistical problems of flying under air traffic control in clouds in the congested Los Angeles air space, no effort was made to chase plumes in the clouds. It is believed that rapid sulfate formation was taking place in the sulfur dioxide-containing plumes which were observed in the clouds in each study year.

The highest sulfate and nitrate concentrations recorded in this series of studies were observed in plumes in the Fontana area the night of 21-22 May 1982 and are reported in Table 1-1. This is the only case observed in which high concentrations of acid species could be attributed to local sources. Emissions in the Fontana area have decreased in recent years and the observation of similar high concentrations in clouds in that area has not occurred again.

1.4.5 Data Volume

A comprehensive Data Volume containing the results of the May-June 1985 flights has been prepared for use by the ARB staff and to make these data available for the evaluation of computer models of cloud chemistry in the Los Angeles Basin.

2. RECOMMENDATIONS

It is recommended that a study be conducted in which the data collected in this and the two prior field studies in this series be used as input to a cloud chemistry computer model appropriate for the Los Angeles Basin. Such a modeling effort could be accompanied by the preparation of journal articles summarizing the more important findings of this series of studies.

If more airborne sampling is done in stratus clouds in the Los Angeles Basin, it is recommended that the range of chemical species determined in the chemical analyses be expanded to include organic compounds. It would be desirable to determine at least the total concentrations of organic compounds in the cloud water and the concentrations of some of the major classes of compounds.

When considering sulfate control strategies, it should be remembered that hydrogen peroxide was found in all cloud water samples analyzed for this species. Therefore, if additional sulfur dioxide were added to the clouds, it would be rapidly oxidized to sulfate.

3. INTRODUCTION

Sonoma Technology, Inc. (STI) conducted a study in May and June 1985 for the California Air Resources Board in which an aircraft was used to collect cloud water, aerosol, and gas samples and to make other air quality and meteorological measurements in stratus clouds in the Los Angeles Basin. This study continued the research on Los Angeles Basin stratus begun in 1981.

The Los Angeles Basin frequently experiences high concentrations of sulfate and nitrate in cloud-free air as well as in clouds and fogs. Prior work in this series of studies and in other studies strongly suggest that stratus clouds have the potential to cause the rapid formation of sulfate. The high concentrations of nitrate always observed in the stratus clouds in Los Angeles also suggest that nitrate may be formed in these clouds. Stratus clouds are most often present at night, and chemical reactions are known which have the potential to cause the rapid nighttime formation of sulfate and nitrate. Because these species can cause visibility degradation, material damage, and when concentrations are high enough, ecological damage and adverse health effects, it is of interest to study the chemistry of stratus clouds in the Los Angeles Basin to learn more about the processes taking place in them which form acid species.

In spite of the potential importance and great current interest in the formation of acid species in clouds and fog, there is almost no unambiguous field data for the rate of these processes. This study was designed to obtain as much chemical conversion rate data as possible within the resources available.

Airplanes provide an ideal means for obtaining chemical conversion rate data in clouds because of their ability to sample where the reactions of interest are taking place. They can also follow air parcels to observe concentration changes with time. It is important to sample clouds because the composition of the atmosphere aloft is different from that at ground level in the Los Angeles Basin, especially at night. Ozone and possibly other oxidants persist aloft at night whereas ozone is consumed at ground level in urban areas by fresh emissions of NO.

It is believed that the best information on the cloud chemistry is obtained by the use of both cloud chemistry computer models and field studies. Therefore, it was also an objective of this study to produce a data base suitable for use in computer models. There is an opportunity to improve the understanding of cloud chemistry in the Los Angeles basin by modeling the data in this report because recent simulations (see, for example, Young et al., 1983) give data which do not agree with the findings described in the following pages. In particular, hydrogen peroxide was always found in the cloud water, whereas most model simulations predict that it is rapidly consumed and has a very small concentration in clouds.

The previous Final Report in this series (Richards *et al.*, 1985) contains a more complete review of the state of knowledge of the chemistry of stratus clouds. The remaining information from this series of studies is contained in the first Final Report (Richards *et al.*, 1983b). Also, a preliminary communication on the chemistry of sulfur (IV) has been published (Richards *et al.*, 1983a). Publications prepared during the current study include an invited paper (Richards *et al.*, 1986a) and a Data Volume (Richards *et al.*, 1986b). The Data Volume gives a complete account of the data obtained from this study.

4. OBJECTIVES

The objectives were to:

1. Determine the rates of formation of sulfate, nitrate, and acidity in clouds in polluted air masses in the Los Angeles Basin.
2. Characterize the air masses in which these rates are measured to provide information on:
    a. The factors which control the rate of sulfate and nitrate formation,
    b. The reaction pathways by which they are formed, and
    c. The distribution of the reaction products between the cloud water and the interstitial aerosol.
3. Determine the spatial relationship of acidity to sources in clouds in and upwind of the Los Angeles Basin.
4. Compare the results with simple model calculations to obtain information on the rates and dominant chemical pathways for the formation of sulfate, nitrate, and acidity in clouds.
5. Make the results available in a Final Report and also a comprehensive Data Volume which can be used by others to evaluate cloud chemistry computer models.

5. EXPERIMENTAL

The experimental equipment and procedures used in this study are described in some detail in this section. It is anticipated that the data contained in this report will be useful to other research workers interested in modeling the chemistry of the stratus clouds in Los Angles. Therefore, the experimental procedures have been described in enough detail to document the strengths and weaknesses of the reported results.

This section begins with a description of the airborne sampling system used to obtain the data followed by an outline of the instrument calibration procedures, and a description of the methods used to chemically analyze the samples collected by the aircraft. The methods used to obtain upper air data are described, followed by a description of the aircraft flight patterns. The section ends with an outline of the data reduction procedures and a description of the Data Volume containing the results of the study.

5.1 AIRCRAFT SAMPLING SYSTEM

The airborne sampling was performed with the STI twin-engine Beechcraft Queen Air, which is an all-weather aircraft with sampling speeds between 180 km/hr and 290 km/hr. There are six sampling ports and manifolds for aerosol and gas sampling, and ports for two warm cloud water collectors. Two inverters provide 1 kW each of 110 V 60 Hz power for instrument use. An engine-driven vacuum pump plus an additional pump driven by a 24 V DC motor provide vacuum for the filter and bubbler sampling. The location of the sample inlet lines and the external probes is shown in Figure 5-1.

5.1.1 Continuous Monitoring Instrumentation

The air quality sampling instruments in the Queen Air are described in Tables 5-1 and 5-2. The sampling manifolds which bring the outside air into the aircraft cabin have a high air flow rate and are drained so that cloud water which collects in them does not flow into the instruments. Most instruments sample from these manifolds at a much smaller flow rate. The manifold for the nephelometer includes a cyclone to remove particles larger than about 2 μm so the nephelometer responds to the accumulation mode aerosol but is relatively insensitive to clouds.

Aerosol size distribution information for particles between 0.1 μm and about 1 μm diameter were obtained by the Active Scattering Aerosol Spectrometer Probe (ASASP-X) manufactured by Particle Measuring Systems, Inc. This is an optical particle counter in which the particles pass through a laser beam within the resonant cavity, and thus are strongly enough illuminated that very small particles can be detected and sized. As indicated in Table 5-2, the instrument has four particle size ranges and can be

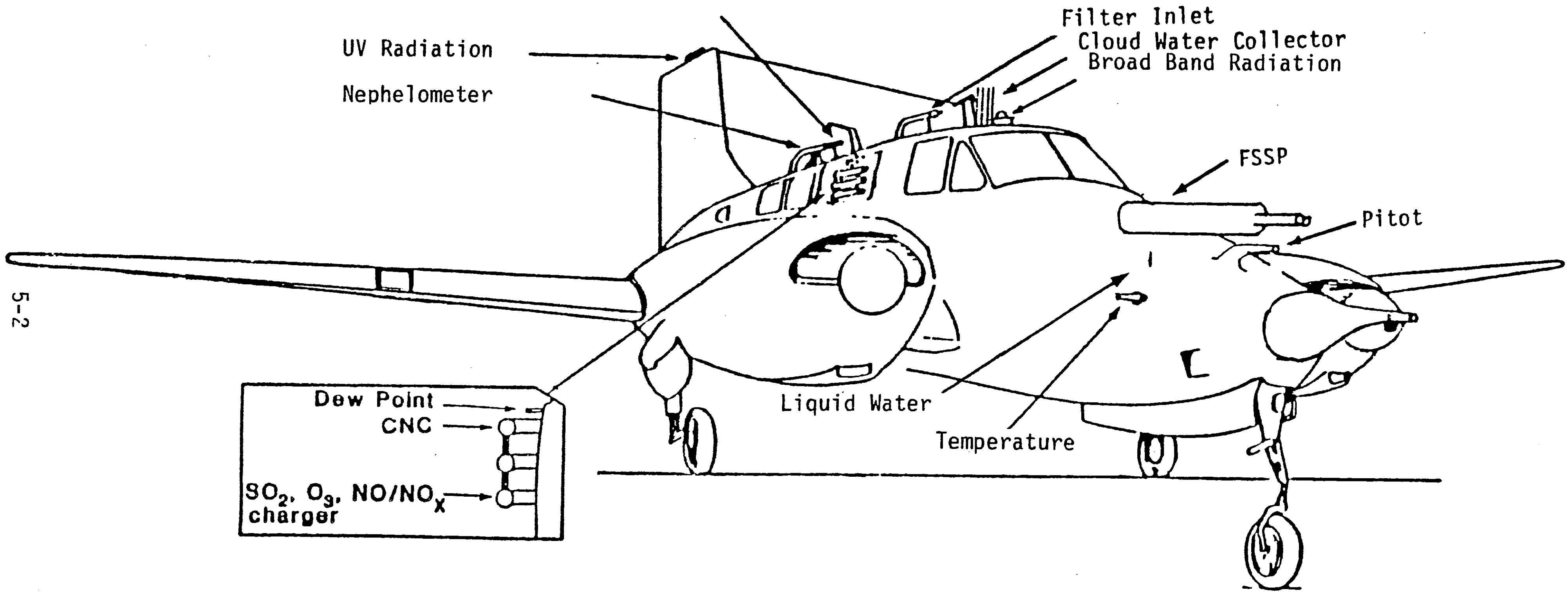

Figure 5-1. Schematic Drawing of STI Queen Air.

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 few minute averages	<10 ppb 1 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}	3s	10^3 cm^{-3}
Aerosol Charge Acceptance	Washington University	Aerosol Charge Acceptance	Primarily responds to .01-.1 μm dia 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
pH	Microelectrodes MI-710	Glass electrode	0-14	>10 s	0.1

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	0.5 s/° C	0.5° C
Dew Point	General Eastern	Cooled Mirror	-50° to +50° C	0.5 s/° C	0.5° C
Liquid Water Content	STI	Heated rod	> 5 g/m^3	< 1 s	0.1 g/m^3
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)
"	II-Morrow	LORAN-C		Updates several times/sec with a 15 sec running avg	15 m
Data Logger (includes time)	MRI Data System	9-track tape - 6 hr 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. Aerosol Size Distribution Instrumentation

Instrument	Nominal Size Range	Method
PMS ASASP-X[†]		Optical Particle Counter Illumination in laser Cavity and ~35° to 120° collection
Range 3	0.090 - 0.195 μm	
Range 2	0.15. - 0.30 μm	
Range 1	0.24 - 0.84 μm	
Range 0	0.60 - 3.0 μm	
PMS FSSP-100[†]		Forward Scattering Spectrometer Probe
Range 3	0.5 - 8 μm	
Range 2	1 - 16 μm	
Range 1	2 - 32 μm	
Range 0	2 - 47 μm	

[†] The Particle Measuring Systems (PMS) opticle particle counters can be manually set to any range, or can be set to automatically cycle through the ranges with one second in each range.

manually set to any range, or can be set to automatically cycle through the ranges with one second in each range. In the automatic mode, four seconds are required to sample the full 0.1 μm to 1 μm size range.

The size distribution of the aerosol particles and cloud water droplets with diameters greater than about 2 μm was measured with the Forward Scattering Spectrometer Probe (FSSP-100) manufactured by Particle Measuring Systems, Inc. This probe is on the nose of the Queen Air and samples particles in the undisturbed air flow. The probe has four ranges and can be set to sample continuously in just one of them or to cycle through the ranges in exactly the same manner as the ASASP-X. In the experiments reported here, the FSSP was set to sample just one range to continuously obtain data for particles in the 2 to 32 μm size range. The data from the FSSP can be used to calculate the cloud liquid water content (LWC).

The cloud LWC was also measured with a probe developed by King et al. (1978) at the CSIRO in Australia. This probe works by monitoring the amount of power needed to maintain a constant temperature in a rod exposed to the air flow. When water impacts on the probe, additional power is required to offset the cooling caused by the evaporation of the water. The LWC of a cloud is calculated from the additional power required to evaporate the water, the thermodynamic properties of water, and the speed of the aircraft. King has shown that the response time of the probe is much less than one second and that the calibration constants of the probe can be calculated from the probe geometry and temperature. He has also experimentally shown that the calculated calibration constants are correct.

Most of the instruments listed in Table 5-1 are standard, commercial instruments. This has the advantage that if an instrument fails, parts can be obtained or a replacement borrowed in a matter of hours and the sampling program can continue on schedule with all instruments operating. When standard instruments are used for airborne sampling, the change in the instrument calibration caused by pressure changes resulting from altitude changes must be taken into account. This is done in the data processing as described in Section 5.6.

5.1.2 The Airborne Collection of Chemical Grab Samples

The equipment for collecting grab samples for chemical analysis is described in this section, but the chemistry of the sample collection and analysis is described in Section 5.3. When stabilizing solutions or filter treatments are used to collect specific chemical compounds, their chemistry is described along with the chemical analysis.

It should be noted that no samples were drawn into bags or other containers before being submitted to the measurement instrument or being drawn through the collection device. It is believed that the intermediate storage of samples in bags can compromise their integrity, especially in clouds where sampling systems tend to become wet.

Cloud water collector. Cloud water was collected by samplers designed by a group at the State University of New York at Albany under the direction of Volker Mohnen (Winters et al. 1979; Mohnen 1980). The cloud water is collected by impaction on the front of 3/8 inch diameter rods which project into the air flow. Grooves in the front of these rods conduct the cloud water downward into the collection bottle, which is in the aircraft cabin so that it can be easily changed during sampling. Immediately after collection, the cloud water sample bottles were placed in an ice chest which keeps the sample temperature near 4° C.

The cloud water collector was designed to collect particles larger than about 3 μm and to be very inefficient at collecting submicron sized particles. Therefore, the cloud water samples collected by this device should be relatively uncontaminated by accumulation mode and nuclei mode size aerosol. It is recognized that the chemical composition of the cloud water collected by this sampler may differ somewhat from the composition of the clouds being sampled due to such factors as the variation in collection efficiency as a function of cloud droplet size and LWC (Huebert and Baumgardner, 1985).

The Queen Air has two cloud water collectors. One is equipped with a miniature pH electrode and a flow system between the water collector and the collection bottle which permits the continuous recording of the pH of the collected water. No stabilizing solutions were added to the water from this collector.

The second cloud water collector was used to collect water directly in stabilizing solutions for labile species. The tubes leading from each of the collector rods were separated into two bundles so that the sample flow was split between two bottles. One of the bottles contained the stabilizing solution for the determination of hydrogen peroxide, and the other was used either for the determination of sulfur (IV) or for carbonyl compounds.

Filter Sampling System.. The air flow for both the filter sampling system and the Integrating Nephelometer passed through a cyclone designed to remove particles larger than about 2 μm and pass particles smaller than about 1 μm with high efficiency. The cyclone prevented the filters from becoming wet and also made it so that the filter samples complimented the cloud water samples. The sample flow for four filter holders was drawn from the sample flow for the Nephelometer. The flow through each filter was controlled by a needle valve downstream from the filter and measured by a rotameter. Records were kept of the air pressure in the rotameters for use when calculating the sample air flow rates.

The filters were loaded into their holders on the ground before the flight, and were stored in Ziploc bags in a tackle box. Each Ziploc bag contained a set of holders to be exposed at the same time. The filter holders were color-coded and numbered for identification. After being exposed, the filter holders were returned to the Ziploc bags. After the flight, the filters were transferred to plastic Petri dishes sealed with Parafilm and stored in a thermoelectrically cooled chest. The filters were cooled during shipment to the chemistry laboratory.

Total Sample Collector. STI constructed a "total sample collector" system which was first used in the May 1984 flights for the ARB in the Los Angeles Basin. The results from these initial experiments with the total sample collector system were reviewed and improvements made in the total sample collector system before it was used in the 1985 flights reported here.

This sampler has an isokinetic inlet so that gases and particles of all sizes are collected with unit efficiency. The sampler contained a combination of filters which retained all the gas, aerosol, and hydrometeor sulfate and nitrate in the sampled air. The objective of this sampler is to accurately determine the total concentration of sulfate and nitrate per volume of ambient air without regard to the distribution of these species among the various particle sizes and (for nitrate) the gas phase. In the absence of sulfate and nitrate data from device such as a total sample collector, it is necessary to estimate the total sulfate and nitrate concentrations from data which are subject to significant uncertainty.

The design of the total sample collector contains the following features:

1. The diameter of the nozzle opening was about 4 mm.
2. The isokinetic sample flow at an airspeed of 60 m/s was about 40 lpm.
3. The Reynolds number of the flow within the sampler was great enough (about 15,000) that the flow rapidly became turbulent.
4. The walls of the sampler were heated to maintain their temperature 5° to 10° C above the dew point during sampling. The heat was turned on a few minutes before the sampler was opened to the air flow and turned off at the end of sample collection.
5. The interior length of the sampler was more than 20 tube diameters, so the sample flow was heated well above the dew point and any water which reached the filters should evaporate.
6. About 1 watt of power is required for each degree of heating of the sample flow. Something like 50 watts of power was required to offset the heat loss to the free airstream. This required about 2 amps from the 24 V DC aircraft power.
7. The interior temperature of the sampler was measured with a thermistor.
8. The filter holder portion of the sampler was a commercially available metal filter holder.
9. The filter holder contained paper, Teflon, and nylon filters in series. The paper filter absorbed liquid water which reached the filters during times when large drops were present. The Teflon filter collected the aerosol which penetrated the paper filter. The nylon filter collected volatile nitrate (nitric acid) which penetrated the Teflon filter.

Bubblers. Gas samples were collected in micro-impingers which contained 10 ml of liquid. A sample flow rate of 1 lpm was used. The air flow was drawn from the manifold which supplied sample air to the O_3, SO_2, and NO/NO_x monitors.

Hydrocarbon Canisters. Gas samples were drawn through a Teflon sampling line by a metal bellows pump into 3.2 liter electropolished stainless steel canisters. The canisters were flushed before being filled. Periodically during the sampling program, the canisters were sent to R. A. Rasmussen for analysis by gas chromatography.

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 every few days during the field study. The following calibration methods were used:

1. SO_2 - The Meloy 285 SO_2 monitor was calibrated by 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 - The NO/NO_x monitor was calibrated using the same methods as for the SO_2 monitor. 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 monitor. 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} - The Integrating Nephelometer was calibrated with Freon-12 and with filtered air.

5. The optical particle counters were calibrated with nebulized polystyrene latex particles and with glass beads. The calibration of the FSSP-100 optical particle counter for cloud droplets was determined using beads obtained from Robert Anderson. In many previous experiments, he had compared cloud liquid water contents determined from FSSP's calibrated with these beads and King probes and found that the effective diameter of these beads was 13.5 μm.

The airborne pH sensor was calibrated against standard pH 4.0 and 7.0 buffer solutions. The purpose of this probe is to measure non-uniformities in the pH of the entering cloud water, so no effort was made to stir the buffer solutions during calibration to obtain the best pH measurement accuracy.

The CSIRO-King liquid water probe is an absolute instrument because its calibration can be calculated from the hardware design and operation parameters and the thermodynamic properties of water (King *et al.*, 1978).

During the reduction of the data, the expression for the power loss from the probe as a function of ambient air temperature and airspeed was tested using in-flight data as well as data recorded during a takeoff. It was found that the calculated liquid water contents (LWC) were rather insensitive to the functional form of the expression for the dry power loss.

To confirm the proper operation of the aircraft system before the aircraft was ferried to the field, test flights were made in the Santa Rosa area. At the conclusion of each test flight, the magnetic tapes of the airplane data were dumped and sufficiently processed to be sure that the measurement systems are performing satisfactorily.

Extensive use was made of checklists and flight log sheets during the field measurements. After the flights, the calibration data were reviewed to check the completeness, accuracy, and precision of the results.

5.3 CHEMICAL ANALYSIS OF AIRCRAFT GRAB SAMPLES

The chemical procedures used for the collection and analysis of the grab samples are described in this section. All analyses were performed by subcontractors or consultants who have special expertise in the analyses they performed. In a number of cases, the analyses were performed or supervised by the person who developed the analytical method. The routine analyses were performed by Environmental Monitoring and Services, Inc. (EMSI) of Combustion Engineering.

5.3.1 Cloud Water Samples

With the exception of the samples to be analyzed for formaldehyde and acetaldehyde, the cloud water samples were collected in polyethylene bottles which were prewashed by EMSI. The cleanliness of the bottles was verified by analyzing the wash water. Shortly before each flight, stabilizing solutions were added to the appropriate bottles and all bottles were cooled and weighed. (If the bottles were weighed at room temperature, the collected samples would have to be warmed to room temperature for weighing after the flight.)

In the aircraft, the cloud water sample bottles were stored in ice chests which maintain the sample temperature near 4° C. A thermometer was used to verify that this temperature was maintained. When the aircraft landed, all bottles were weighed to determine the amount of water collected. The sampling and analysis protocol for the cloud water samples is outlined in Table 5-3 and discussed in the following paragraphs.

Unstabilized cloud water. The cloud water samples which were not stabilized were kept refrigerated until delivered to EMSI for the analyses listed in Table 5-3. When the sample volume was limited, the analyses were performed in the order listed until the sample was exhausted. All the analyses could be performed on nearly all of the unstabilized water samples.

In some cases, enough stabilized cloud water was collected in a pass that aliquots could be taken for other determinations. When cloud water samples stabilized for sulfur (IV) were not collected, aliquots of unstabilized cloud

Table 5-3. Cloud water chemistry

Unstabilized cloud water

Environmental Monitoring and Services, Inc. sample

pH
Conductivity
Ion chromatography: sulfate, nitrate, chloride
Colorimetry: ammonium
Atomic absorption spectroscopy: Na, K, Ca, Mg, Fe, Mn, Pb

Cloud water collector with stabilizing solutions

Environmental Monitoring and Services, Inc. sample

Collect cloud water in DNPH solution to determine formaldehyde and acetaldehyde (Fung and Grosjean 1981)

Texas Tech University sample

Collect cloud water in formaldehyde solution to determine sulfur (IV) (Dasgupta et al., 1980)

National Center for Atmospheric Research sample

Collect cloud water in p-hydroxyphenylacetic acid solution to determine hydrogen peroxide (Kunen et al., 1983, Kok and Wilson, 1984).

water were added to the sulfur (IV) stabilizing reagent after the aircraft landed. Aliquots of unstabilized water were also added to the reagents for the determination of hydrogen peroxide after the aircraft landed to see how the analytical results depend on the length of time between water collection and stabilization.

Hydrogen peroxide. The horseradish peroxidase method was used to determine the concentration of hydrogen peroxide in the cloud water (Kunen et al., 1983; Kok and Wilson, 1984; Kok, Thompson, Lazrus, and McLaren, 1986). The cloud water was collected directly into a solution containing horseradish peroxidase and p-hydroxyphenylacetic acid, which is the monomer of the fluorescent dimer formed in the horseradish peroxidase method for hydrogen peroxide. Thus, the first step in the hydrogen peroxide analysis was carried out immediately as the cloud water was collected. The resulting solution is stable for a week or more and was shipped to Boulder, CO for the remainder of the hydrogen peroxide determination (Kok and Wilson, 1984; Kok, Thompson, Lazrus, and McLaren, 1986). Calibration standards were prepared in the field using known amounts of hydrogen peroxide and were delivered along with the unknowns to provide calibration standards and to assure that the samples were not degraded. Also, some samples of unstabilized cloud water were first treated with catalase to destroy the hydrogen peroxide then added to the reagents described above. These samples were used to see of organic peroxides or fluorescent organic materials were interfering with the analyses.

G. L. Kok at NCAR was responsible for the hydrogen peroxide analyses and provided the equipment and chemicals used in the field to carry out the above procedures.

Carbonyl compounds. To minimize contamination, the samples to be determined for formaldehyde and acetaldehyde were collected in glass bottles. The analytical method used has been described by Fung and Grosjean (1981) and by Grosjean (1982). The aqueous solution of 2,4-dinitrophenylhydrazine (DNPH) and the organic layer were added to the sample bottles by EMSI. These bottles were cooled and weighed before the flight, and cloud water was collected directly into these bottles. The DNPH derivatives of the carbonyl compounds were thus formed in flight as the water samples were collected. The concentrations of the derivatives were determined by liquid chromatography at EMSI using methods described by Fung and Grosjean (1981) and by Grosjean (1982).

Daniel Grosjean served as a consultant for these determinations.

Sulfur (IV). Cloud water samples to be analyzed for sulfur (IV) were collected directly into a buffered formaldehyde solution. Sulfur (IV) in these solutions is stable for a week or more (Dasgupta et al., 1980). These samples were shipped to P. K. Dasgupta at Texas Tech University for analysis (Dasgupta, 1981).

Dr. Dasgupta was a consultant to this project. He advised on the collection and analytical methods for sulfur (IV) and all of the sulfur (IV) analyses were performed in his laboratory. (Dasgupta and Gupta, 1986).

5.3.2 Filter Samples

The analytical methods and the species to be determined on each filter are listed in Table 5-4. The laboratory which performed each analysis is also indicated.

Teflon filters from the Teflon-nylon filter pack were extracted in buffer (to prevent the loss of ammonium) and analyzed for anions by ion chromatography and ammonium by colorimetry.

Teflon filters from the Teflon-carbonate filter pack were typically archived. About 10% of these filters were analyzed in the same manner as the Teflon filter from the Teflon-nylon filter pack to provide replicate data for quality control.

Nylon filters from the Teflon-nylon filter pack were extracted in the eluent solution used for ion chromatography and nitrate determined by ion chromatography. The nitrate on the nylon filter was used to estimate ambient nitric acid concentrations, and was combined with the nitrate concentrations on the Teflon filter to determine total nitrate concentrations. It is known nitrate can be volatilized from the Teflon filter by acidic species, especially in clouds in Los Angeles, and be carried onto the nylon filter. Thus, not all nitrate on the nylon filter was in the gas phase in the clouds. Also, other species such as HONO, NO_3 radical, and N_2O_5 may be retained by the nylon filter and reported as nitrate.

Carbonate impregnated filters were prepared at EMSI using procedures developed at the Brookhaven National Laboratory (Forrest et al., 1981). The filters were analyzed by water extraction, peroxide oxidation to convert any sulfur (IV) on the filter to sulfur (VI), dilution to prevent carbonate interference, and determination of sulfate by ion chromatography. The observed sulfate levels were used to calculate the ambient sulfur dioxide concentration.

Quartz filters were collected to determine elemental carbon concentrations by a visual ranking of the darkness of the filters.

Total sample collector filters were analyzed by the same methods as the filters from the Teflon-nylon filter pack. Sulfate and nitrate on each of the three filters were determined by ion chromatography.

Blank filters were carried on each flight and analyzed along with the samples. The analytical laboratories were not aware which filters were blank when they performed the analyses.

5.3.3 Bubbler and Canister Samples

Bubblers for Carbonyl Compounds. Air samples were drawn through bubblers containing an aqueous solution of 2,4-dinitrophenylhydrazine (DNPH) and an organic layer (Fung and Grosjean, 1981; Grosjean, 1982). The contents of these bubblers were analyzed for formaldehyde and acetaldehyde by EMSI using the same procedures as for the cloud water samples collected into DNPH.

Table 5-4. Filter and bubbler chemistry

ID code letter	Flow (lpm)	Diam. (mm)	Filter medium	Method and analytes	Analytical laboratory
Filters collected behind 2 μm cut cyclone.					
H	50	47	Teflon	Ion Chromatography (IC): sulfate and nitrate Colorimetry: ammonium	EMSI
			Carbonate impregnated	IC sulfate to determine sulfur dioxide	EMSI
N	30	47	Teflon	Replicate IC & Colorimetry on selected filters. Archive others as backup	EMSI
			Nylon	IC nitrate to determine nitric acid	EMSI
Q	30	47	Quartz (masked to 10 mm)	Visual reflectance for elemental carbon.	STI
X	25	25	Teflon	Archived for replicate or trace metal analysis.	---
Total sample collector					
T	50	47	Paper Teflon Nylon	Ion Chromatography: sulfate and nitrate Colorimetry: ammonium	EMSI
Bubblers					
Bubbler sample collected at about 1 lpm with 2,4-dinitrophenylhydrazine solution for formaldehyde and acetaldehyde (Fung and Grosjean 1981).					EMSI
Bubbler sample collected at 1 lpm in which the air flow is passed first through water then through 0.1 N KOH. The KOH solution was analyzed for acetate as an indicator of PAN.					TTU

EMSI: Environmental Monitoring and Services, Inc. of Combustion Engineering
STI: Sonoma Technology Inc.
TTU: Texas Tech University.

Bubblers for PAN. It was desired to place an upper limit on the PAN concentration in the clouds to determine whether or not PAN could contribute to the readings of the chemiluminescent NO_x monitor. This was accomplished by a bubbler system in which the air was first drawn through water to remove soluble acetate compounds, then through 10 ml of 0.01 N KOH solution, which collected PAN in the form of acetate. The bubbler tubes containing KOH were prepared by EMSI and were analyzed by P. K. Dasgupta at Texas Tech University by an ion chromatographic procedure. Formaldehyde was added to each bubbler immediately after the flight to prevent bacterial alteration of the acetate concentrations.

Canisters for Hydrocarbons. One stainless steel canister was flushed and filled with a sample of ambient air during the first or second orbit of each flight which was designed to observe chemical changes. These canisters were shipped to R. A. Rassmussen at Biospherics Research, Inc. for analysis by gas chromatography.

5.4 RAWINSONDES

The aircraft flights designed to observe chemical conversion rates were supported by upper air soundings which measured the wind speed and direction in the clouds. One sounding was made about one hour before takeoff and the other during the middle of the flight. These data were worked up immediately and were then transmitted to the aircraft crew as part of the information used to guide the flight.

The equipment used was a manually guided RD-62 Rawinsonde.

5.5 METEOROLOGICAL FORECASTS AND FLIGHT LOGISTICS

The Ontario International Airport was used as a base for all sampling flights. After the aircraft was prepared, the crew and Queen Air remained in Santa Rosa until a suitable 3 to 5 day weather forecast was obtained. Then the aircraft and crew traveled to Ontario and made flights on a day-to-day forecast basis.

Contact was initiated with air traffic control personnel several months in advance of the planned flights to acquaint them with our plans and needs. As the time for the study drew near, instructions on people to contact and procedures to be followed were obtained. These contacts were reinforced with personal visits on arrival at Ontario and occasionally after that.

Most flights were made at night. The 9:00 am (local time) weather data were used to make a decision whether or not to prepare for a flight that night. If a flight was planned, the weather was examined again that afternoon and just before the planned takeoff time. Some planned flights were delayed because the clouds were not forming as early as expected, and others scrubbed because of lack of clouds.

The noise complaints encountered in previous years led to the design of a new flight pattern for the flights designed to observe chemical changes. Instead of circling over one location and generating a continuous noise for some residents, the aircraft flew back and forth along a line between 15 and 20 km long as shown Figure 5-2. These flight lines were selected to be roughly perpendicular to the expected wind direction and separated by about the distance the clouds were expected to move in one hour. Clearance to fly these patterns was obtained well before the start of the field program. A plot generated by computer from LORAN data for the actual flight patterns during Flight 435 in the Ontario area on 26 May 1985 are shown in Figure 5-3. These flight patters were quite effective in abating noise complaints.

The three-dimensional distribution of pollutants in the basin was explored by means of a flight pattern which included missed approaches at a number of airports. When an aircraft is making an approach to an airport under instrument conditions, it can stop descending at any time and fly above the glide slope until it reaches the departure route for missed approaches. It then must climb as specified by the departure route. Using a missed approach allows sampling at lower altitudes than would otherwise be possible.

After each flight, the aircraft was met and the grab samples were immediately taken back to the motel. All of the operations specified in the above descriptions of the chemical procedures for the cloud water samples were carried out immediately and the samples placed in a refrigerator. The filter samples were typically unloaded after a few hours sleep and the petri dishes containing the filters placed in Ziploc bags in a refrigerator.

5.6 DATA REDUCTION

At the conclusion of the sampling, all aircraft magnetic tapes were processed to obtain magnetic tapes of data in engineering units. The Meloy 285 SO_2 monitor is known to shift its zero as a function of pressure. This effect is compensated for during data processing by using results recorded during a "zero spiral" at the end of several of the flights. The zero spirals cover the range of altitudes over which sampling was done. The SO_2, NO/NO_x, and O_3 monitors are operated in a zero mode during this spiral to document any pressure effects on the instrument zeros. Instrument zeros recorded at sampling altitude from time to time during each flight were also used in the data processing.

The data from the FSSP-100 optical particle counter which determines particle concentrations in the size range of cloud droplets were processed to give continuous records of the particle volume concentration (cloud liquid water content), particle number concentration, and mean particle diameter. The data from the CSIRO-King probe were processed to give the cloud liquid water content in units of ml/m^3.

Continuous "stripchart" plots of the more important channels of data on the engineering unit data tape were prepared for review.

The volumes of air drawn through all filter and bubbler samples were calculated. The average pressure and temperature in the flow meters during each of the time intervals during which filter samples were collected were calculated from the continuous records of these parameters on the data tape.

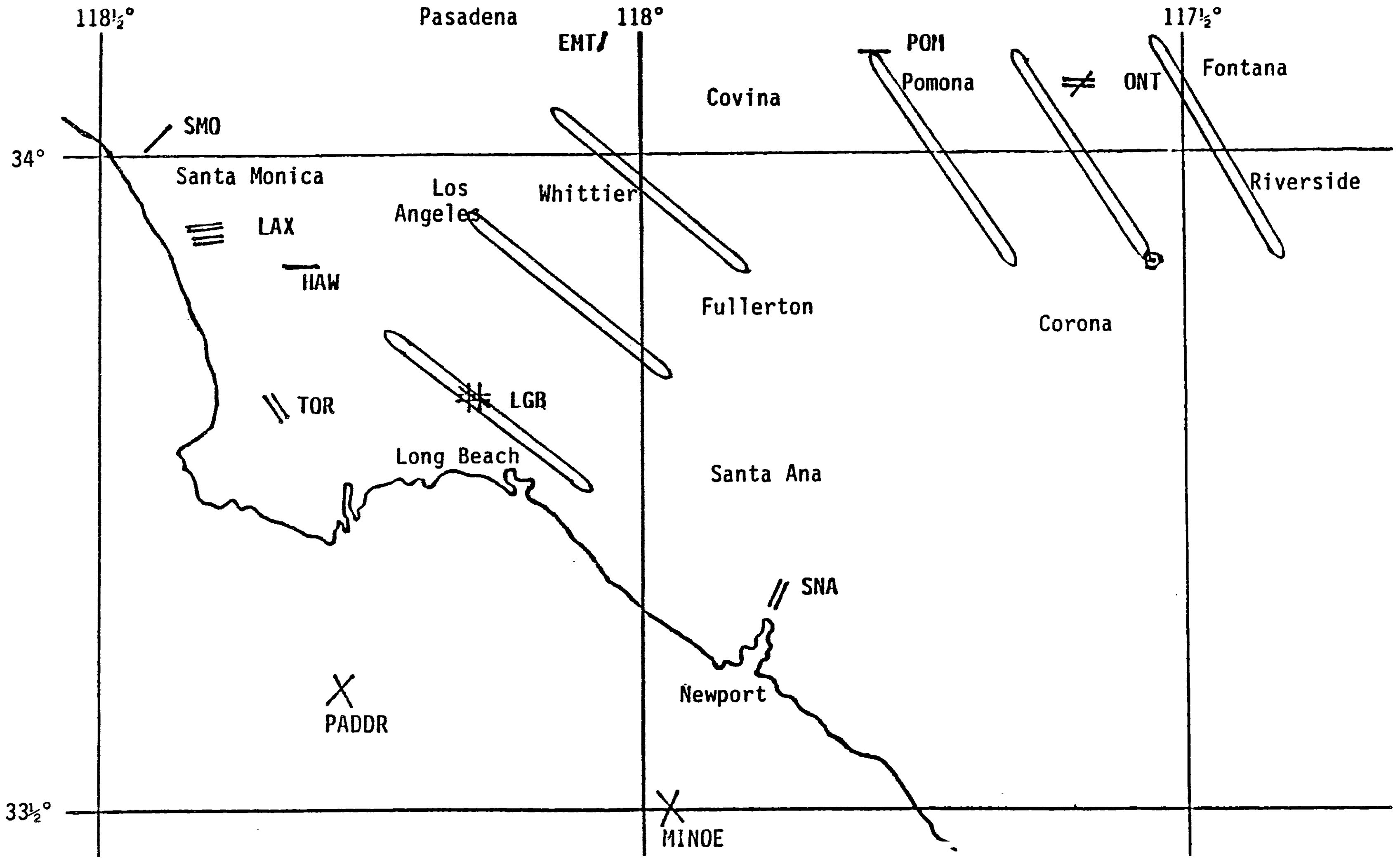

Figure 5-2. Planned flight patterns for use when following air parcels to obtain data for the changes in cloud chemical composition with time.

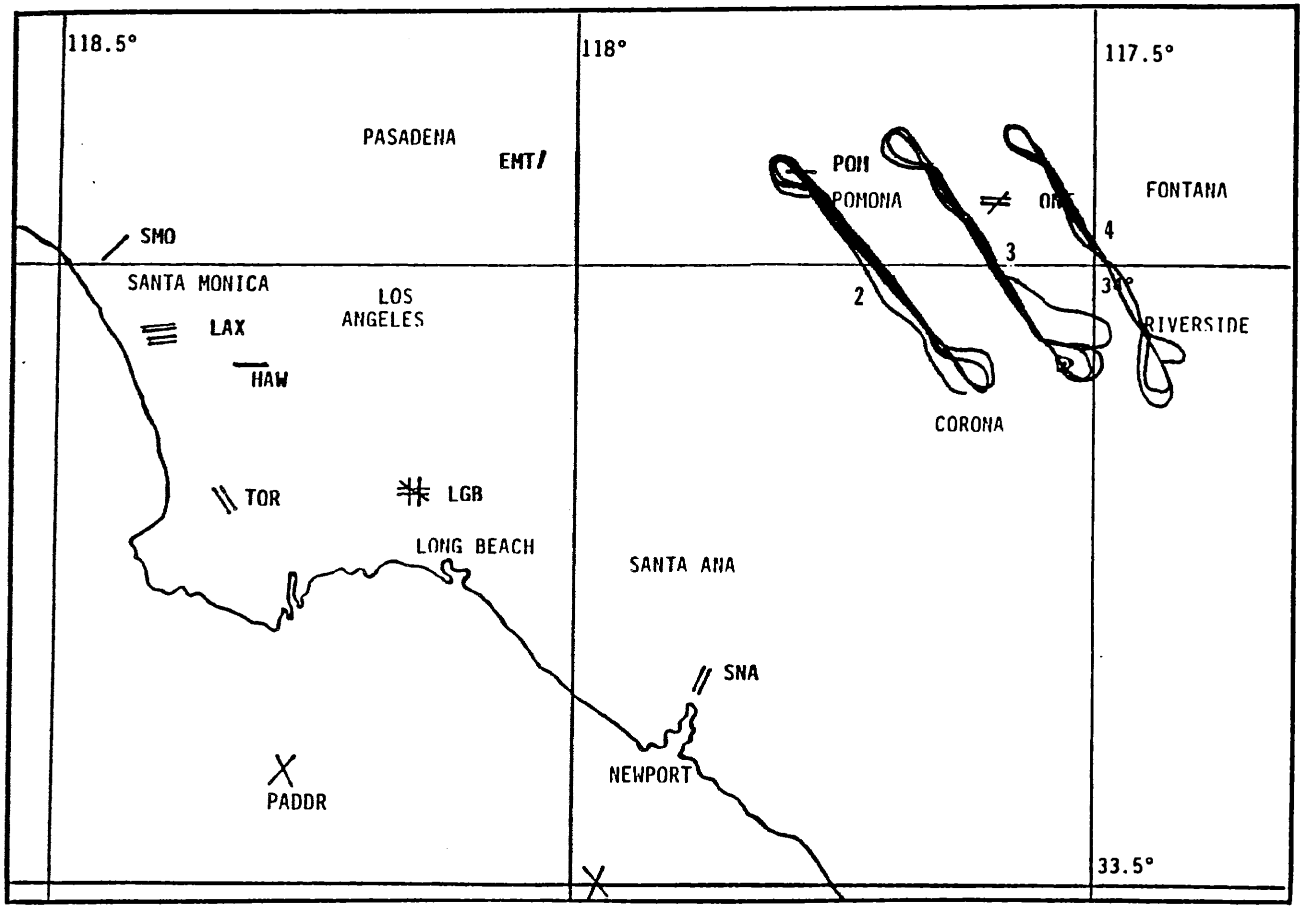

Figure 5-3. An example of the actual flight patterns used when following air parcels. These data are from Flight 435, 26 May 1985.

These results were combined with the flow meter readings to calculate the volumes of air drawn through each filter sample. The sample volumes are calculated for standard conditions of 25 ^{o}C and 1 atm.

Averages of the continuously recorded parameters listed in Table 5-1 as well as derived parameters such as the cloud liquid water content were calculated for the time intervals corresponding to the collection of filters and cloud water samples and tabulated. Plots giving the value of the more important continuously recorded parameters as either a function of time or of altitude were prepared for the Data Volume.

All grab sample data were entered into a spreadsheet program which facilitated combining laboratory results with sample volumes to calculate ambient concentrations. Most of the tables of grab sample data in this Final Report were printed from these spreadsheets.

5.7 DATA VOLUME

Appendix A of this report contains the flight summaries describing the sampling date, times, altitudes, and grab samples collected during each pass. It also contains flight maps showing the sampling locations. The results from the chemical analysis of the grab samples are contained in the body of this report. The remainder of the data from this study are contained in a data volume (Richards et al., 1986b).

The Data Volume contains a section for each sampling flight. Each section contains:

1. A table giving a summary of the flight, the identification codes of the grab samples, and the time intervals during which the grab samples were collected.
2. Maps generated from LORAN data for the flight route during each sampling pass.
3. Plots of the data recorded during each sampling pass.
4. Means, standard deviations, and maximum and minimum values for the air quality, meteorological, and navigational parameters recorded during each sampling pass.

Items 1. and 2. appear in Appendix A of this report.

A final section in the Data Volume contains the rawinsonde data in the form of tabulations of wind speed, wind direction, temperature, and relative humidity as a function of altitude.

6. SUMMARY OF THE RESULTS

The experimental results obtained from the May-June 1985 flights in the South Coast Air Basin are summarized in this section. Calculations to examine the quality of the data and intercomparisons between replicate measurements are also included here. All analysis and interpretation of these data appears in Sections 7 and 8.

6.1 FLIGHT TIMES AND LOCATIONS

Table 6-1 gives an overview of the date, time, general location, and flight pattern for each flight. The sampling time intervals listed in the table are from the beginning of the first data collection to the end of the last data collection for each flight. Almost all data were collected between midnight and 6:00 AM because that is the time when stratus clouds were present. When orbits were flown, the aircraft flew back and forth along a line which was progressively moved downwind as described in Section 5.5. The objective of the orbits was to observe changes in the cloud water composition. Missed approaches at various airports in the Basin were used to explore the three-dimensional distribution of pollutants in and near the clouds. The general area of the flights is indicated in Table 6-1, and maps showing the exact flight paths are in Appendix A.

6.2 METEOROLOGICAL SUMMARY

While forecasts were being made to decide when to fly, notes were kept on the meteorological conditions during the field study. The following text is a summary of those notes.

Variable Conditions, 16 - 20 May 1985.

Inland penetration of coastal stratus took place to a varying degree during the period from 15 May to 19 May, 1986. This was a period when higher pressure aloft was trying to build in along the southern California coast following the earlier passage of a long wave trough. However, despite the somewhat higher pressure, the period was one which lacked specific broad scale troughing or ridging and was more marked by fast moving small lows and sharp ridges. Prior to the 19th, surface temperatures in the California and Nevada deserts reached near 100 F and onshore pressure gradients at the surface increased. As a result, some incursion of marine air into the L.A. Basin took place because of the thermal differential even though the weak ridging along the coast was encouraging slight offshore flow. This resulted in the ocean stratus, which penetrated inland during the evening, but was rather shallow and tended to be broken when it reached the inland valleys and eastern portion of the coastal plain. By 19 May, a closed low aloft off the Washington-Oregon coast reduced pressures and encouraged a deeper onshore marine layer in

Table 6-1. Summary of flights

Date 1985	Time interval for sampling PDT	Type of flight	Location
21 May	02:24 - 06:38	Orbits	Long Beach
24 May	01:07 - 02:57	Missed approaches	Coastal
25 May	00:33 - 03:05	Orbits	Long Beach
26 May	23:57 - 03:11	Orbits	Ontario
27 May	00:57 - 04:21	Orbits	Ontario
1 June	02:48 - 03:34	Orbits*	Ontario
10 June	01:12 - 05:17	Orbits	Long Beach
11 June	00:56 - 01:48	Missed approaches	Coastal

*Flight discontinued due to lack of clouds.

southern California. This feature enabled a thicker stratus layer to develop over the L.A. Basin and inland valleys during the night of the 19th and early morning of the 20th with solid clouds from 1500 to 4000 feet above ground level (ft AGL).

Sharp Ridging, 21 - 23 May 1985.

The closed low aloft moved rapidly southeastward from the Oregon coast and was situated over southern Nevada by the morning of the 21st. As the low moved inland, stratus cloudiness still penetrated into the valleys early on the morning of the 21st and a solid overcast persisted over the coastal plain with bases at 1200 to 1600 ft AGL and tops near 3500 ft AGL. However, by 0400 PDT on the 21st, even the coastal stratus broke up as flow began to shift from southeasterly to west-north-westerly. A small but sharp omega ridge quickly built off the coast behind the low on the 21st, switching flow aloft to a more northerly direction and thus reducing the marine layer and nighttime coastal stratus during the period from the 21st to early on the 23rd. During this time, marine stratus only penetrated the inland areas in a spotty fashion while the coastal plains experienced shallow clouds below 1500 feet. The sharp but short ridge quickly moved inland by the 23rd and dissipated rapidly. A moderate long wave trough aloft, extending from the Gulf of Alaska southward to off Baja, began to affect west coast weather by that day. Flow aloft shifted once again back into the southwest along the west coast as the axis of the trough approached to within 500 miles of California.

Moderate Offshore Trough, 23 - 27 May 1985.

With the onset of the southerly flow from the approaching trough, the marine layer began to deepen and strengthen again and produced thicker stratus cloudiness more extensively over the coastal regions as well as the inner valleys by the evening of the 23rd. Overcast stratus with ceilings just under 1000 ft AGL moved into the LAX area by late afternoon and included most of the coastal plain by sunset. Inland areas such as Burbank and Ontario remained clear but hazy through the early evening hours but also experienced development of ceilings around 800 to 1000 ft AGL by 0300 PDT on the 24th. Tops of the clouds were around 2000 ft AGL during most of the evening rising to around 2500 ft AGL by 0600 PDT on the 24th. Skies became hazy again but relatively clear inland by late morning and in the coastal regions by noon or early afternoon.

During the 24th the trough aloft had reached to within 400 miles of the coast as it elongated southward from the Gulf of Alaska. As it slowly approached southern California, the marine layer continued to deepen and stratus cloudiness persisted over the coastal plains and inland valleys during the evening of the 24th and early morning of the 25th. Low overcast conditions were reported in the Long Beach area by 2200 PDT on the 24th and also spread across most of the coastal plain between then and midnight. Bases were around 900 ft AGL with tops between 2000 and 2500 ft AGL. The clouds spread into the inland areas shortly after midnight with Ontario and Burbank both reporting ceilings less than 1000 ft AGL by that time. Cloud bases became higher in the coastal areas during the early morning hours of the 25th with bases up to 1400 ft AGL at Long Beach by 0300 PDT and tops extending above 2500 ft AGL. Cloud bases in inland locations remained less than 1000 ft AGL but tops in those areas were also above 2500 ft AGL. The stratus remained over the inland areas until midmorning while it persisted throughout the entire morning in the coastal areas before dissipating into hazy sunshine by early afternoon.

The trough aloft remained about 400 miles off the coast during the 25th but began to weaken as the main energy of the system was re-established in a deeper, closed low in the northern Gulf of Alaska. However, the trough in the southern reaches still maintained onshore southwesterly flow and thus enabled the continued penetration of the marine layer inland during the 25th and early on the 26th. Broken marine stratus with bases between 1500 and 2000 ft AGL began to appear in the coastal areas by 2000 PDT on the 25th but did not spread inland until later. Scattered stratus above 2000 ft AGL appeared in the Burbank area by 2200 PDT and the entire area from the San Fernando Valley through San Gabriel Valley to Riverside became overcast with stratus ceiling around 1500 ft AGL by 2300 PDT. This stratus persisted into the morning of the 26th with tops above 3500 ft AGL. As the early morning hours progressed on the 26th, the cloud bases became more ragged and increased in height to as high as 2500 ft AGL in both the inland valleys and coastal areas by 0600 PDT. The tops of the cloud deck increased to as high as 4500 ft AGL by that time. The clouds persisted in this manner throughout the remainder of the morning in all areas and became scattered during the afternoon in the inland valleys but continued broken along the coast.

By the evening of the 26th, the trough aloft had become more disorganized and the axis had moved to just off the southern California coast when the main low in the Gulf of Alaska began to move southward. The southern end of the trough then broke off from the main feature and moved inland as a weak short wave during the morning of the 27th. Because of the weakening of the troughing in southern California and the deeper mixing prompted by the advancing short wave, the marine stratus onset was later on the 26th than on previous evenings. Coastal areas did not experience clouds until after 2200 PDT and the inland areas from Burbank through Ontario did not have ceilings until almost 0100 PDT on the 27th. Cloud bases in the coastal areas were around 2500 ft AGL and just below 2000 ft AGL in the inland areas. Cloud tops were as high as 5000 ft AGL. By 0400 PDT on the 27th, breaks in the cloud decks over the inland valleys began to occur and the clouds began to show increased puffiness and vertical mixing. Clouds became scattered by late morning of the 27th in the inland areas but remained broken into the early afternoon near the coast. By midmorning, clouds had taken on a more strato-cumulus form and cloud thicknesses had become more multi-layered as the short wave moved inland toward the east.

Weak Ridging, 27 - 28 May 1985.

By the morning of the 27th, the main closed low aloft which had been located in the Gulf of Alaska, had moved to just north of Vancouver Island and continued to sink southward along the North American coast. As it did so, it caused a southwestward digging of a new long wave trough with an axis running from the main low center several hundred miles off Portland to about 700 miles off of the Baja Coast. Weak high pressure wedged northward slightly between the new trough off the coast and the dying short wave inland during the 27th, bringing cooler, less stable air to southern California and an increase in mixing and drying which the higher cloud bases and tops indicated. The main trough continued to retrograde in its southern extension as it dug southwestward on the 27th and 28th, while the weak ridge between it and the coast broadend out and weakened. This produced continued southwest to west-southwest flow at the coast, but a less onshore impetus. During the late evening of the 27th and the early morning of the 28th, marine cloudiness in the form of stratus to stratocumulus formed in patches along the coast and did move inland in several areas. This cloud deck produced only a broken to scattered ceiling in the Ontario area during that time and was inconsistent throughout the southern California area. Clouds remained variably scattered with bases at 3000 to 4000 ft AGL and haziness persisted throughout the 28th and during the 29th.

Subtropical Fetch, 29 - 30 May 1985.

By the morning of the 29th, the offshore troughing aloft had split into two sections, with the main closed low centered over Oregon and a secondary low 800 miles off the Baja coast. The southern California area was in between the two patterns and experienced an increase in high and middle level cloudiness from subtropical areas due to the southerly fetch aloft from the secondary low. As the subtropical flow became more dominant during the 29th and into the 30th of May, very little low coastal stratus developed in the southern California area as only broken high cirrus and middle altitude cloudiness prevailed. At the same time, rain shower activity broke out along the mountains and spilled into the inland valleys during the afternoon hours.

Winterlike Closed Low, 31 May - 3 June 1985.

The split flow situation aloft ended by the morning of 31 May 1985 as the closed low, which had been oscillating around the Oregon coast, became the dominant feature. As this took place, the trough, which extended southwestward from the low, shifted towards the coast and began to strengthen onshore flow into southern California. The low and trough, however, were very deep for this time of year and resembled the type of system which is more prevalent during winter months. The increased onshore flow induced the reappearance of marine cloudiness along the coast and inland early on the morning of the 31st. These clouds were layered and rather stratocumulus in form and had broken bases at around 1500 ft AGL with the main cloud bases at around 2500 ft AGL. The tops of the clouds were around 5000 ft AGL. During the day on the 31st, the trough associated with the closed low along the Oregon coast moved rapidly onshore in southern California and shifted flow from the southwest to the west-northwest. This resulted in an increase in the vertical development of the stratocumulus clouds and continued to allow the marine layer to deepen. By the late afternoon of the 31st, broken stratocumulus type cloudiness had covered the L.A. Basin area from the coast to the San Gabriel mountains. However, by that time, the bases of those clouds had risen to above 5000 ft AGL as the mixing layer continued to deepen. This cloud deck finally dissipated by 2300 PDT. Patchy broken marine stratus did form by 0100 PDT on 1 June 1985, but a consistent solid overcast never persisted at the inland locations or along the coastal plain, except well to the south of Long Beach. The broken clouds extended from around 2000 ft AGL to around 5500 ft AGL and were multilayered and tended to be stratocumulus form. The clouds dissipated by 1000 PDT and reformed into cumulus clouds along the mountains during the afternoon of the 1st.

The period from 1 to 4 June 1985 was characterized by variable cloudiness and considerable winterlike instability, as the closed low aloft drifted southward from Oregon and over inland California. The low moved along the west slopes of the Sierra during the 2nd and passed through southern California on the 3rd. By the morning of 4 June 1985, it was located over southern Arizona.

Broad Ridging, 4 - 9 June 1985.

A small ridge of high pressure wedged inland from the Pacific over central and southern California on 4 June 1985 as the closed low aloft which had dominated the weather during the previous four days dissipated over the Arizona deserts. The ridge produced northerly flow aloft over southern California but the associated stability and inland heating enabled a shallow onshore southwesterly seabreeze flow to develop in the lower levels. The light onshore flow produced shallow coastal stratus by 0100 PDT on 5 June 1985, with bases at 600 to 900 ft AGL. The tops of these clouds were only around 1500 ft AGL. Most of this stratus stayed south of Long Beach through the morning of the 5th, with only scattered clouds reported at LAX and broken ceilings at Long Beach from only 0030 PDT to 0230 PDT.

After the morning of the 5th, the high pressure ridge aloft built in strongly over the southern half of California and the southwest U.S. High pressure also strengthened in the lower levels and an extended period of light offshore flow with only weak, thermally induced afternoon sea breezes began which lasted through 8 June 1985. During that period, several air quality alerts were necessary in parts of the L.A. Basin but only shallow, short-lived stratus appeared near the coast while only local fog formed at night at inland locations. By early morning on 9 June 1985, the high ridge which had been dominating the west coast for several days was weakening as a closed low aloft deepened in the central Gulf of Alaska.

Weak Catalina Eddy, 10 - 14 June 1985.

The strengthening of the semi-stationary closed low aloft in the Gulf of Alaska induced the formation of a short ridge aloft to its east which approached the Pacific Coast of North America early on 10 June 1985. As a result, a short wave trough developed in the lower level in the Pacific Northwest and moved southeastward into California ahead of the short ridge aloft. As the low level short wave approached California, it induced the formation of a weak Catalina eddy along the southern California coast. This caused a slight deepening of the marine layer and increased the depth and extent of the coastal stratus. However, because of the continued general high pressure aloft over the Pacific and the southwest U.S., subsidence and weak offshore flow still prevented the marine layer from strengthening and deepening to the extent to allow much penetration of marine stratus to the inland basin and valleys. Coastal stratus did penetrate the coastal plain by early on the 10th, but did not intrude to the inland valleys. Cloud bases during this episode were below 800 ft AGL and tops were only around 1700 ft AGL. Some stratus did penetrate inland as far as Burbank but only local shallow fog was reported at Ontario.

The formation of a weak but closed high pressure aloft about 600 miles off the southern California coast during 11 June 1985, induced slightly increased troughing at the coast which then allowed the Catalina eddy in the lower levels to remain intact. However, the depth of the marine layer did not increase appreciably during that time. As a result, marine stratus clouds once again penetrated the coastal plain and moved into some interior areas during the evening of the 11th and early morning hours of the 12th, but only local shallow fog at Ontario and the inland valleys was reported. Stratus cloud bases were again between 600 and 1000 ft AGL during that period with tops between 1500 and 2000 ft AGL. The eddy circulation continued on through the 12th and 13th but general high pressure aloft still prevailed through the southern portion of California with the main long wave trough still staying well to north and west in the Gulf of Alaska. As a result, no further deepening of the marine layer took place during the period after 12 June 1985 and marine stratus development decreased.

6.3 CLOUD WATER MEASUREMENTS

The laboratory results from the chemical analysis of the cloud water samples are presented in this section. The first subsection presents the results of a physical measurement, the cloud liquid water content, which is required to convert the laboratory data for the solute concentrations in the collected water (amount of solute per ml of water) into ambient concentrations (amount of solute per m^3 of air). The first chemical data are for the unstabilized water samples collected in clean polyethylene bottles. Then the data for species whose concentrations may change on sample storage are presented. Water samples to be analyzed for these species were collected directly into stabilizing solutions to eliminate the possible effects of sample storage. The sampling equipment and analytical methods used to obtain these data are described in Section 5.

6.3.1 Liquid Water Content

Data for the liquid water content (LWC) of the clouds were determined by two methods. In one, the signals from the CSIRO-King probe were processed to determine the LWC from the measured heat loss due to the evaporation of the cloud water impinging on the probe. In the other method, the counts from the FSSP optical particle counter were multiplied by the volume of droplet associated with each count and the results were summed. Both of these data reduction methods gave LWC data with a time resolution of one second.

Both methods were subject to experimental difficulties caused by the high values of LWC encountered in these flights. The FSSP sometimes became wet enough that the laser beam was attenuated and the droplet size counts were placed in channels corresponding to smaller droplets than were actually present. The CSIRO-King probe data were sometimes affected by the fact that the electronic control circuit for this instrument can become unstable and oscillate when the rate of heat loss is very large. This caused some CSIRO-King probe data to be lost in the more dense clouds.

Data from both probes were reviewed and combined to obtain the LWC data in Table 6-2. In general, the CSIRO-King probe is regarded as being more reliable than the FSSP. Therefore, data from the CSIRO-King probe were used during times when its signal was free of oscillations to calibrate the FSSP

Table 6-2. Cloud liquid water contents

Tape/Pass	Sample ID	LWC ml/m^3
432/2	U1	0.61
432/3	U3	0.59
432/4	U5	0.21
432/5	U6	0.47
433/1,2	U10	0.40
433/3	U11	0.25
433/4	U12	0.40
433/4	U13	0.40
434/2	U15	0.82
434/2	U16	0.82
434/3	U17	1.20
434/3	U18	1.20
434/4	U19	0.93
434/4	U20	0.93
435/2	U21	1.00
435/3	U24	1.20
435/4	U26	0.90
436/2	U31	0.44
436/3	U33	0.30
436/4	U34	0.36
440/2	U52	0.60
440/3	U54	0.30
440/4	U55	0.40
440/5	U56	0.30

data. The calibrated FSSP data were then used to determine the LWC during times when the CSIRO-King probe output was oscillating.

6.3.2 Unstabilized Samples

Table 6-3 gives the results from the analytical laboratory analysis of the unstabilized water samples collected during time periods for which the data were processed and included in the Data Volume (Richards et al., 1986b). These time periods are called passes. Data for water samples collected in between passes are not included in this table. (The column of data with the heading "Sulfur (IV) as SO_2" was obtained from the analysis of separate water samples collected in a stabilizing solution, and is discussed in Section 6.3.5 below.)

Several averages appear at the bottom of this table as well as in a number of the following tables. The first row gives the average of all values in that column in the table. The row labeled "First pass" gives the average of results from all flights from the first pass in that flight during which grab samples were collected. The row labeled "Last pass" gives similar data from all flights for the last pass in which grab samples were collected, and the row labeled "Middle passes" gives the average of the data from all flights for the one or two passes between the first and last. These averages were calculated to see if there are trends in the data.

Two internal checks on the quality of these data were calculated, and the results are shown in Table 6-4. The first check was to multiply the concentration of each ion by its conductivity and sum the results to obtain the calculated conductivity. No corrections were made for the effect of ionic strength on the equivalent conductivities of the ions. Both the measured conductivity and the conductivity calculated from the ionic concentrations are reported in Table 6-4 along with the ratio of these two values. With few exceptions, the ratios are in the interval from 0.92 to 0.98. Two samples, U11 for 433/3 and U62 for 441/1 were omitted from this table because the sample volumes were small enough that it was not possible to determine the concentrations of all the ions. The consistency of the reported ratios indicates that the analytical data are precise, and the fact that the ratios are close to unity indicates that the most important ions were included in the analyses.

Table 6-4 gives the fraction of the calculated conductivity due to hydrogen ions, which ranges from about 45% to 70%. The hydrogen ion is the dominant contributor to the conductivity of the water samples. The samples with the highest conductivity also have the lowest pH values, indicating that conductivity can be used as a rough indicator of the hydrogen ion concentration.

The agreement between the calculated and measured conductivities is very sensitive to the pH measurements. Decreasing all pH readings by 0.03 to 0.04 units would cause the calculated conductivities to be essentially equal to the measured conductivities.

The other calculation in Table 6-4 to check the analytical data is the ion balance. Nearly all ratios of the concentrations of cations and anions

Table 6-3. Analytical results for unstabilized cloud water samples

Tape/Pass	Sample ID	pH	Solute concentration										
			Cl^- µg/ml	NO_3^- µg/ml	$SO_4^=$ µg/ml	S(IV) as SO_2 µg/L	NH_4^+ µg/ml	Na^+ µg/ml	K^+ µg/ml	Ca^{++} µg/ml	Mg^{++} µg/ml	Fe^{+++} µg/ml	Mn^{++} µg/L	Pb^{++} µg/ml
432/2	U1	3.41	10.32	39.20	19.2	3.2	6.88	7.70	0.690	2.200	1.170	0.484		0.331
432/3	U3	3.35	6.63	30.30	15.2	≤1.5	4.67	4.48	0.332	0.775	0.663			
432/4	U5	2.90	11.85	107.20	36.0	27.7	15.41	9.71	1.100					
432/5	U6	3.12	8.03	80.10	24.8		13.83	7.81	0.736	1.920	1.255	0.703	31.20	0.444
433/1,2	U10	3.43	9.68	31.30	21.3	22.9	4.06	9.14	0.923	1.810	1.240	0.444		
433/3	U11	3.26	6.40	42.00	29.0									
433/4	U12	2.97	5.71	68.90	32.9	18.1	8.69	5.63	0.637	1.860	0.975	0.755		0.376
433/4	U13	2.98	4.45	62.30	29.0		7.56	3.94	0.301	0.759	0.644			
434/2	U15	3.26	3.66	19.10	15.0	21.7	2.03	2.46	0.166	0.415	0.354	0.108		0.359
434/2	U16	3.26	4.95	24.60	19.6		2.53	3.82	0.227	0.508	0.555	0.168	10.40	0.317
434/3	U17	3.25	4.00	26.20	18.5	≤1.5	2.99	2.72	0.163	0.427	0.416	0.175	7.26	0.355
434/3	U18	3.40	4.38	21.10	13.7		2.66	3.22	0.185	0.428	0.463	0.073	6.82	
434/4	U19	3.37	2.31	28.20	11.5	25.6	3.36	2.00	0.274	0.473	0.328	0.142	7.97	0.496
434/4	U20	3.35	2.18	28.60	12.2		3.50	1.95	0.191	0.459	0.334	0.134	8.26	0.366
435/2	U21	3.35	3.24	36.80	14.6	≤1.5	5.86	2.97	0.378	1.250	0.518	0.315	16.90	0.336
435/3	U24	3.31	2.39	33.70	12.9	4.0	4.86	1.68	0.142	0.578	0.286	0.131	7.69	0.447
435/4	U26	3.65	1.72	27.30	9.8	≤1.5	8.30	0.89	0.081	0.310	0.143	0.063	3.81	0.341
436/2	U31	3.32	3.58	44.30	14.5		7.78	3.29	0.366	1.130	0.571	0.267	17.60	0.295
436/3	U33	3.14	3.41	59.30	16.0		8.11	2.45	0.295	1.320	0.502	0.335	17.60	
436/4	U34	3.42	3.80	63.50	17.3		15.71	4.21	0.455	1.920	0.796	0.478	24.00	0.234
440/2	U52	3.82	3.64	8.60	6.8		1.14	2.58	0.217	0.656	0.385	0.080	6.53	
440/3	U54	3.20	17.26	37.10	32.0		6.25	13.05	0.758	1.530	1.736	0.341		0.301
440/4	U55	3.25	8.42	43.30	25.7		8.87	7.51	0.608	1.420	1.130	0.404	17.70	0.209
440/5	U56	3.60	18.29	17.70	12.3		1.84	4.69	0.325	0.729	0.654	0.165	8.55	0.252
441/1	U61	3.75	20.02	12.70	12.6		2.11	12.50	0.658	1.800	1.559	0.149	0.00	
441/1	U62	3.65					1.50	13.25	0.585	0.930	1.604	0.097	5.68	
441/1	U63	3.57	19.13	18.20	16.5		2.95	12.85	0.617	1.080	1.610	0.122	7.69	
Averages														
All data		3.35	7.29	38.91	18.8	11.2	5.90	5.63	0.439	1.067	0.796	0.267	12.10	0.341
First pass		3.45	7.39	27.07	15.4		4.05	5.56	0.45	1.22	0.79	0.25	12.86	0.328
Middle passes		3.27	6.47	40.02	19.9		6.15	6.45	0.46	0.93	0.85	0.22	10.46	0.338
Last pass		3.34	7.29	43.87	18.5		7.30	4.89	0.40	1.06	0.75	0.32	13.07	0.358

Table 6-4. Comparison of measured and calculated cloud water conductivites and the ion balances

Tape/Pass*	Sample ID	Conductivity (µmho/cm)				Ion balance			
						Sums		Ratios	
		Measured	Calculated	Ratio Calc./Obs.	Fraction due to H^+	Cations	Anions	+/-	-/+
432/2	U1	315	294	0.93	0.46	1358	1323	1.03	0.97
432/3	U3	280	265	0.95	0.59	1002	992	1.01	0.99
432/4	U5	782	736	0.94	0.60	2564	2813	0.91	1.10
432/5	U6	522	504	0.97	0.53	2126	2035	1.04	0.96
433/1,2	U10	280	272	0.97	0.48	1234	1222	1.01	0.99
433/4	U12	600	582	0.97	0.64	2032	1958	1.04	0.96
433/4	U13	560	541	0.97	0.68	1736	1734	1.00	1.00
434/2	U15	242	264	1.09	0.73	832	724	1.15	0.87
434/2	U16	302	287	0.95	0.67	945	945	1.00	1.00
434/3	U17	300	288	0.96	0.68	919	921	1.00	1.00
434/3	U18	230	218	0.95	0.64	754	749	1.01	0.99
434/4	U19	240	228	0.95	0.66	770	759	1.01	0.99
434/4	U20	250	236	0.95	0.66	792	777	1.02	0.98
435/2	U21	280	268	0.96	0.58	1036	989	1.05	0.95
435/3	U24	280	264	0.94	0.65	900	880	1.02	0.98
435/4	U26	179	168	0.94	0.47	759	693	1.09	0.91
436/2	U31	318	297	0.93	0.56	1184	1117	1.06	0.94
436/3	U33	420	402	0.96	0.63	1414	1386	1.02	0.98
436/4	U34	340	328	0.96	0.41	1636	1492	1.10	0.91
440/2	U52	99	96	0.97	0.55	401	383	1.05	0.95
440/3	U54	448	422	0.94	0.52	1805	1752	1.03	0.97
440/4	U55	399	372	0.93	0.53	1584	1471	1.08	0.93
440/5	U56	162	192	1.18	0.46	667	1057	0.63	1.58
441/1	U61	200	190	0.95	0.33	1081	1032	1.05	0.95
441/1	U63	240	235	0.98	0.40	1201	1177	1.02	0.98
Averages									
All data		331	318	0.97	0.56	1229	1215	1.02	0.99
First pass		254	246	0.97	0.54	1009	967	1.05	0.95
Middle passes		392	371	0.95	0.61	1368	1370	1.01	0.99
Last pass		344	335	0.98	0.54	1302	1298	1.00	1.03

* Data for 433/3 and 441/1 sample U62 were incomplete and hence were omitted.

are close to unity. There is a small bias in the data indicating that on the average, cation concentrations were higher than anion concentrations. This suggests that there were more anions than cations among the species which were not determined, for example, organic compounds. The hydrogen ion is the cation which makes the largest contribution to the total cation concentration, so the ion balance is very sensitive to errors in pH measurements.

Both of these checks on the data give information only on the quality of the chemical analysis of the samples received in the analytical laboratory. They provide no information about possible contamination or alteration of the samples before analysis, nor do they give any indication of the relationship between the analytical results and the composition of the cloud water as it existed in the atmosphere.

6.3.3 Hydrogen Peroxide

Table 6-5 reports the hydrogen peroxide concentrations for the collected cloud water samples. The data under the heading "Stabilized during flight" are from samples collected directly into a stabilizing solution containing horseradish peroxidase and p-hydroxyphenylacetic acid. These reagents produce a stable fluorescent dimer from hydrogen peroxide, and the concentration of this dimer can be measured at a later time.

When the quantities of unstabilized water were large enough to permit, aliquots were taken from the unstabilized samples after the flight and added to the stabilizing reagents for hydrogen peroxide. Typically, this was done one to two hours after the airplane landed, or two to six hours after sample collection. These data appear under the heading "Stabilized after flight" and are on the same row in the table as the data from the sample simultaneously collected in the stabilizing solution.

Figure 6-1 compares the two sets of data for hydrogen peroxide. The hydrogen peroxide concentrations determined from the samples stabilized after the flight were always in good agreement with the concentrations from samples stabilized during collection. The small bias in the results suggest that a few micromoles per liter of peroxide may be lost by the delay in adding the stabilizing reagents.

The middle column in Table 6-5 gives the ambient concentration of hydrogen peroxide in the cloud water calculated from the concentrations measured in the samples stabilized in flight and the measured liquid water content (LWC) of the clouds.

6.3.4 Formaldehyde and Acetaldehyde

The geometry of the cloud water collectors allowed the simultaneous use of only two stabilizing solutions. In the May-June 1985 flights, hydrogen peroxide samples were always collected and either sulfur (IV) or carbonyl samples were collected. The sulfur (IV) concentrations were very low, so carbonyl samples were collected on most flights. The formaldehyde and acetaldehyde data are shown in Table 6-6.

Table 6-5. Cloudwater hydrogen peroxide concentrations

Tape/Pass	Stabilized during flight Sample ID	Stabilized during flight Concentration (μM)	Ambient concentration in water (μg/m^3)	Stabilized after flight Sample ID	Stabilized after flight Concentration (μM)
432/2	P1	163.0	3.38		
432/3	P3	62.0	1.24		
432/4	P5	53.6	0.38		
432/5	P6	44.3	0.71		
433/4	P11	12.3	0.17		
434/2	P15	102.0	2.84	PU16	106.3
434/3	P16	33.4	1.36	PU17	30.6
434/3	P17	44.3	1.81		
434/4	P18	55.1	1.74	PU20	45.0
434/4	P19	44.3	1.40		
435/2	P22	30.6	1.04	PU23	30.0
435/3	P26	25.2	1.03	PU25	22.4
435/4	P25	28.8	0.88	PM	21.8
436/2	P31	40.1	0.60	PU31	37.6
436/3	P32	43.0	0.44	PU33	35.0
436/4	P33	50.7	0.62	PU34	43.0
440/2	P52	81.3	1.66		
440/4	P54	72.4	0.98		
440/5	P55	97.4	0.99		
441/1	P61	52.8			
441/1	P62	60.1			
441/1	P63	63.5			
Averages					
All data		57.3	1.23		41.3
First pass		78.3	1.90		58.0
Middle passes		49.2	1.04		29.3
Last pass		49.5	0.93		36.6

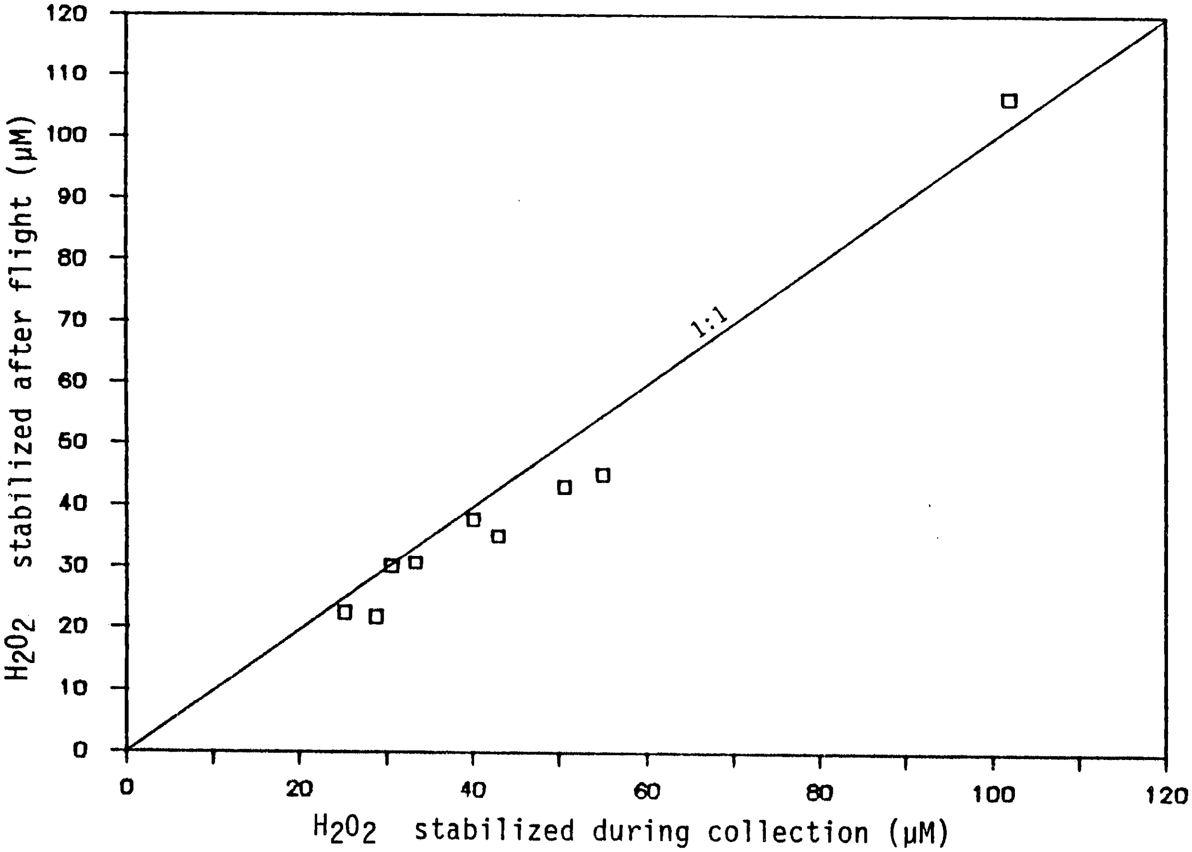

Figure 6-1. Comparison of cloud water hydrogen peroxide concentrations for simultaneously collected samples stabilized after the flight and during sample collection.

Table 6-6. Cloudwater formaldehyde and acetaldehyde concentrations

Tape/Pass	Sample ID	Weight of carbonyl collected (μg)		Weight of cloud water collected	Carbonyl conc. in cloud water (μg/ml)		Ambient concentrations (μg/m^3)	
		Formal.	Acetal.	(g)	Formal.	Acetal.	Formal.	Acetal.
433/4	D1	2.30	1.18	6.39	0.296	0.160	0.12	0.06
434/2	D15	6.45	1.40	12.77	0.473	0.097	0.39	0.08
434/3	D16	7.31	2.54	10.51	0.656	0.226	0.79	0.27
434/4	D18	7.63	1.53	7.76	0.930	0.176	0.87	0.16
435/2	D21	12.10	2.76	10.19	1.147	0.255	1.15	0.25
435/3	D22	19.62	2.65	11.95	1.607	0.208	1.93	0.25
435/4	D23	14.23	2.17	10.90	1.268	0.184	1.14	0.17
436/2	D31	11.80	2.46	10.07	1.131	0.228	0.50	0.10
436/3	D32	11.08	2.92	8.52	1.252	0.324	0.38	0.10
436/4	D33	10.74	2.35	7.42	1.392	0.295	0.50	0.11
440/3	D51	4.22	1.04	5.13	0.743	0.172	0.22	0.05
440/4	D52	5.11	1.70	4.67	1.006	0.330	0.40	0.13
440/5	D53	5.00	0.64	14.56	0.315	0.033	0.09	0.01
441/1	D61	2.19	0.44	4.14	0.430	0.068		
441/1	D62	6.63	1.31	15.14	0.411	0.076		
	blank	0.41	0.16					
Averages								
All data		8.43	1.81	9.34	0.871	0.189	0.56	0.12
First pass		8.13	1.76	9.29	0.795	0.162	0.51	0.11
Middle passes		8.99	2.03	9.32	0.946	0.223	0.62	0.13
Last pass		7.98	1.57	9.41	0.840	0.170	0.54	0.10

The analytical laboratory reported total formaldehyde and acetaldehyde per sample. Field data for the weight of water collected in each bottle were used to convert these results into water concentrations in μg/ml. These data were then multiplied by the cloud LWC to obtain ambient concentrations in μg/m^3. The averages at the bottom of the table were calculated as described in Section 6.3.2 above.

6.3.5 Sulfur (IV)

Cloud water was collected directly into the buffered formaldehyde solution to stabilize sulfur (IV) on the first two sampling flights, 21 and 24 May. These flights were in the Long Beach and coastal areas, where the chance of observing significant sulfur (IV) concentrations was believed to be at a maximum. On later flights, aliquots were removed from some unstabilized cloud water samples after the aircraft landed and added to the stabilizing solutions.

Only a few data points were obtained, so they have been reported in Table 6-3 along with the data from the unstabilized water samples. When the sulfur (IV) concentration was below the limit of detection, the upper limit for the sulfur (IV) concentration is reported with the $\leqq$ sign. When no sulfur (IV) determination was made, the space for it was left blank.

It was found that it was necessary to filter the water samples to be analyzed for sulfur (IV) before making the colorimetric measurement. If this was not done, light absorbing particles in the water samples gave readings which were high by more than 100 μg/L (or about 2 μM). For comparison, the highest sulfur (IV) concentration reported in Table 6-3 is 27.7 μg/L.

6.4 AEROSOL FILTER SAMPLES

Table 6-7 contains the data from the analysis of filter samples collected behind a cyclone, which removed the cloud water from the sample flow. The affect on these data of the absorption and desorption of gases (such as nitric acid) in the sample inlet plumbing and the cyclone is unknown, but may well not be negligible. In the ideal case, these filter data give information on the concentration of interstitial aerosol and gases. In practice, the data must be used with caution.

It is apparent that more nitrate was collected by the nylon filters than could have been present in the clouds as interstitial nitrate. It is expected that nitric acid would not be present in the gas phase in clouds (Levine and Schwartz, 1982). The data for the blank filters indicates that contamination may have contributed to these high readings. It is also likely that evaporation of cloud water in the inlet plumbing may have also contributed to the high nitrate values on the nylon filters.

6.5 TOTAL SAMPLE COLLECTOR

The sulfate data from the total sample collector (TSC) are shown in Table 6-8 and the nitrate data in Table 6-9. These results are not as useful as it

Table 6-7. Filter chemistry data

Tape/Pass	Teflon filter					Nylon filter			Ambient concentrations ($\mu g/m^3$)							
	Filter ID	Mass per filter (μg)			Sample volume (m^3)	Filter ID	NO_3^- mass per filter (μg)	Sample volume (m^3)	Teflon filter			Nylon filter	Total	Teflon filter	Total	Teflon filter equivalent balance +/-
		$SO_4^=$	NO_3^-	NH_4^+					$SO_4^=$	NO_3^-	NH_4^+	NO_3^-	NO_3^-	mass	mass	
432/2	H-1	7.28	5.37	3.47	1.55	N-1	1.57	0.62	4.34	2.44	2.11	-0.5	2.0	8.89	8.43	0.90
432/3	H-2	7.96	3.70	3.28	2.28	N-2	19.10	0.68	3.25	0.92	1.35	25.4	26.3	5.52	30.88	0.91
432/4	H-3	15.14	3.37	5.59	1.57	N-3	70.30	0.47	9.29	1.13	3.43	145.6	146.8	13.86	159.48	0.90
432/5	H-4	11.52	5.72	5.72	1.28	N-4	59.70	0.38	8.57	3.22	4.31	152.2	155.4	16.11	168.33	1.04
Blank	H-5	0.67	0.98			N-5	60.60									
433/1,2,3	H-10	14.30	5.49	6.31	2.05				6.71	1.90	2.98		1.9	11.59	11.59	0.97
433/4	H-11	13.86	2.39	5.74	1.89				7.04	0.42	2.93		0.4	10.39	10.39	1.06
Blank	H-12	0.75	2.58													
434/2	H-15	2.20	1.53	0.74	0.95	N-15	162.60	0.28	1.73	-0.07	0.57	574.1	574.0	2.24	576.33	0.90
434/3	H-16	1.26	1.53	0.57	1.39	N-16	60.90	0.42	0.51	-0.04	0.27	140.6	140.5	0.73	141.31	1.50
434/4	H-17	4.67	2.54	1.53	1.19	N-17	26.90	0.36	3.46	0.80	1.12	69.6	70.4	5.37	74.94	0.73
Blank	H-18	0.06	4.67			N-18	4.67									
435/2	H-21	3.85	7.53	1.54	1.54	N-21	4.32	0.46	2.14	3.86	0.87	5.4	9.2	6.87	12.23	0.45
435/3	H-22	2.47	1.36	1.11	1.32	N-22	19.30	0.40	1.45	-0.18	0.69	43.6	43.4	1.97	45.58	1.40
435/4	H-23	2.60	2.24	1.42	1.44	N-23	4.27	0.43	1.42	0.45	0.85	5.6	6.1	2.72	8.33	1.28
Blank	H-24	0.56	0.38			N-24	1.27									
Blank	H-25	0.54	0.44	0.25		N-25	0.92									
436/2	H-31	7.85	6.24	4.41	1.60	N-31	3.53	0.48	4.56	2.90	2.63	3.5	6.4	10.10	13.59	1.03
436/3	H-32	11.54	5.02	5.37	1.61	N-32	6.04	0.48	6.82	2.13	3.21	8.7	10.8	12.16	20.88	1.01
436/4	H-33	16.82	12.81	8.98	1.97	N-33	8.67	0.59	8.26	5.69	4.46	11.5	17.2	18.41	29.96	0.94
Blank	H-34	0.58	0.74			N-34	0.56									
440/2	H-51	3.94	2.57	1.53	1.13				3.00	0.86	1.18		0.9	5.04	5.04	0.86
440/3	H-52	7.71	2.50	3.38	1.12				6.39	0.81	2.84		0.8	10.04	10.04	1.08
440/4	H-53	7.24	3.37	3.31	1.11				6.02	1.60	2.80		1.6	10.43	10.43	1.03
440/6	H-54	2.72	1.70	0.90	1.11				1.95	0.10	0.63		0.1	2.68	2.68	0.83
440/7	H-55	16.61	2.55	6.46	1.99				8.07	0.48	3.15		0.5	11.70	11.70	0.99
441/1	H-61	7.67	2.07	2.82	1.89				3.77	0.25	1.39		0.2	5.40	5.40	0.93
441/2	H-62	0.78	0.39		0.02											
Blank	H-63	0.60	1.97	0.34												
Data from the replicate Teflon filter																
434/2	NT-15	1.25	0.51	0.56	0.28				2.49	-3.87	1.29		570.2	-0.09	574.00	-6.83
434/3	NT-16	1.13	1.17	0.44	0.42				1.37	-1.01	0.57		139.6	0.94	141.52	2.56
434/4	NT-17	1.74	1.54	0.86	0.36				3.30	-0.15	1.83		69.4	4.99	74.56	1.53
Blank	NT-18	0.66	0.98	0.31												

Table 6-8. Sulfate data from the total sample collectors

Sample ID	Flight/Pass	Sample volume (m3)	Sulfate mass per sample (µg)					Ambient conc. (µg/m3)	Without washings		
			Paper	Teflon	Wash	Total	Blank		Total	Blank	Ambient conc. (µg/m3)
1	432/2	1.31	3.80	1.27	22.77	27.84	41.11	-10.1	5.07	2.02	1.7
2	432/3	1.93	6.86	0.59	30.90	38.35	41.11	-1.4	7.45	2.02	2.4
3	432/4	1.33	6.78	0.57	25.78	33.13	41.11	-6.0	7.35	2.02	3.4
4	432/5	1.08	9.01	0.47	34.75	44.23	41.11	2.9	9.48	2.02	6.2
5	432/Blank		1.49	0.53	39.09	41.11	41.11		2.02	2.02	
15	434/2	0.80	7.88	1.21	19.70	28.79	6.71	27.6	9.09	2.47	8.6
16	434/3	1.18	7.97	0.92	21.79	30.68	6.71	20.3	8.89	2.47	5.7
17	434/4	1.01	7.26	0.79	6.15	14.20	6.71	7.4	8.05	2.47	5.8
18	434/Blank		2.34	0.13	4.24	6.71	6.71		2.47	2.47	
21	435/2	1.31	5.91	0.41	12.77	19.09	4.19	11.4	6.32	2.81	4.8
22	435/3	1.12	4.61	0.42	7.28	12.31	4.19	7.2	5.03	2.81	2.4
23	435/4	1.22	5.74	0.40	3.92	10.06	4.19	4.8	6.14	2.81	5.0
24	435/Blank		2.17	0.64	1.38	4.19	4.19		2.81	2.81	
25	434,435/Blank		12.27		8.84	21.11	4.19		12.27		
31	436/2	1.36	4.97	0.68	7.64	13.29	2.92	7.6	5.65	2.17	4.2
32	436/3	1.36	5.66	0.81	5.14	11.61	2.92	6.4	6.47	2.17	4.8
33	436/4	1.67	7.95	0.70	4.51	13.16	2.92	6.1	8.65	2.17	5.2
34	436/Blank		1.79	0.38	0.75	2.92	2.92		2.17	2.17	
Average of all samples		1.28	6.49 28%	0.71 3%	15.62 68%	22.83	15.84	6.48	7.20	2.34	4.63
Average of samples from 434 through 436		1.23	6.44 38%	0.70 4%	9.88 58%	17.02	4.61	10.99	7.14	2.48	5.17

Table 6-9. Nitrate data from the total sample collectors

			Nitrate mass per sample (μg)							Without washings		
Sample ID	Flight/Pass	Sample volume (m3)	Paper	Teflon	Nylon	Wash	Total	Blank	Ambient conc. (μg/m3)	Total	Blank	Ambient conc. (μg/m3)
1	432/2	1.31	7.54	1.39	5.41	8.35	22.69	9.75	9.9	14.34	9.57	3.6
2	432/3	1.93	24.50	1.02	7.19	10.11	42.82	9.75	17.1	32.71	9.57	12.0
3	432/4	1.33	21.10	0.75	2.70	5.98	30.53	9.75	15.6	24.55	9.57	11.3
4	432/5	1.08	28.00	0.52	2.83	10.64	41.99	9.75	29.9	31.35	9.57	20.2
5	432/Blank		0.68	0.79	8.10	0.18	9.75	9.75		9.57	9.57	
15	434/2	0.80	14.70	1.61	11.81	5.16	33.28	2.80	38.1	28.12	2.03	32.6
16	434/3	1.18	23.30	1.30	8.74	8.93	42.27	2.80	33.4	33.34	2.03	26.5
17	434/4	1.01	17.90	0.62	1.72	6.43	26.67	2.80	23.6	20.24	2.03	18.0
18	434/Blank		0.48	0.91	0.64	0.77	2.80	2.80		2.03	2.03	
21	435/2	1.31	21.30	0.78	1.77	12.77	36.62	4.58	24.5	23.85	4.12	15.1
22	435/3	1.12	18.80	2.82	4.47	7.90	33.99	4.58	26.3	26.09	4.12	19.6
23	435/4	1.22	16.70	0.42	2.28	6.85	26.25	4.58	17.8	19.4	4.12	12.5
24	435/Blank		0.90	0.58	2.64	0.46	4.58	4.58		4.12	4.12	
25	434,435/Blank		20.90		1.09	1.16	23.15	4.58		21.99		
31	436/2	1.36	16.00	0.68	1.92	7.15	25.75	5.67	14.8	18.6	5.02	10.0
32	436/3	1.36	18.80	1.53	4.48	5.37	30.18	5.67	18.0	24.81	5.02	14.5
33	436/4	1.67	22.20	0.82	2.14	9.74	34.90	5.67	17.5	25.16	5.02	12.1
34	436/Blank		0.57	2.07	2.38	0.65	5.67	5.67		5.02	5.02	
Average of all samples		1.28	19.29 59%	1.10 3%	4.42 13%	8.11 25%	32.92	6.01	22.03	24.81	5.52	16.00
Average of samples from 434 through 436		1.23	18.86 59%	1.18 4%	4.37 14%	7.81 24%	32.21	4.35	23.77	24.40	3.72	17.89

was hoped they would be because the blank values were high and variable. The blanks were determined from the analysis of the filters and the nozzle washings from TSC's which were flown but were not opened to the air flow. Much of the blank was due to sulfate and nitrate in the washings from the nozzle.

The results from TSC no. 25, which was flown as a blank on both flights 434 and 435 are higher than for all but one of the other blanks, which were flown only once. This suggests that much of the sulfate and nitrate in the blanks is due to the failure to seal the TSC's tightly before and after the sample collection. The one exception is the sulfate in TSC no. 5, which was the blank for the first flight. The sulfate data from all of the samples from the first flight (432) suggest that even though the TSC nozzles were washed several times before the start of the sampling, some contamination remained and even more washing would have been beneficial.

Averages of the data from the all samples (but not from the blanks) are reported at the bottom of the table. The percentages indicate how, on the average, the collected sulfate and nitrate was distributed among the filters and the nozzle washings. Because the sulfate data for the first flight are significantly different from the remainder of the data, averages which omit the data from the first flight are also reported.

It is interesting to note that on the average, most of the collected sulfate was deposited on the nozzle of the TSC. Most of the rest of the sulfate was on the paper filter, and only an average of 3 to 4% of the sulfate penetrated to the Teflon filter. Most of the nitrate was collected on the paper filter, and the second greatest amount was collected in the nozzle washings. Only 13 to 14% penetrated to the nylon filter.

The high and variable blank values for the TSC data indicate that the TSC samplers did not provide the reliable data for total concentrations of sulfate and nitrate needed for precise calculation of chemical conversion rates. It is still believed that the total sample collector is an essential device if accurate total concentrations of sulfate and nitrate are to be measured in clouds, and accurate total concentrations must be measured if chemical conversion rates are to be determined.

The data from the TSC's in Tables 6-8 and 6-9 emphasize one very important point, which is the difficulty of drawing samples of air containing cloud droplets through sampling tubes in an aircraft. Even though the inlet nozzles of the TSC's were short and straight, large amounts of the sulfate and nitrate were collected there. These data clearly demonstrate that the composition of air containing cloud droplets can be altered when it is drawn through sampling tubes into an aircraft.

6.6 OTHER GRAB SAMPLES

Several other types of grab samples were collected to address specific issues.

6.6.1 Bubblers for Formaldehyde and Acetaldehyde Gas

Bubblers were used to obtain information on the gas phase concentrations of formaldehyde and acetaldehyde. Limited data from sampling in earlier years (Richards et al., 1985) suggest that the gas phase concentrations are rather small in the clouds. Therefore, one bubbler was run for all passes in each flight in an attempt to collect samples with concentrations above the analytical detection limit. The sample flow through the bubblers was turned off between passses to make it possible to compare the bubbler data with other results.

The data are reported in Table 6-10. In most cases, the amount of sample collected is only slightly above the value of the blank, so the calculated ambient concentrations are small and somewhat uncertain. As with other measurements, there is the possibility that cloud droplets impacted on the walls of the sampling lines and released formaldehyde and acetaldehyde. Therefore, it is recommended that the ambient concentrations in Table 6-10 be regarded as approximate upper limits to the true ambient concentrations.

6.6.2 Bubblers for PAN

It was known from data collected in prior years that the NO/NO_x monitor often gives NO_x readings in the 5 to 10 ppb range in the clouds and that these readings are not due to NO. Because of the possibility that peroxyacetylnitrate (PAN) might contribute to these readings, bubbler samples were collected to place an upper limit on the gas phase PAN concentrations in the clouds. If the upper limit to the PAN concentration is sufficiently low, it is assured that PAN does not interfere with the calculation of nitrogen dioxide concentrations from the NO/NO_x monitor readings.

The air sample flow for the PAN bubblers was first passed through a water bubbler to remove acetate, then through 10 ml of 0.01 N KOH in a bubbler to collect PAN and hydrolyze it to acetate. One bubbler was exposed during each flight, so the volume of air sampled by each bubbler was in excess of 0.1 m^3. The acetate concentrations in the KOH bubblers were always found to be below the detection limit of 0.25 μM. Therefore, the upper limit for the average gas phase PAN concentration during each flight was approximately 0.5 ppb.

6.6.3 Hydrocarbons

Table 6-11 summarizes the non-methane hydrocarbon concentrations measured in the gas chromatographic analysis of the grab samples collected in the stainless steel canisters. The complete data from these analyses are reported in the Data Volume. The main purpose for collecting the hydrocarbon data was to make the data base from this study more useful for the evaluation of cloud chemistry computer models.

Table 6-10. Bubbler data for gas phase formaldehyde and acetaldehyde

Tape/Pass	Bubbler ID	Sample volume	Formaldehyde			Acetaldehyde		
		(liters)	µg/sample	µg/m^3	ppb	µg/sample	µg/m^3	ppb
432/3,4,5	B-2	139.68	0.60	1.36	1.11	0.12	-0.29	-0.12
434/3,4	B-3	69.65	0.59	2.58	2.10	0.26	1.44	0.60
435/2,3,4	B-4	119.60	1.29	7.36	5.98	1.16	8.36	3.47
436/2,3,4	B-5	134.62	1.00	4.38	3.56	0.22	0.45	0.18
440/3,4,6,7	B-51	120.13	0.93	4.33	3.52	0.19	0.25	0.10
	Blank		0.41			0.16		

Table 6-11. Summary of Hydrocarbon Data

Tape/Pass	Sample ID	CH_4 ppbv	CO ppbv	TNMHC ppbC	Fraction identified %	Fraction unidentified %	Alkanes %	Alkenes %	Aromatics %	C_2H_2 ppbC	C_2H_6 ppbC
432/3	TV675	1812	288	48	78	22	77	7	16	1.7	7.3
434/3	TV250	1739	261	2940	2	98	66	7	27	1.5	4.7
435/2	TV667	1789	376	158	37	63	70	7	22	2.1	5.4
436/2	TV659	1754	248	41	75	25	66	10	24	1.5	4.4
440/3	TV264	1778	163	47	81	19	82	6	12	0.7	5.6
441/1	TV245	1798	231	67	77	23	78	8	13	1.2	7.0

6.7 CONTINUOUSLY MEASURED PARAMETERS

Data for the parameters listed in Table 5-1 were recorded once per second throughout each flight. Most of these data are plotted as a function of time or altitude in the Data Volume (Richards et al., 1986b). Averages, standard deviations, and maximum and minimum values of these continuously recorded parameters have also been calculated and are reported in the Data Volume.

A special experiment was performed with the NO/NO_x analyzer to see if there was any evidence for gas phase nitric acid. The reason for this experiment was to guard against the unlikely possibility that gas phase nitric acid concentrations might be high enough in the clouds to interfere with the calculation of the nitrogen dioxide concentration from the readings of the NO/NO_x monitor. On flights when orbits were flown, the nylon filter was removed from the inlet to the NO/NO_x monitor for one round trip in the orbit pattern during each pass. During data processing, the NO_x data were averaged during the times the nylon filter was removed. The data in Table 6-12 compare the NO_x readings during the times the filter was removed with the readings during the remainder of the pass when the filter was in place. These data show that the NO_x readings with the nylon filter removed are not significantly greater than the readings with the filter in place. Therefore, nitrogen dioxide concentrations can be calculated from the NO/NO_x monitor readings without significant interference from gas phase nitric acid.

Table 6-12. NO_x averages with and without a nylon filter in the sample inlet.

Tape/Pass	Total pass		Without nylon filter		With nylon filter		Difference* (without minus with)
	Mean	No. of records	Mean	No. of records	Mean	No. of records	
434/3	9.2	2249	7.6	960	10.39	1289	-2.79
434/4	10.4	1930	10.9	859	10.00	1071	0.90
435/2	7.1	2571	6.8	483	7.17	2088	-0.37
435/3	7.5	2203	8.2	493	7.30	1710	0.90
435/4	6.4	2402	6.3	488	6.43	1914	-0.13
436/2	5.3	2675	5.5	489	5.26	2186	0.24
436/4	5.8	2701	6.4	447	5.68	2254	0.72
440/2	17.7	1801	16.4	512	18.22	1289	-1.82
440/3	21.8	1801	21.5	445	21.90	1356	-0.40
440/4	21.7	1801	21.7	468	21.70	1333	0.00

Mean difference and standard deviation -0.27 ± 1.19

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* The difference is equal to the contribution of nitric acid to the NO_x signal when there is no nylon filter in the sample inlet.

7. CLOUD WATER COMPOSITION

The analysis of the airborne cloud sampling data is divided into two sections. This section presents a discussion of the data for the cloud water composition as a function of time and location within the Los Angeles Basin. Comparisons are made between the May-June 1985 data and results obtained in prior years (Richards et al. 1983b, 1985). Section 8 contains a discussion of the implications of these cloud water composition data for the formation and fate of acid species in the clouds.

7.1 CLOUD WATER COMPOSITION

Figure 7-1 is a pie diagram showing the average composition by mass of the cloud water samples collected in May-June 1985. Only species for which analyses were performed are shown in this diagram, and no effort has been made to estimate the mass of undetermined species. The data in this diagram are taken from the averages appearing at the bottom of Tables 6-3, 6-5, and 6-6.

The average composition of the cloud water expressed as ionic equivalents is shown as a pie diagram in Figure 7-2. Only ionic species for which analyses were performed are shown, and no effort has been made to estimate the concentrations of undetermined ionic species. In rough terms, the data in Figure 7-2 can be summarized as follows:

> The average ionic composition of the cloud water collected in May-June 1985 is:
>
> 42% nitric acid,
> 27% ammonium sulfate,
> 18% sodium chloride, and
> 13% other metal sulfates and nitrates.

The average composition of the cloud water has changed little from year to year. The percentages given here fall within the range given for the average cloud water composition in the first Final Report of this series (Richards et al., 1983b), which was:

> 40-50% nitric acid,
> 20-30% ammonium sulfate, and
> 10-20% sodium chloride.

These recipes for the cloud water composition are intended to be a simple summary of the observed compositions, and are not intended to imply that the sources of hydrogen ion and nitrate are related nor that the sources of ammonium and sulfate are related.

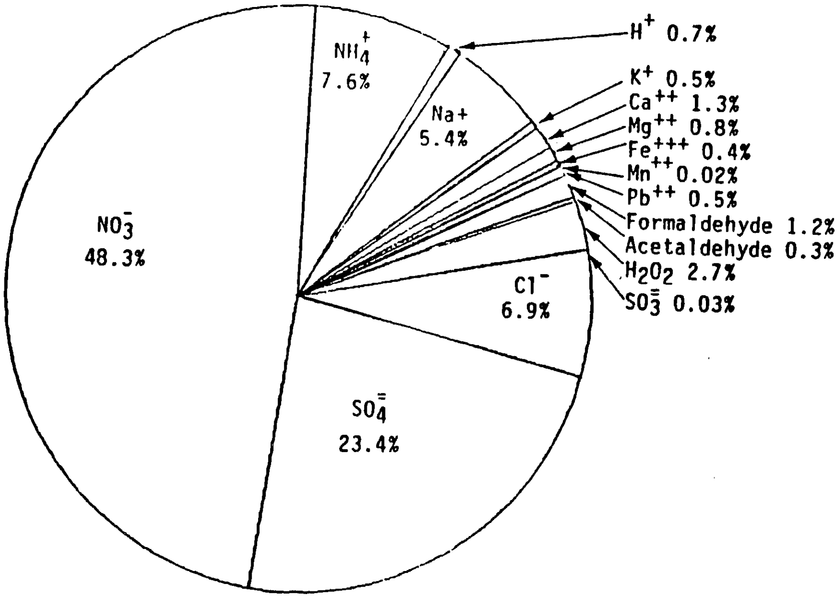

Figure 7-1. May-June 1985 average cloud water composition by mass. Only species determined are included.

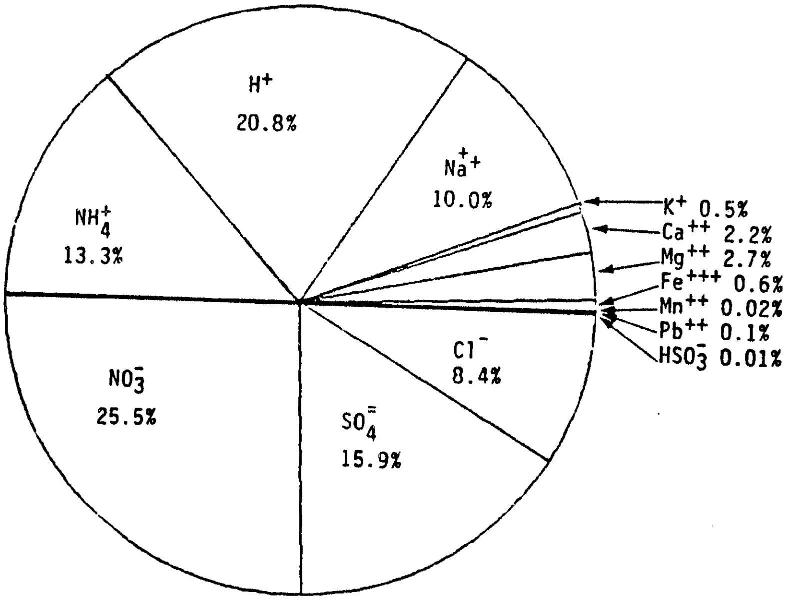

Figure 7-2. May-June 1985 average cloud water composition by equivalents. Only ionic species determined are included.

Table 7-1 shows the ambient concentrations of the species determined in the cloud water. These data were obtained by multiplying the concentrations of the solutes in the collected water reported in Tables 6-3, 6-5, and 6-6 by the liquid water content (LWC) data in Table 6-2. The averages at the bottom of this table have the same format as in previous tables.

Table 7-2 gives the mean and range of the concentration of some of the more important cloud water species observed each of the years in this series of studies. Except for the high maximum concentrations of sulfate, nitrate, and ammonium observed in May 1982, no significant trends appear in these data. The extreme concentrations observed in May 1982 are discussed in Section 7.3.3 below, and are believed to have been due to local plumes present at that time.

7.2 HENRY'S LAW CALCULATIONS

Henry's Law calculations have been performed to estimate the distribution of formaldehyde, acetaldehyde, and hydrogen peroxide between the gas and liquid phase. Henry's Law states that the liquid and gas phase concentrations are proportional to each other at equilibrium. For these calculations, it was assumed that the gas and liquid phases were in equilibrium, then the measured liquid phase concentrations and published data for the Henry's Law constant were used to estimate the gas phase concentrations.

Results of the Henry's Law calculations for formaldehyde and acetaldehyde are shown in Table 7-3. Henry's Law constant for formaldehyde was obtained from Dong and Dasgupta (1986), and for acetaldehyde from Gaffney and Senum (1984). The results for formaldehyde appear reasonable, but those for acetaldehyde are certainly not. The calculated gas phase concentrations are too high by at least a factor of 100, indicating that the published Henry's Law constant is probably incorrect.

The calculations for hydrogen peroxide are in Table 7-4. The Henry's Law constant was obtained from Hwang and Dasgupta (1985). Laboratory data show that hydrogen peroxide in aqueous solution oxidizes sulfur (IV) to sulfate very rapidly. Therefore, model calculations show that if more sulfur dioxide were mixed into the clouds, the hydrogen peroxide would be rapidly consumed and sulfate would be produced. Table 7-4 contains calculated values for the amount of additional sulfate that would be produced if enough sulfur dioxide were added to the clouds to consume all the hydrogen peroxide. Additional columns in the table give the ratio of the additional sulfate that would be formed to the sulfate already existing, and also the total amount of sulfate that would be present. Note that in three cases, these calculations show that the additional sulfate formed would cause the total sulfate concentration in the cloud water to exceed the California standard of 25 $\mu g/m^3$.

7.3 COMPOSITION CHANGES WITH LOCATION

Large changes in the composition of the atmosphere with height above ground were typically observed. The vertical profiles are discussed first to provide a setting in which to discuss the horizontal variations in the composition of the clouds in the Los Angeles Basin.

Table 7-1. Ambient concentrations of cloud water solutes

Tape/Pass	Sample ID	LWC ml/m^3	pH	Ambient Concentrations (µg/m^3)															
				Cl^-	NO_3^-	$SO_4^=$	$SO_3^=$	NH_4^+	Na^+	K^+	Ca^{++}	Mg^{++}	Fe^{+++}	Mn^{++}	Pb^{++}	H^+	H_2O_2	Form-aldehyde	Acet-aldehyde
432/2	U1	0.61	3.41	6.29	23.9	11.7	0.002	4.20	4.70	0.421	1.342	0.714	0.295		0.202	0.237	3.38		
432/3	U3	0.59	3.35	3.91	17.9	9.0		2.75	2.64	0.196	0.457	0.391				0.264	1.24		
432/4	U5	0.21	2.90	2.49	22.5	7.6	0.007	3.24	2.04	0.231						0.264	0.38		
432/5	U6	0.47	3.12	3.77	37.6	11.7		6.50	3.67	0.346	0.902	0.590	0.330	0.01466	0.209	0.357	0.71		
433/1,2	U10	0.40	3.43	3.87	12.5	8.5	0.011	1.62	3.66	0.369	0.724	0.496	0.178			0.149			
433/3	U11	0.25	3.26	1.60	10.5	7.2										0.137			
433/4	U12	0.40	2.97	2.28	27.6	13.2	0.009	3.48	2.25	0.255	0.744	0.390	0.302		0.150	0.429	0.17	0.12	0.06
433/4	U13	0.40	2.98	1.78	24.9	11.6		3.02	1.58	0.120	0.304	0.258				0.419			
434/2	U15	0.82	3.26	3.00	15.7	12.3		1.66	2.02	0.136	0.340	0.290	0.089		0.294	0.451			
434/2	U16	0.82	3.26	4.06	20.2	16.1	0.022	2.07	3.13	0.186	0.417	0.455	0.138	0.00853	0.260	0.451	2.84	0.39	0.08
434/3	U17	1.20	3.25	4.80	31.4	22.2		3.59	3.26	0.196	0.512	0.499	0.210	0.00871	0.426	0.675	1.36	0.79	0.27
434/3	U18	1.20	3.40	5.26	25.3	16.4		3.19	3.86	0.222	0.514	0.556	0.088	0.00818		0.478	1.81		
434/4	U19	0.93	3.37	2.15	26.2	10.7		3.12	1.86	0.255	0.440	0.305	0.132	0.00741	0.461	0.397	1.74	0.87	0.16
434/4	U20	0.93	3.35	2.03	26.6	11.3	0.030	3.25	1.81	0.178	0.427	0.311	0.125	0.00768	0.340	0.415	1.40		
435/2	U21	1.00	3.35	3.24	36.8	14.6		5.86	2.97	0.378	1.250	0.518	0.315	0.01690	0.336	0.447	1.04	1.15	0.25
435/3	U24	1.20	3.31	2.87	40.4	15.5	0.006	5.83	2.02	0.170	0.694	0.343	0.157	0.00923	0.536	0.588	1.03	1.93	0.25
435/4	U26	0.90	3.65	1.55	24.6	8.8		7.47	0.80	0.073	0.279	0.129	0.057	0.00343	0.307	0.201	0.88	1.14	0.17
436/2	U31	0.44	3.32	1.57	19.5	6.4		3.42	1.45	0.161	0.497	0.251	0.117	0.00774	0.130	0.211	0.60	0.50	0.10
436/3	U33	0.30	3.14	1.02	17.8	4.8		2.43	0.73	0.088	0.396	0.151	0.100	0.00528		0.217	0.44	0.38	0.10
436/4	U34	0.36	3.42	1.37	22.9	6.2		5.66	1.52	0.164	0.691	0.287	0.172	0.00864	0.084	0.137	0.62	0.50	0.11
440/2	U52	0.60	3.82	2.18	5.2	4.1		0.68	1.55	0.130	0.394	0.231	0.048	0.00392		0.091	1.66		
440/3	U54	0.30	3.20	5.18	11.1	9.6		1.87	3.91	0.227	0.459	0.521	0.102		0.090	0.189		0.22	0.05
440/4	U55	0.40	3.25	3.37	17.3	10.3		3.55	3.00	0.243	0.568	0.452	0.162	0.00708	0.084	0.225	0.98	0.40	0.13
440/5	U56	0.30	3.60	5.49	5.3	3.7		0.55	1.41	0.097	0.219	0.196	0.049	0.00256	0.076	0.075	0.99	0.09	0.01
441/1	U61		3.75															0.00	0.00
441/1	U62		3.65															0.00	0.00
441/1	U63		3.57																
Averages																			
All data		0.63	3.35	3.13	21.8	10.6	0.013	3.44	2.43	0.211	0.571	0.379	0.158	0.0080	0.249	0.313	1.23	0.56	0.12
First pass		0.67	3.41	3.46	19.1	10.5		2.79	2.78	0.255	0.709	0.422	0.168	0.0093	0.244	0.291	1.90	0.51	0.11
Middle passes		0.63	3.23	3.39	21.6	11.4		3.31	2.68	0.197	0.514	0.416	0.136	0.0077	0.257	0.337	1.04	0.62	0.13
Last pass		0.59	3.31	2.55	24.5	9.6		4.13	1.86	0.186	0.501	0.308	0.167	0.0074	0.232	0.304	0.93	0.54	0.10

Table 7-2. Summary of cloud water concentrations

Analyte	Time Period	Mean	Maximum	Minimum
Ambient concentrations of water species in $\mu g/m^3$				
Sulfate	May 1982	15.4	38.4	4.0
	Jun 1984	6.5	12.1	3.3
	May-Jun 85	10.6	15.5	3.7
Nitrate	May 1982	35.8	91.0	7.6
	Jun 1984	16.5	24.0	7.3
	May-Jun 85	21.8	40.4	5.2
Ammonium	May 1982	5.8	18.	0.6
	Jun 1984	1.6	2.3	0.8
	May-Jun 85	3.4	7.5	0.6
Water concentrations in μM				
H2O2	May 1982	33	88	1
	Jun 1984	55	127	16
	May-Jun 85	57	167	12
HCHO	May 1982	37	72	6
	Jun 1984	43	73	20
	May-Jun 85	29	53	11
pH	May 1982	2.98	3.59	2.34
	Jun 1984	3.01	3.60	2.83
	May-Jun 85	3.35	3.82	2.90

Table 7-3. Henry's Law calculations for formaldehyde and acetaldehyde

		Formaldehyde					Acetaldehyde				
Tape/Pass	ID	Conc. in water (µM)	Calc. gas conc. (ppb)	Ambient conc. in water (ppb)	Total ambient conc. (ppb)	Fraction in water (%)	Conc. in water (µM)	Calc. gas conc. (ppb)	Ambient conc. in water (ppb)	Total ambient conc. (ppb)	Fraction in water (%)
433/4	D1	9.86	2.85	0.096	2.94	3.3	3.63	242	0.026	242	0.011
434/2	D15	15.77	4.40	0.315	4.71	6.7	2.21	147	0.033	147	0.022
434/3	D16	21.88	5.96	0.640	6.60	9.7	5.15	343	0.113	343	0.033
434/4	D18	31.01	8.23	0.703	8.93	7.9	4.01	267	0.068	268	0.025
435/2	D21	38.24	9.99	0.933	10.92	8.5	5.80	387	0.106	387	0.027
435/3	D22	53.58	13.65	1.568	15.22	10.3	4.74	316	0.104	316	0.033
435/4	D23	42.26	10.96	0.928	11.89	7.8	4.19	279	0.069	279	0.025
436/2	D31	37.70	9.86	0.405	10.26	3.9	5.19	346	0.042	346	0.012
436/3	D32	41.74	10.83	0.305	11.14	2.7	7.36	491	0.040	491	0.008
436/4	D33	46.41	11.95	0.407	12.36	3.3	6.71	447	0.044	447	0.010
440/3	D51	24.76	6.68	0.181	6.86	2.6	3.90	260	0.021	260	0.008
440/4	D52	33.55	8.85	0.327	9.18	3.6	7.49	500	0.055	500	0.011
440/5	D53	10.51	3.02	0.077	3.10	2.5	0.75	50	0.004	50	0.008
441/1	D61	14.33	4.03				1.54	102			
441/1	D62	13.69	3.86				1.73	115			
Averages											
All data		29.02	7.67	0.530	8.78	5.60	4.29	286	0.056	313	0.018
First pass		26.51	7.07	0.551	8.63	6.39	3.68	246	0.060	293	0.021
Middle passes		31.53	8.30	0.605	9.80	5.79	5.06	337	0.067	382	0.019
Last pass		28.01	7.40	0.442	7.84	4.95	3.86	257	0.042	257	0.016

Formaldehyde Henry's Law constant from Dong and Dasgupta (1986).

Acetaldehyde Henry's Law constant from Gaffney and Senum (1984). These data suggest that the value used is in error by at least a factor of 100.

Table 7-4. Henry's Law calculations for hydrogen peroxide and calculation of potential additional sulfate formation

Tape/Pass	Sample ID	Hydrogen peroxide concentrations				Fraction of H_2O_2 in water	Sulfate formed if all H_2O_2 reacted		
		Meas-ured in water	Gas conc. from Henry's Law	In water in units of	Total		Sulfate formed	Ratio existing sulfate	Existing total sulfate
		(µM)	(ppb)	(ppb)	(ppb)	(%)	(µg/m^3)	(%)	(µg/m^3)
432/2	P1	163.0	1.63	2.43	4.06	60	15.96	136.30	27.68
432/3	P3	62.0	0.62	0.89	1.51	59	5.95	66.38	14.92
432/4	P5	53.6	0.54	0.28	0.81	34	3.19	42.18	10.75
432/5	P6	44.3	0.44	0.51	0.95	53	3.74	32.11	15.40
433/1,2									
433/3									
433/4	P11	12.3	0.12	0.12	0.24	49	0.96	7.27	14.12
433/4									
434/2									
434/2	P15	102.0	1.02	2.05	3.07	67	12.05	74.97	28.12
434/3	P16	33.4	0.33	0.98	1.31	75	5.17	23.27	27.37
434/3	P17	44.3	0.44	1.30	1.74	75	6.85	41.67	23.29
434/4	P18	55.1	0.55	1.25	1.80	69	7.09	66.31	17.79
434/4	P19	44.3	0.44	1.01	1.45	69	5.70	50.25	17.05
435/2	P22	30.6	0.31	0.75	1.05	71	4.15	28.40	18.75
435/3	P26	25.2	0.25	0.74	0.99	75	3.90	25.18	19.38
435/4	P25	28.8	0.29	0.63	0.92	69	3.62	41.08	12.44
436/2	P31	40.1	0.40	0.43	0.83	52	3.27	51.29	9.65
436/3	P32	43.0	0.43	0.32	0.75	42	2.93	61.04	7.73
436/4	P33	50.7	0.51	0.45	0.95	47	3.75	60.16	9.97
440/2	P52	81.3	0.81	1.19	2.01	59	7.88	193.24	11.96
440/3	P53								
440/4	P54	72.4	0.72	0.71	1.43	49	5.63	54.76	15.91
440/5	P55	97.4	0.97	0.71	1.69	42	6.64	179.86	10.33
441/1	P61	52.8	0.53		0.53		2.07		
441/1	P62	60.1	0.60		0.60		2.36		
441/1	P63	63.5	0.63		0.63		2.50		
Averages									
All data		57.3	0.57	0.88	1.33	59	5.24	65.04	16.45
First pass		78.3	0.78	1.37	1.92	62	7.56	96.84	19.23
Middle passes		49.2	0.49	0.74	1.14	58	4.50	44.92	17.05
Last pass		49.5	0.50	0.67	1.08	57	4.25	62.43	13.87

7.3.1 Vertical Spatial Distributions

Almost all of the flights reported in this series of studies were conducted at night when stratus clouds were present in the Los Angeles Basin. Under these conditions, most pollutants show large variations in concentration with height above ground. The stratus clouds which can be sampled by aircraft occupy an altitude range only a few hundred feet deep approximately 2000 ft above ground level. Because of the interest of these studies in cloud chemistry, most of the data reported here apply to the thin layer where clouds were available for sampling. Collecting and analyzing a set of grab samples requires half to one hour of flying time and hundreds of dollars of analytical costs, so few grab samples were collected above and below the clouds.

Data are easily obtained for the vertical profiles of species, such as ozone, which can be measured continuously. The previous Final Report (Richards et al. 1985) presented vertical profiles for ozone. The data obtained in May-June 1985 are consistent with prior results, and show that even though ozone concentrations often fall to zero at night at ground level, they never do so in the clouds. Ozone concentrations in the clouds were usually between 50 and 100 ppb.

Again this year, it was observed that ozone concentrations just above cloud tops where typically 10 to 60 ppb greater than ozone concentrations in the clouds. However, the ozone concentrations are not always greater above the clouds and can be quite variable. As an example of the variability, the morning of 24 May 1985, a missed approach to the Santa Ana Airport (John Wayne Airport) found ozone concentrations of 80 to 90 ppb in clouds and greater than 200 ppb above the clouds. A missed approach at the Long Beach Airport about 20 min later and roughly 30 km to the northwest found ozone concentrations in the clouds near 75 ppb and 90 to 100 ppb above the clouds. High ozone concentrations above the clouds were typically accompanied by high aerosol light scattering readings by the integrating nephelometer.

7.3.2 Horizontal Spatial Distributions in 1985

In 1985 and in prior years, it was found that the concentration of nitrate and sulfate in the cloud water were relatively constant throughout the Basin. The map in Figure 7-3 shows all the cloud water sulfate concentrations measured in 1985 at the location where the measurements were made. These results show that within the narrow vertical altitude range where stratus clouds were sampled, the cloud water sulfate concentrations were quite uniform. The nitrate concentrations in the cloud water are shown in a similar map in Figure 7-4, and again the concentrations are rather uniform.

In 1985, enough hydrogen peroxide data were obtained to explore the spatial distribution of the concentration of this species. Figure 7-5 shows the spatial distribution of the hydrogen peroxide concentrations in the cloud water. Results of the Henry's Law calculations in Table 7-4 show that a very similar spatial distribution is obtained if the total ambient concentrations are plotted on a map. The data show a definite trend; the highest hydrogen peroxide concentrations were observed offshore, and the hydrogen peroxide

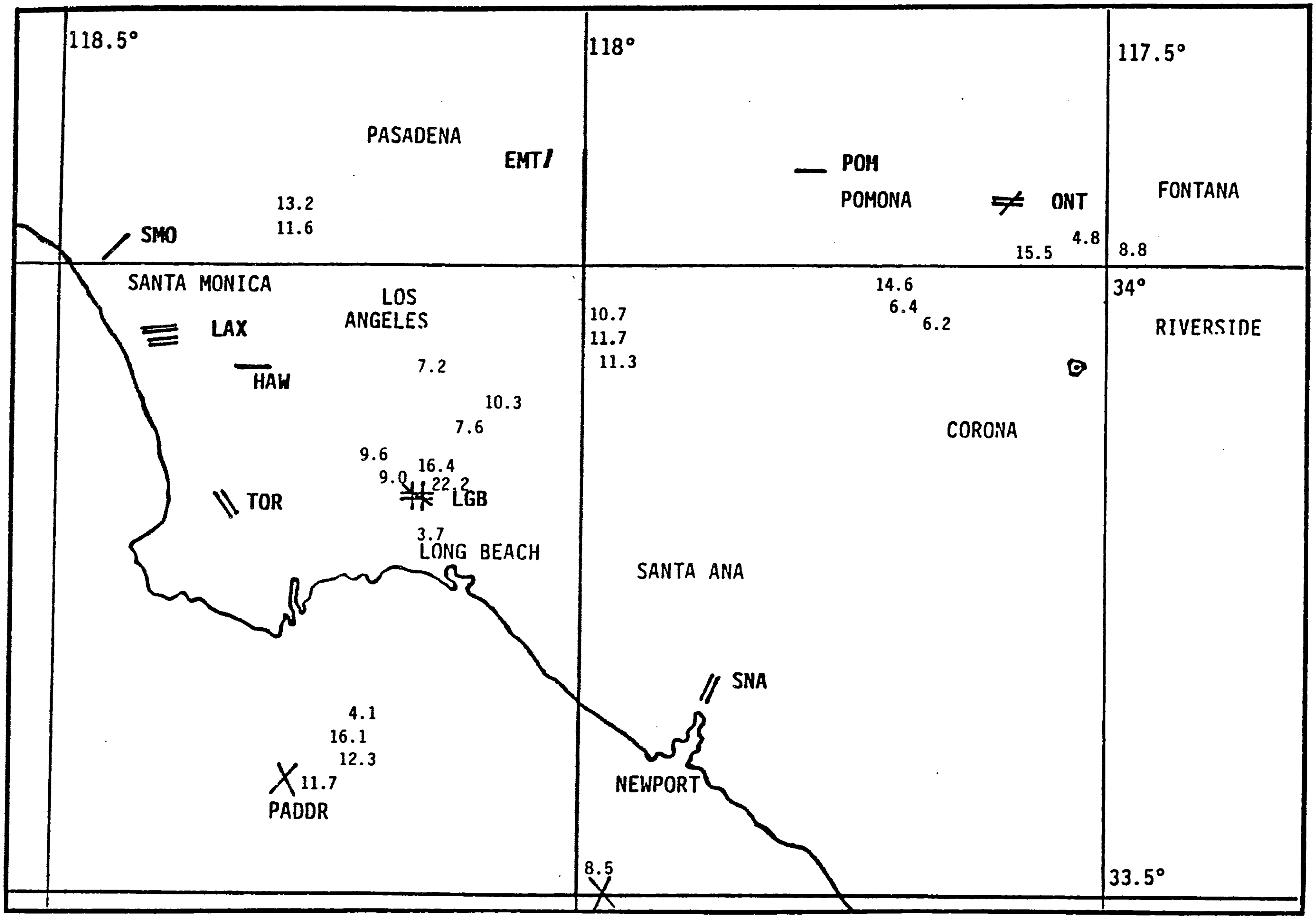

Figure 7-3. Spatial distribution of all 1985 measurements of cloud water sulfate concentrations ($\mu g/m^3$).

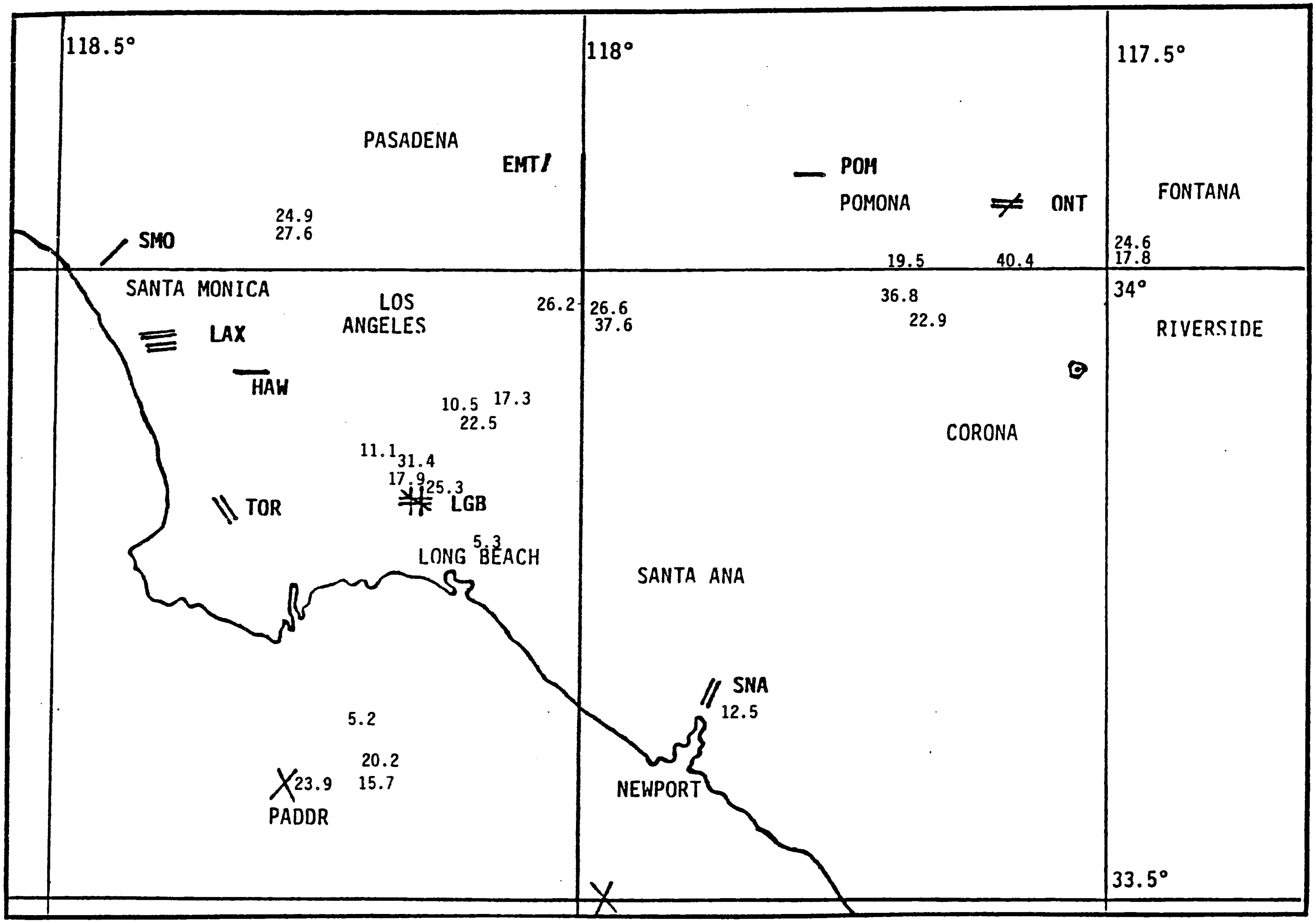

Figure 7-4. Spatial distribution of all 1985 measurements of cloud water nitrate concentrations (μg/m^3).

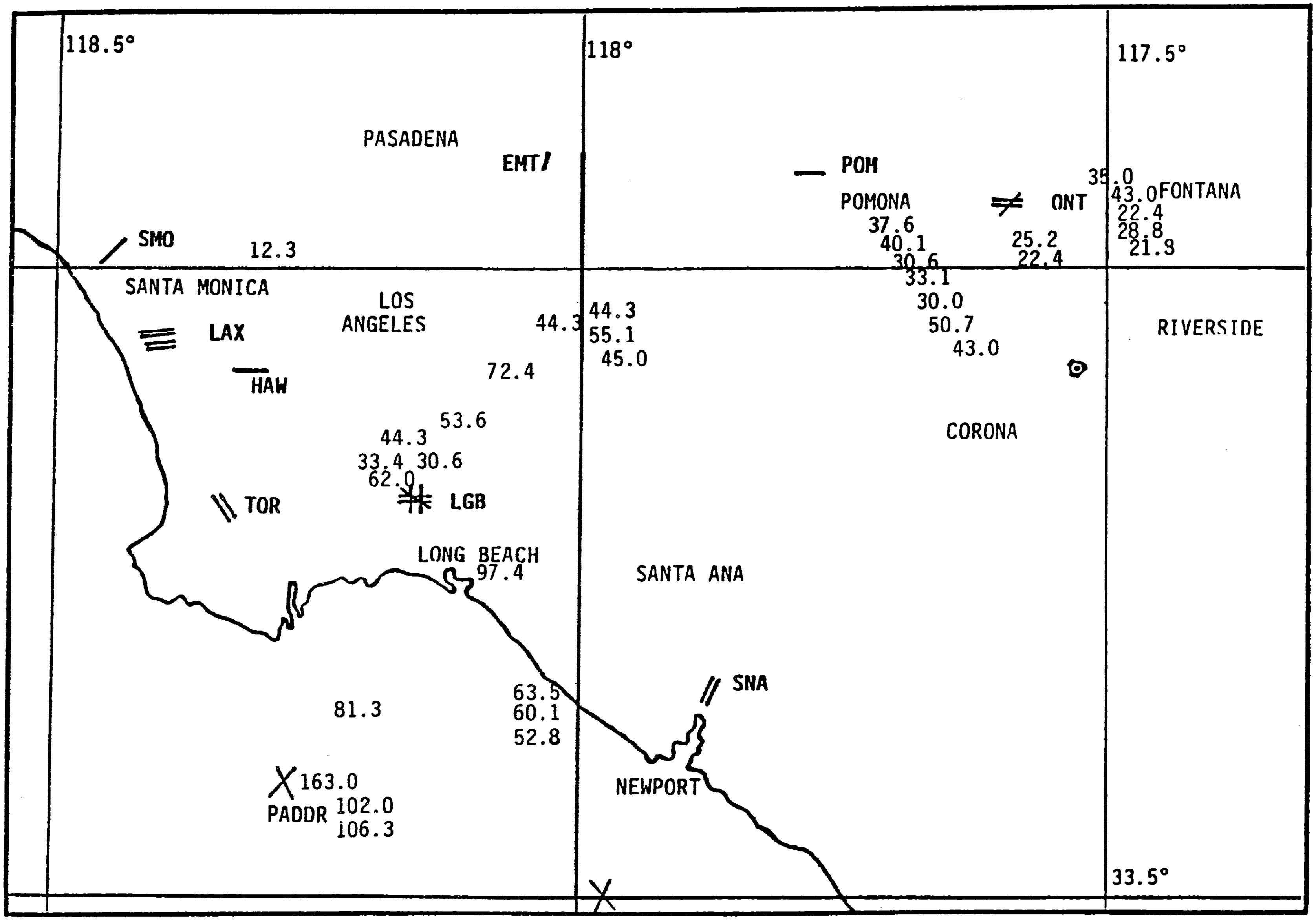

Figure 7-5. Spatial distribution of all 1985 measurements of cloud water hydrogen peroxide concentrations (μM).

concentrations decreased with increasing distance inland. On the average, the hydrogen peroxide concentrations in the cloud water were roughly 30% as great in the Fontana area as along the coast and just offshore.

The ozone concentrations observed at the times the offshore hydrogen peroxide samples were collected were 68, 80, and 97 ppb, indicating that the clouds had formed in relatively polluted air masses. Lead and soot data provide additional evidence that the offshore samples contained urban emissions. Sufficient meteorological data are not available to perform a back trajectory analysis to determine the prior history of the air masses sampled offshore.

Again in 1985 it was noticed that when the aircraft was flying in and out of clouds at constant altitude, the ozone concentrations typically were higher out of the clouds than in the clouds. An extreme example of such data is shown in Figure 7-6, where the ozone concentrations are more than 50 ppb greater out of the clouds than in. Usually, the ozone concentrations do not differ this much. In the previous report in this series (Richards et al., 1985), all the data collected in horizontal flights were averaged in clouds and out of clouds. It was found that on the average, the ozone concentrations were 7.6 ppb greater out of the clouds, but there were significant day-to-day variations in this difference.

The relative importance of meteorological and chemical effects in causing the ozone concentrations to be lower in the clouds than in clear air is not known. In extreme cases, such as shown in Figure 7-6, it is not likely that only chemical processes could cause the observed ozone concentration variations.

7.3.3 Plumes

The only notable exception to the uniform concentrations of sulfate and nitrate in the Los Angeles Basin was observed the night of 21-22 May 1982 in the Fontana area (Richards et al., 1983b). The sulfate and nitrate concentrations observed on that flight are roughly double the highest concentrations observed in more recent years. The continuous data for NO/NO_x, O_3, and SO_2 indicate that plumes containing appreciable quantities of sulfur and nitrogen oxides had become mixed with the clouds. This is the only case in which the contribution of local sources to sulfate and nitrate concentrations in stratus clouds has been definitely observed in this series of studies. Emissions in the Fontana area have decreased since 1982, so the maximum sulfate and nitrate concentrations are likely to be lower at the present time.

Isolated plumes have been observed in the clouds in coastal areas every year flights have been made. These plumes have always been small enough that only a small fraction of each grab sample was collected in a plume. Therefore, the plumes themselves have had only a minor effect on the data collected in them. In the data reported here, the emissions in these plumes are mixed with all the other nearby emissions to make a general contribution to the pollution found in the clouds in the Basin. No effort was made to "chase" these plumes to collect data in them because of the logistical problems of flying under air traffic control in clouds in the congested air space in the Los Angeles Basin.

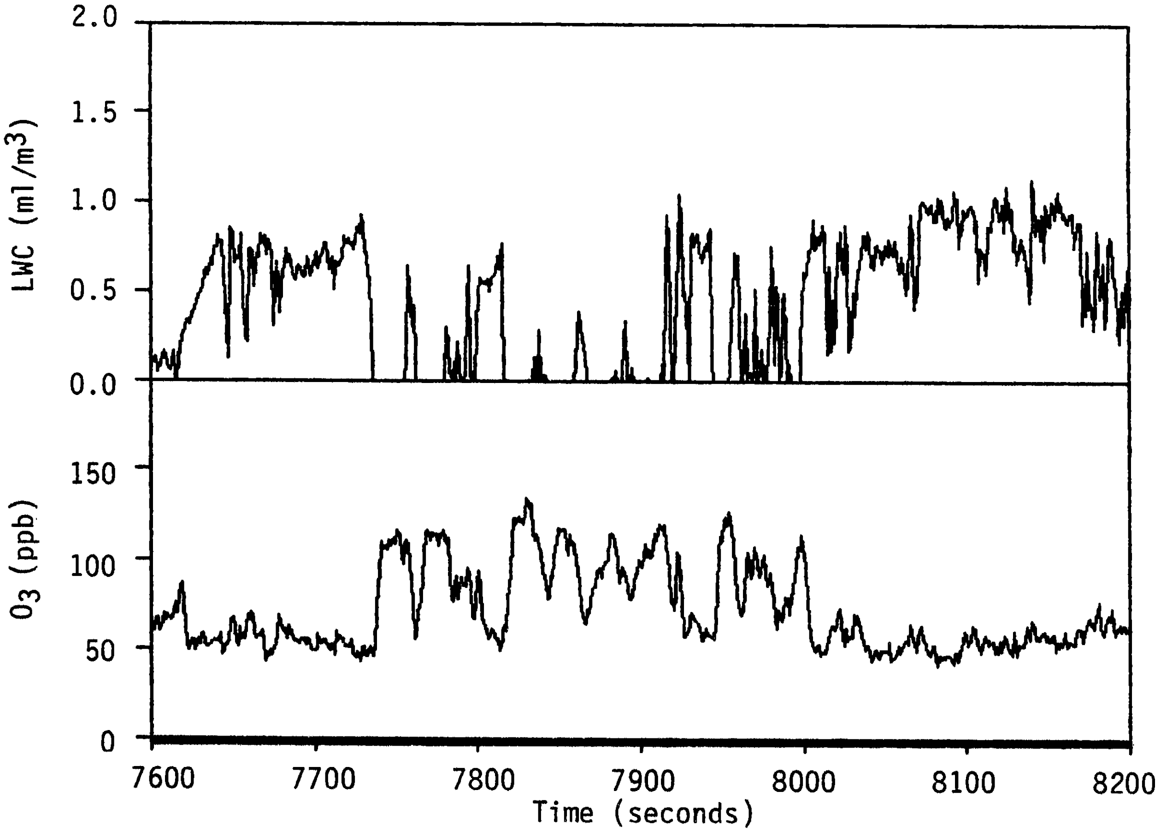

Figure 7-6. An example where ozone concentrations were much higher out of the clouds than in. The upper panel shows the cloud liquid water content (LWC) measured by the FSSP and the lower panel shows the ozone concentration. The time resolution is 1 s. These data were recorded at constant altitude during Flight 434 Pass 4 over the Whittier Narrows (near the middle of the Los Angeles Basin) on 25 May 1985.

7.4 COMPOSITION CHANGES WITH TIME

In this study, a significant effort was directed toward attempting to follow air parcels and to measure the change of composition with time in the clouds. To accomplish this, the flight patterns shown in Figure 5-2 were planned and cleared in advance with air traffic control. Radiosonde data were then used to determine the length of time which should be allowed to elapse between the collection of samples in each location.

The restrictions of air traffic control, variability of the wind, and vertical mixing make it impossible to exactly follow an air parcel. However, air flows in the Los Angeles Basin are predictable enough that this flight pattern permitted following air parcels rather closely on several nights.

Five flights were made in 1985 with the objective of measuring changes in the cloud composition with time. Two flights were made near Long Beach, then two near Ontario, and finally one more was made near Long Beach. In general, cloud water concentrations of non-volatile species decreased with time. This is shown in Figures 7-7 and 7-8, which show averages of the data for all five flights. The three bars for each chemical species show average concentrations for the first sample collected each flight, the intermediate sample(s), and the last sample. The usual time interval between the three samples was between 45 min and 1 h.

Because of the great concentration differences for the various species, a logarithmic concentration scale is used in these bar graphs. This format has the additional advantage that a given relative change in the concentration of any species will be shown by the same difference in height of the bars.

Figure 7-9 shows the ambient concentration data from each of the five flights individually. It is approximately true that the concentrations of the metals sodium, potassium, calcium, and magnesium tend to vary together as if their concentration variations were all controlled by exactly the same factors. These elements are neither produced nor destroyed by chemical reactions in the clouds, so these factors must be physical or meteorological processes.

The data in Figure 7-10 were calculated in an attempt to remove the effect of these physical processes on the data. Separate calculations were performed for each flight. A multiplier was found for the data represented by the second bar, and another multiplier for the data represented by the third bar, so that when the data were normalized by these multipliers, the concentrations of sodium, potassium, calcium, and magnesium remained constant on the average. The average of these normalized concentration data is shown in Figure 7-11.

One of the most prominent trends in the normalized data is that the concentrations of lead and ammonium tend to increase with time. This shows that air below the clouds is mixed into the clouds during the sampling time interval. Other trends in these data are discussed in the following Section. An analysis of these data showed that none of the trends in the ambient

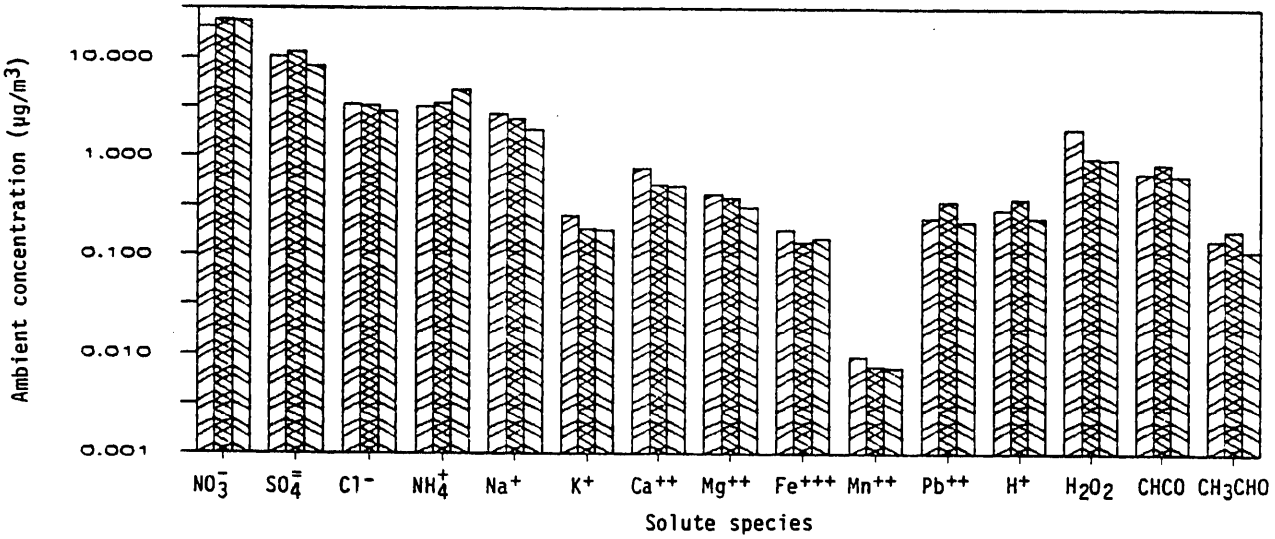

Figure 7-7. Trends with time in the average ambient concentrations of cloud water species measured in flights in which air parcels were approximately followed. Note the logarithmic concentration scale. The three bars for each species show average concentrations measured at approximately one hour intervals.

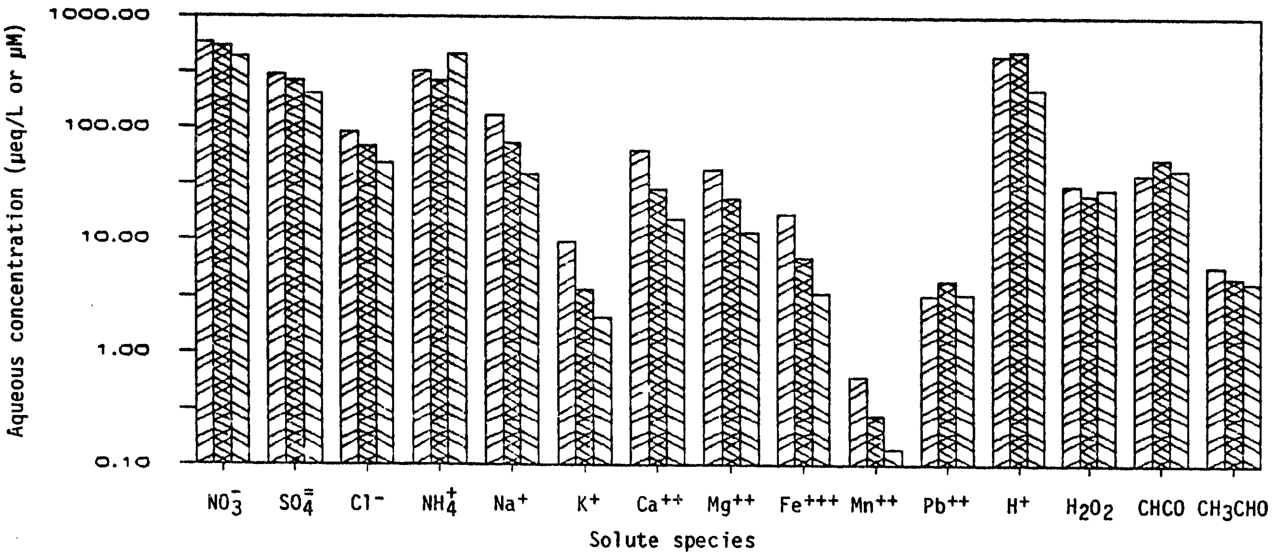

Figure 7-8. Trends with time in the average cloud water concentrations of species measured in flights in which air parcels were approximately followed. These are the same data as in Figure 7-7, except that here the concentrations are in units of microequivalents per liter of cloud water for the ionic species and micromolar for the other species.

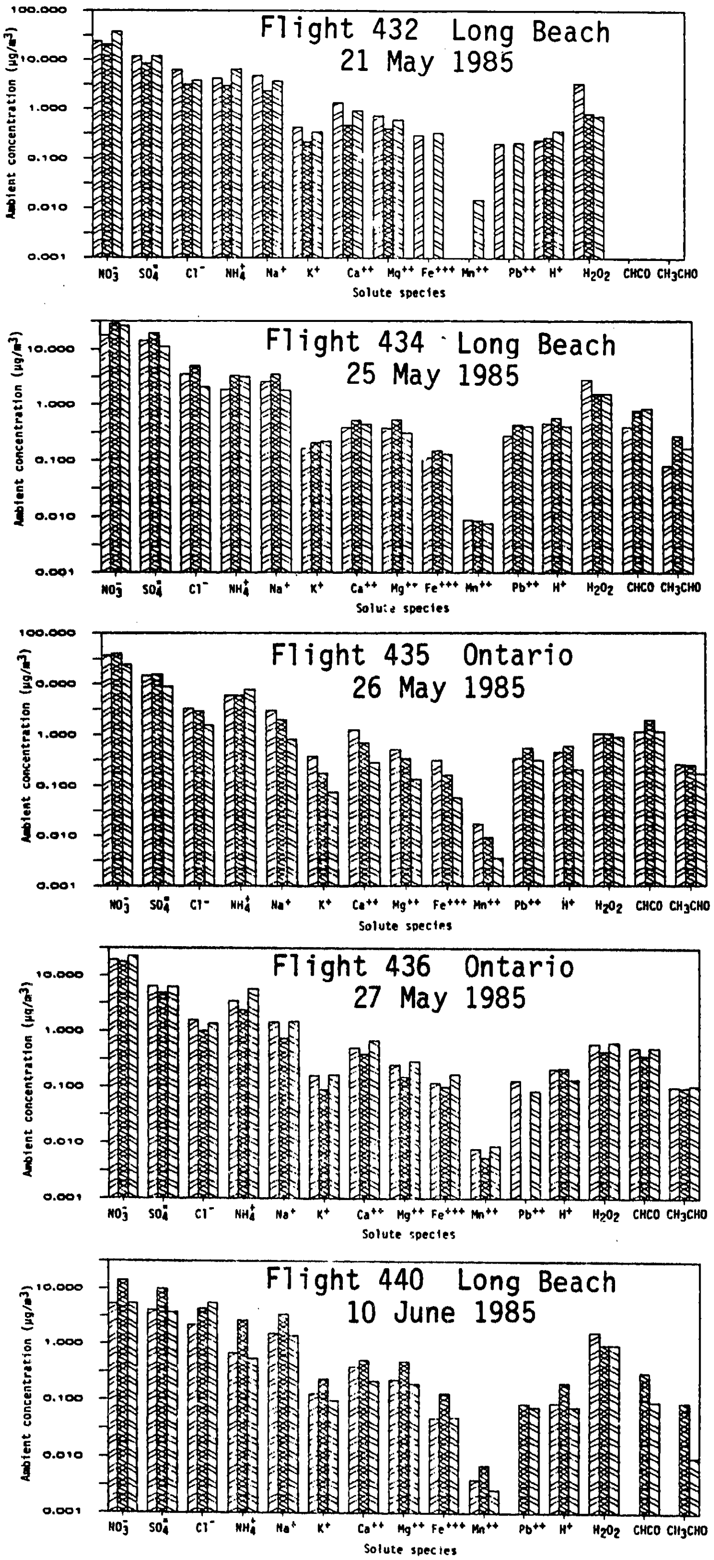

Figure 7-9. Ambient concentrations ($\mu g/m^3$) measured in the flights which approximately followed air parcels. The three bars for each species show data collected at about one hour intervals.

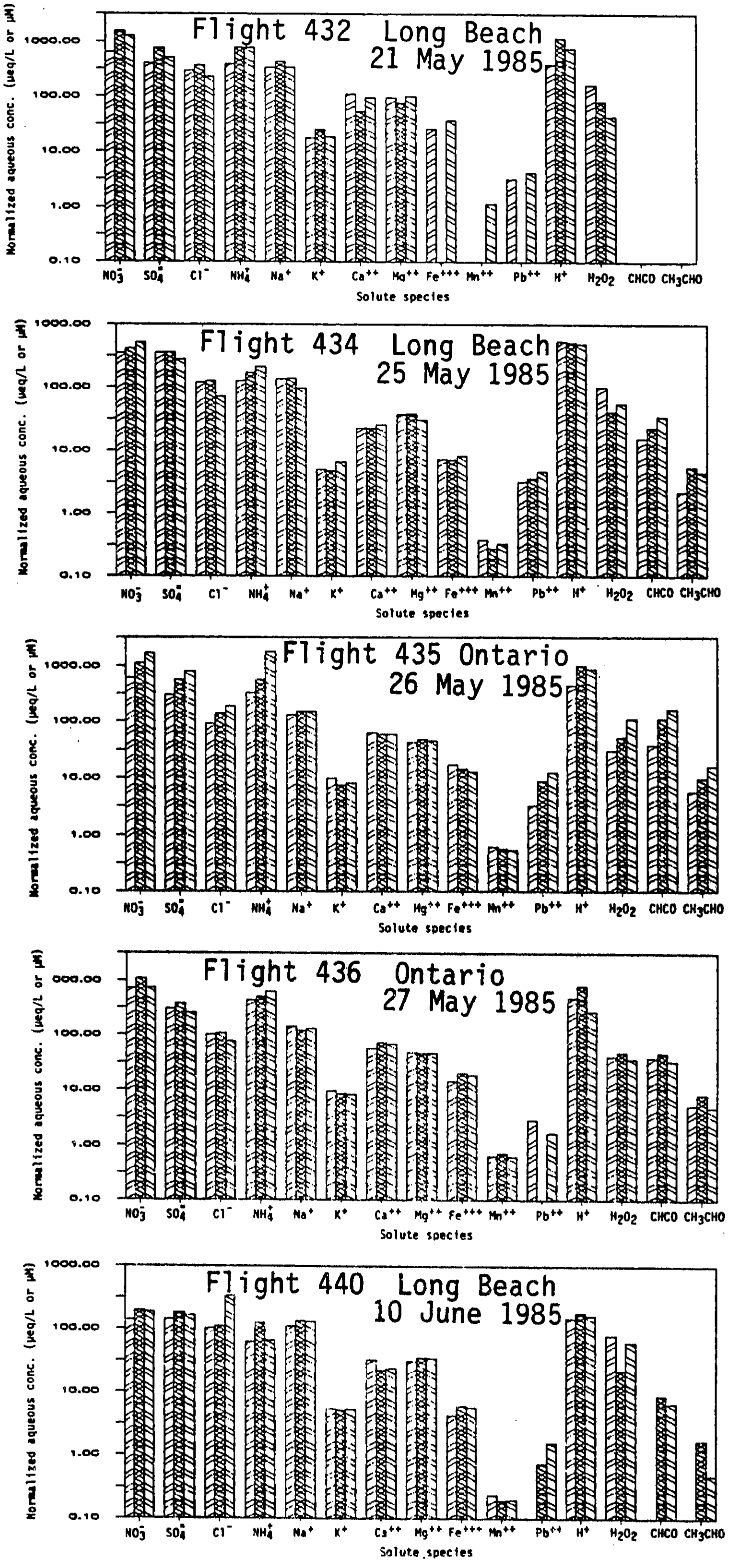

Figure 7-10. Normalized concentrations for the flights which approximately followed air parcels. The data for the second and third orbits for each flight have been normalized so that on the average, the concentrations of Na^+, K^+, Ca^{++}, and Mg^{++} remain constant with time.

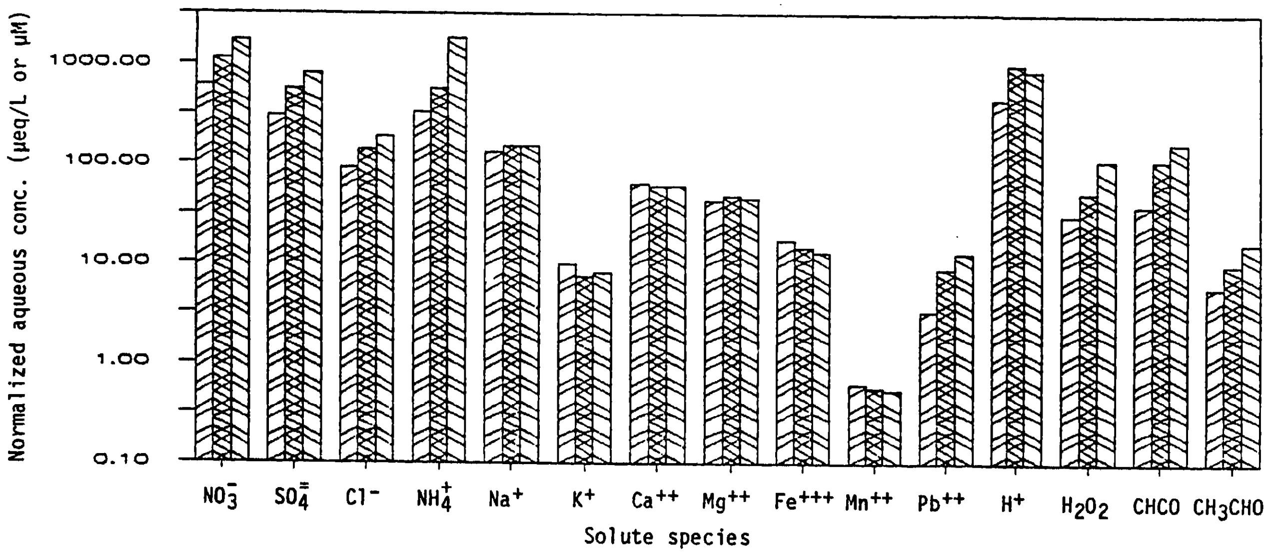

Figure 7-11. The average of the normalized concentration data in Figure 7-10. The data for the second and third orbits for each flight have been normalized so that on the average, the concentrations of Na^+, K^+, Ca^{++}, and Mg^{++} remain constant with time.

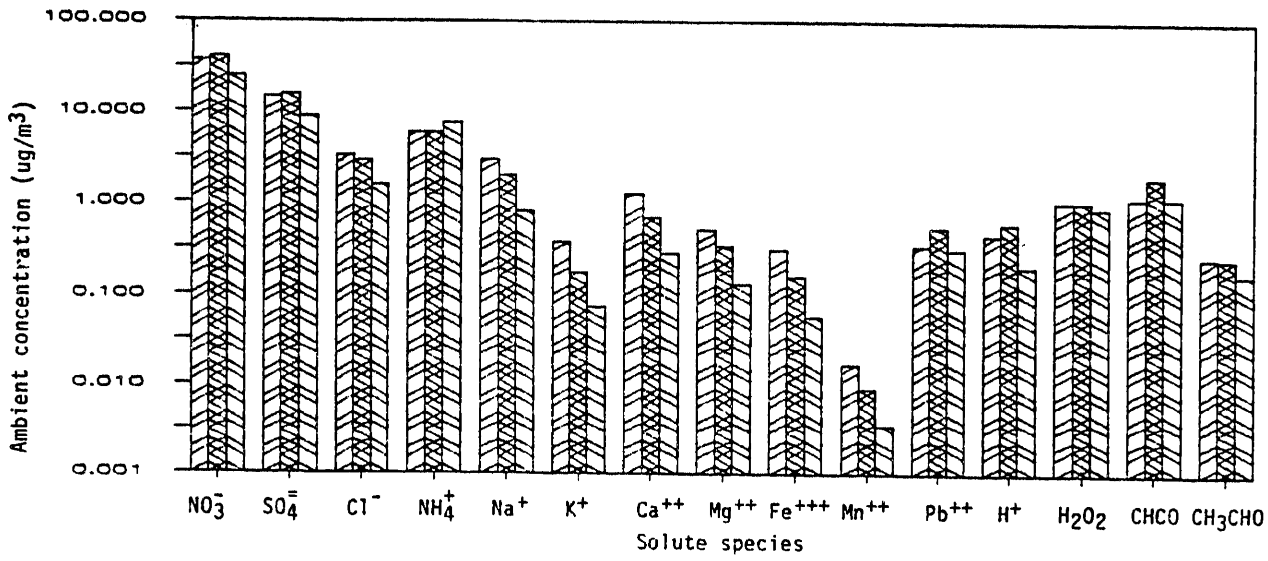

Figure 7-12. Ambient concentration by mass of species in the cloud water on a night when there was significant drizzle. The three bars for each species show concentrations measured at one hour intervals.

concentrations and the normalized concentrations were consistent enough to be statistically significant.

The one time in May-June 1985 when a significant concentration trend was observed during a flight was the morning of 26 May, when there was enough drizzle where the aircraft was sampling to cause some runoff from paved areas. Figure 5-3 on page 5-18 shows the flight patterns used by the aircraft to collect these data. Figure 7-12 shows on a logarithmic scale the ambient concentrations of species in the cloud water during this event. The average concentration of sodium, potassium, calcium, and magnesium in the cloud water decreased by about a factor of 2 each hour. The concentrations of nitrate and sulfate decreased less than that, and the ammonium and lead concentrations changed little. These data show that the settling of large droplets out of the clouds during drizzle can be a significant removal process.

8. FORMATION AND FATE OF ACID SPECIES

The airborne sampling data from May-June 1985 and from prior studies in this series show that the stratus clouds in the Los Angeles Basin contain relatively high concentrations of nitrate and sulfate and that the pH of the cloud water is typically close to 3.0. This section summarizes the information about the processes leading to the formation of sulfate and nitrate in cloud water which can be inferred from the data collected in these studies without the aid of computer models. Processes removing these species from the clouds as well as the fate of these species when the clouds evaporate are also discussed.

The objective of the discussion in this section is to present the conclusions which can easily be drawn from the data. The best information on the relative importance of various chemical pathways for the formation of acid species in the clouds will be obtained from the combination of these data with cloud chemistry computer models.

8.1 REMOVAL PROCESSES

The data in Figures 7-7 and 7-8 show a general trend for the concentrations of most species in the cloud water to decrease between the time of the first and last samples during the flights that approximately followed air parcels. Thus, during the time intervals these data were collected, processes which removed dissolved species from the clouds were dominant. The data in Figure 7-12 show that this was particularly true the morning of 26 May 1985, when drizzle caused large concentration decreases. Because of their dominance, removal processes are discussed first.

8.1.1 Droplet Settling

The data in Figure 7-12 show that the concentrations of most species in the cloud water decreased by a factor of two each hour when there was drizzle during the time the cloud water samples were collected. This shows that at least in one case, droplet settling was an important process in removing dissolved species from the stratus clouds in Los Angeles.

Drizzle and droplet settling are not uncommon when stratus clouds are present. Concentration decreases have been observed in California fogs (Jacob et al., 1986), and droplet settling has been shown to be an important process causing these decreases (J. M. Waldman, 1986). The fact that the concentrations of most of the non-volatile species measured in the cloud water decreased during the majority of the time intervals during which samples were collected suggests that droplet settling was usually important at the times these experiments were performed.

Droplet settling from the low clouds that frequently form at night in the Los Angeles Basin provides a mechanism for the formation of the large particle nitrate which has been observed in a number of studies (See Appel et al., 1981 for an early reference). The data in Section 7.4 show that the ammonia concentrations in the cloud water tend to increase with time. This ammonia is mixed into the clouds from the urban and agricultural emissions below the clouds. Ammonia concentrations are known to be high near and down wind from agricultural sources in the inland portion of the Basin. Therefore, it is expected that cloud drops which settle out of the clouds will encounter significant ammonia concentrations, especially in the inland portion of the basin. This ammonia will tend to neutralize the high nitric acid concentrations always found in cloud water. Cloud droplets which evaporate before reaching the ground will leave behind a large aerosol particle. When the ammonia concentrations are adequate, this particle will contain significant quantities of nitrate.

Because the droplets that settle are at the large end of the cloud droplet size distribution, the resulting aerosol will have a particle size distribution at the large end of the size aerosol size distribution left when the cloud evaporates. Calculations in the first Final Report in this series (Richards et al. 1983b) indicate that aerosol particles remaining from the evaporation of the larger cloud droplets have diameters in excess of 1 μm.

An order of magnitude calculation indicates that this mechanism is feasible. A cloud droplet with a settling velocity of 1000 ft/h or 8.5 cm/s has a diameter between 50 and 60 μm. For typical cloud water solute concentrations, such a cloud droplet will yield an aerosol particle between 2 and 3 μm diameter when it dries.

8.1.2 Vertical Mixing

The data in Figure 7-8 for the change with time of the concentrations of the measured species in clouds show that on the average, ammonia concentrations tended to increase with time. The data in Figure 7-12 show that the ammonia concentrations even increased when other species were being rapidly removed by drizzle. Since there is no known reaction for producing ammonia in the clouds, this result implies that vertical mixing is bringing ammonia into the clouds faster than it is being removed by droplet settling. The data also show that the lead concentrations in the cloud water tend to remain more nearly constant than do the concentrations of other metals. These data suggest that either lead is preferentially contained in the smaller cloud droplets and the other metals in the larger droplets, or lead is also mixed into the clouds from below.

These results show that at least some vertical mixing brings species from lower levels into the clouds. This mixing will tend to decrease the concentrations of species in the clouds for which the ambient concentrations below the clouds are smaller than in the clouds.

The data from this study do not provide enough information to establish the relative importance of vertical mixing and droplet settling as removal processes. It can only be concluded that both droplet settling and vertical mixing do take place.

8.2 SULFATE FORMATION

The demonstration that removal processes are typically important in the clouds shows that it is possible for species to be formed in the clouds and yet have their concentrations remain relatively constant, or even decline slightly. The data in Figure 7-7 show that on the average, sulfate concentrations in the sampled clouds tended to decline slightly, but not as rapidly as the concentrations of most trace metals. Thus, either some sulfate formation was taking place or sulfate was being mixed into the clouds from below.

Hydrogen peroxide has been found in every sample of cloud water which has been subjected to analysis for this species. Concentrations in the range from 1 to 167 μM have been observed. The mean hydrogen peroxide concentration in May-June 1985 was 57 μM. Hydrogen peroxide concentrations this high will oxidize sulfur dioxide gas to sulfate in the cloud water as rapidly as the sulfur dioxide is mixed into the clouds.

The data for sulfur dioxide and sulfur (IV) concentrations in the clouds show that these species were essentially absent. Thus, it appears that sulfate formation in the clouds was limited by the availability of these species.

Table 7-4 contains calculations estimating the amount of additional sulfate that would be formed in the clouds if sulfur dioxide were made available. These calculations show that if enough sulfur dioxide were added to the clouds to consume all the hydrogen peroxide, the sulfate concentration would increase by an average of 5.2 $\mu g/m^3$ or 65%.

Concentrations of other species which may oxidize sulfur (IV) to sulfate, such as iron and manganese, have also been measured. Calculations in the second Final Report (Richards et al. 1985) show that the iron-manganese catalyzed oxidation of sulfur (IV) is about 1000 times slower than the oxidation by hydrogen peroxide. The iron and manganese concentrations found in May-June 1985 were somewhat smaller than those found previously, so it continues to be true that the iron-manganese catalyzed oxidation of sulfur (IV) is unimportant in the clouds that were sampled.

The results obtained in this series of studies clearly show that the stratus clouds in Los Angeles have a significant capacity to oxidize sulfur dioxide to sulfate. Sulfate formation will take place very rapidly in these clouds when sulfur dioxide is mixed into them. The highest sulfate concentration observed in this series of studies was about 100 $\mu g/m^3$ measured the night of 21-22 May in sulfur dioxide-containing plumes near Fontana. Should such plumes return to the Basin, it is expected that they would again produce high sulfate concentrations in the clouds.

8.3 NITRATE FORMATION

Chemical reactions are known which are capable of forming large quantities of nitrate in the Los Angeles clouds at night. One of these is the reaction of ozone and NO_2 to form NO_3, which reacts with additional NO_2 to form N_2O_5, the anhydride of nitric acid (see, for example, Heikes et al., 1983; Richards, 1983). However, no clear experimental demonstration that nitrate is formed rapidly in clouds at night has been published. For the Los Angeles Basin, perhaps the strongest evidence for the presence of this reaction is found in the work of Russell, McRae, and Cass (1985). They modeled ground level nitrate concentration data for selected days, and found that it was necessary to include the NO_3 and N_2O_5 reactions in the model to obtain satisfactory agreement between experimental data and model results.

The data from this series of studies are consistent with nitrate formation at night in the Los Angeles stratus clouds. The average concentrations of nitrate in cloud water in Table 7-2 are relatively high. No data are available for the nitrate concentrations in the sampled air masses before clouds formed in them, but typical concentrations are less than this (Russell and Cass, 1984). In addition, the data in Figures 7-9 and 7-10 show that nitrate is second only to ammonia for its tendency to increase with time in the clouds. For the nitrate concentrations to increase at the same time that droplet settling is removing dissolved species from the clouds, it is necessary either for nitrate concentrations to be higher out of the clouds and mixing to take place, or it is necessary for nitrate to be formed in the clouds. It is suggested that the latter process is more probable.

8.4 CHANGES IN COMPOSITION ON CLOUD EVAPORATION

Chemical species can leave the stratus clouds by several pathways. Removal by vertical mixing and droplet settling take place while cloud is still present. The stratus clouds formed at night in the Los Angeles Basin typically evaporate during the following day to produce an aerosol which contains less nitrate and chloride than was in the cloud water.

The first Final Report in this series contains a full discussion of the methods used to estimate the composition and size distribution of the aerosol which remains when the clouds evaporate (Richards et al., 1983b). The same assumptions and calculation methods have been used here. The assumptions are:

1. All cloud droplets have a composition equal to that of the collected cloud water sample.

2. All species which make a significant contribution to the dry aerosol mass have been determined. The dry aerosol has a density of 1 g/cm^3. (It is believed that neither of these assumptions are very good, but that the errors in them tend to cancel.)

3. All water, nitric acid, and hydrochloric acid are volatilized.

It is apparent that the assumptions, and hence the results of the calculations, are only approximately correct.

Table 8-1 shows the 1985 results for the calculated composition of the dry aerosol remaining after the sampled clouds evaporated. The average calculated dry aerosol composition is shown in Figure 8-1. It is interesting to compare the aerosol composition in Figure 8-1 with the composition of the cloud water before cloud evaporation in Figure 7-1. The aerosol particle size distribution calculations have not been done for the 1985 data, but it is expected that the results would be similar to those reported previously (Richards *et al.* 1983b). These calculations show that the evaporation of clouds can account for the aerosol particles in the upper end of the 0.1 to 1 μm particle size range frequently observed in the Los Angeles Basin (Hering and Friedlander, 1981).

Table 8-1. Change in composition on cloud evaporation

Tape/Pass	Sample ID	Ambient concentrations before evaporation (ug/m^3)			Fraction lost		Mass NO_3^- & Cl^- lost	Ambient concentrations after evaporation (ug/m^3)			
		Cl^-	NO_3^-	Mass	NO_3^- & Cl^-	H^+	(ug/m^3)	Mass	Cl^-	NO_3^-	H^+
432/2	U1	6.29	23.9	54.0	0.421	1.000	12.7	41.1	3.64	13.84	0.00
432/3	U3	3.91	17.9	37.5	0.661	1.000	14.4	22.8	1.33	6.06	0.00
432/4	U5	2.49	22.5	38.3	0.610	1.000	15.3	22.8	0.97	8.78	0.00
432/5	U6	3.77	37.6	66.0	0.500	1.000	20.7	44.9	1.89	18.84	0.00
433/1,2	U10	3.87	12.5	32.1	0.478	1.000	7.8	24.1	2.02	6.54	0.00
433/3	U11	1.60	10.5	19.5	0.640	1.000	7.7	11.6	0.58	3.77	0.00
433/4	U12	2.28	27.6	51.0	0.842	1.000	25.1	25.4	0.36	4.35	0.00
433/4	U13	1.78	24.9	44.0	0.926	1.000	24.7	18.8	0.13	1.83	0.00
434/2	U15	3.00	15.7	36.2	1.000	0.748	18.7	17.2	0.00	0.00	0.11
434/2	U16	4.06	20.2	47.4	1.000	0.976	24.2	22.8	0.00	0.00	0.01
434/3	U17	4.80	31.4	67.8	1.000	0.952	36.2	30.9	0.00	0.00	0.03
434/3	U18	5.26	25.3	55.9	0.858	1.000	26.2	29.2	0.74	3.59	0.00
434/4	U19	2.15	26.2	46.1	0.820	1.000	23.3	22.4	0.39	4.71	0.00
434/4	U20	2.03	26.6	46.9	0.854	1.000	24.5	22.0	0.29	3.87	0.00
435/2	U21	3.24	36.8	66.7	0.652	1.000	26.1	40.2	1.13	12.80	0.00
435/3	U24	2.87	40.4	69.1	0.802	1.000	34.7	33.8	0.57	8.02	0.00
435/4	U26	1.55	24.6	44.3	0.458	1.000	12.0	32.1	0.84	13.32	0.00
436/2	U31	1.57	19.5	33.7	0.587	1.000	12.4	21.1	0.65	8.05	0.00
436/3	U33	1.02	17.8	27.7	0.688	1.000	12.9	14.6	0.32	5.55	0.00
436/4	U34	1.37	22.9	39.2	0.336	1.000	8.1	30.9	0.91	15.18	0.00
440/2	U52	2.18	5.2	14.5	0.627	1.000	4.6	9.9	0.81	1.92	0.00
440/3	U54	5.18	11.1	33.3	0.581	1.000	9.5	23.6	2.17	4.66	0.00
440/4	U55	3.37	17.3	39.3	0.601	1.000	12.4	26.6	1.34	6.91	0.00
440/5	U56	5.49	5.3	17.2	0.313	1.000	3.4	13.7	3.77	3.65	0.00
441/1	U61										
441/1	U62										
441/1	U63										
Averages											
All data		3.13	21.8	42.8	0.677	0.987	17.4	25.1	1.04	6.51	0.01
First pass		3.46	19.1	40.7	0.681	0.961	15.2	25.2	1.18	6.16	0.02
Middle passes		3.39	21.6	43.2	0.716	0.995	18.8	24.0	0.89	5.26	0.00
Last pass		2.55	24.5	44.3	0.631	1.000	17.7	26.3	1.07	8.22	0.00

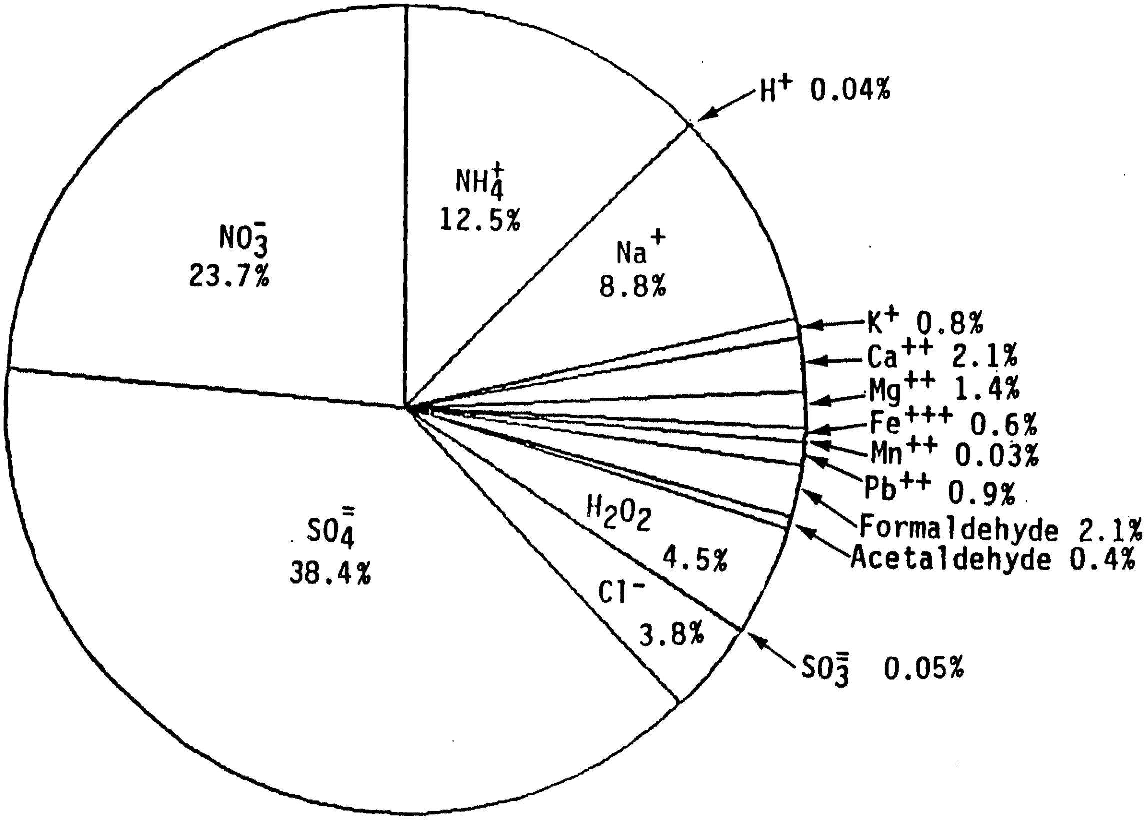

Figure 8-1. Calculated May-June 1985 average composition by mass of the aerosol remaining after cloud evaporation. Only species determined are included. Compare with Figure 1-1.

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APPENDIX A

Flight Summaries and Flight Maps

The following pages contain the flight summary for each flight followed by the maps for that flight. Each flight is divided into periods of time known as passes, during which grab samples were collected and all instruments were operated in the data collection mode. Between passes, grab sample equipment was changed and some instruments were zeroed.

The flight summaries give the time for each pass and the codes of all grab samples collected during that pass. Other pertinent information, such as sampling altitude, are also given.

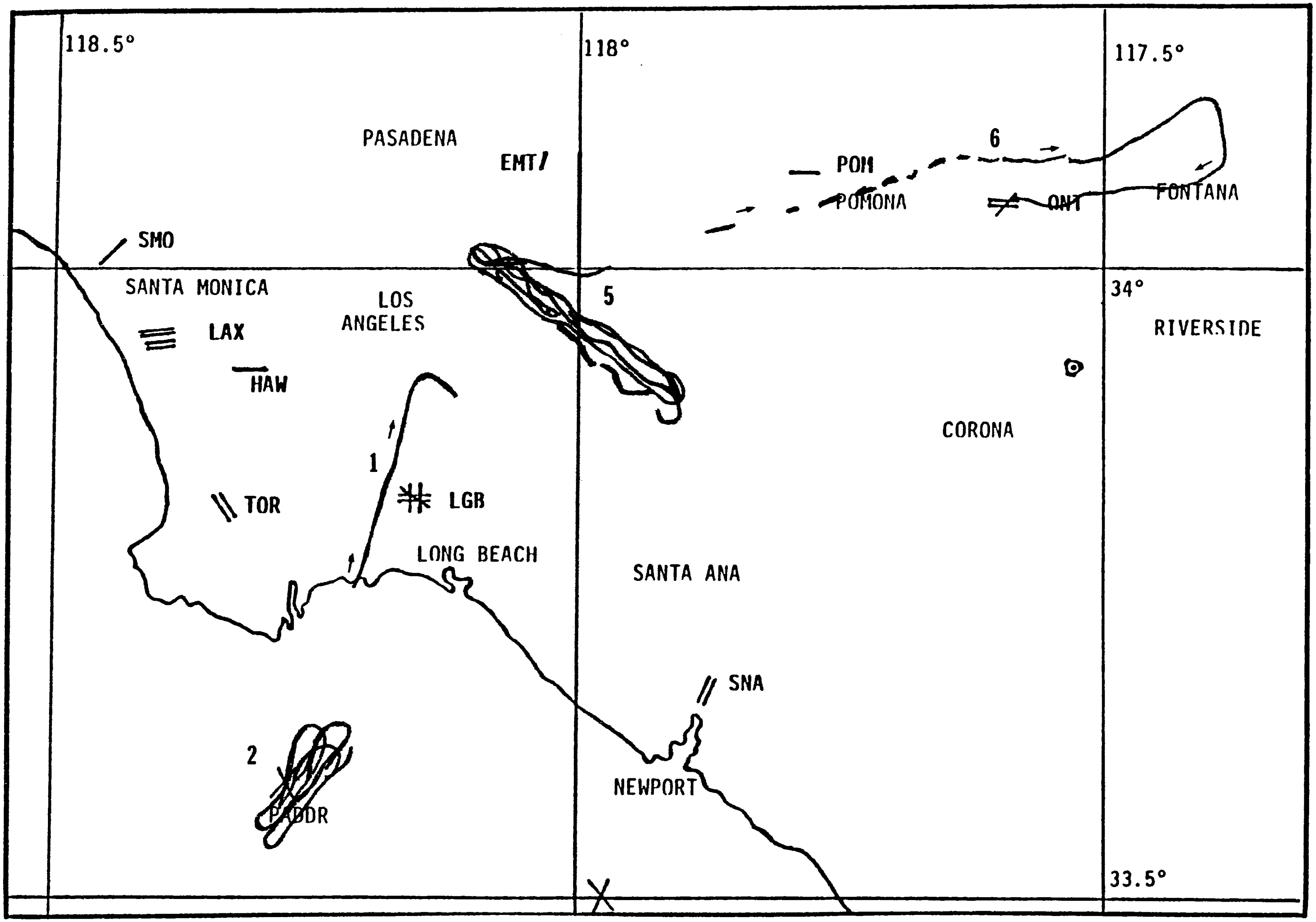
The flight trajectories were drawn by computer using the LORAN data, then transferred to the flight maps. The exact path of the aircraft during every pass is shown in the maps.

Flight Summary
CARB Cloud Sampling
Date: 21 May 1985

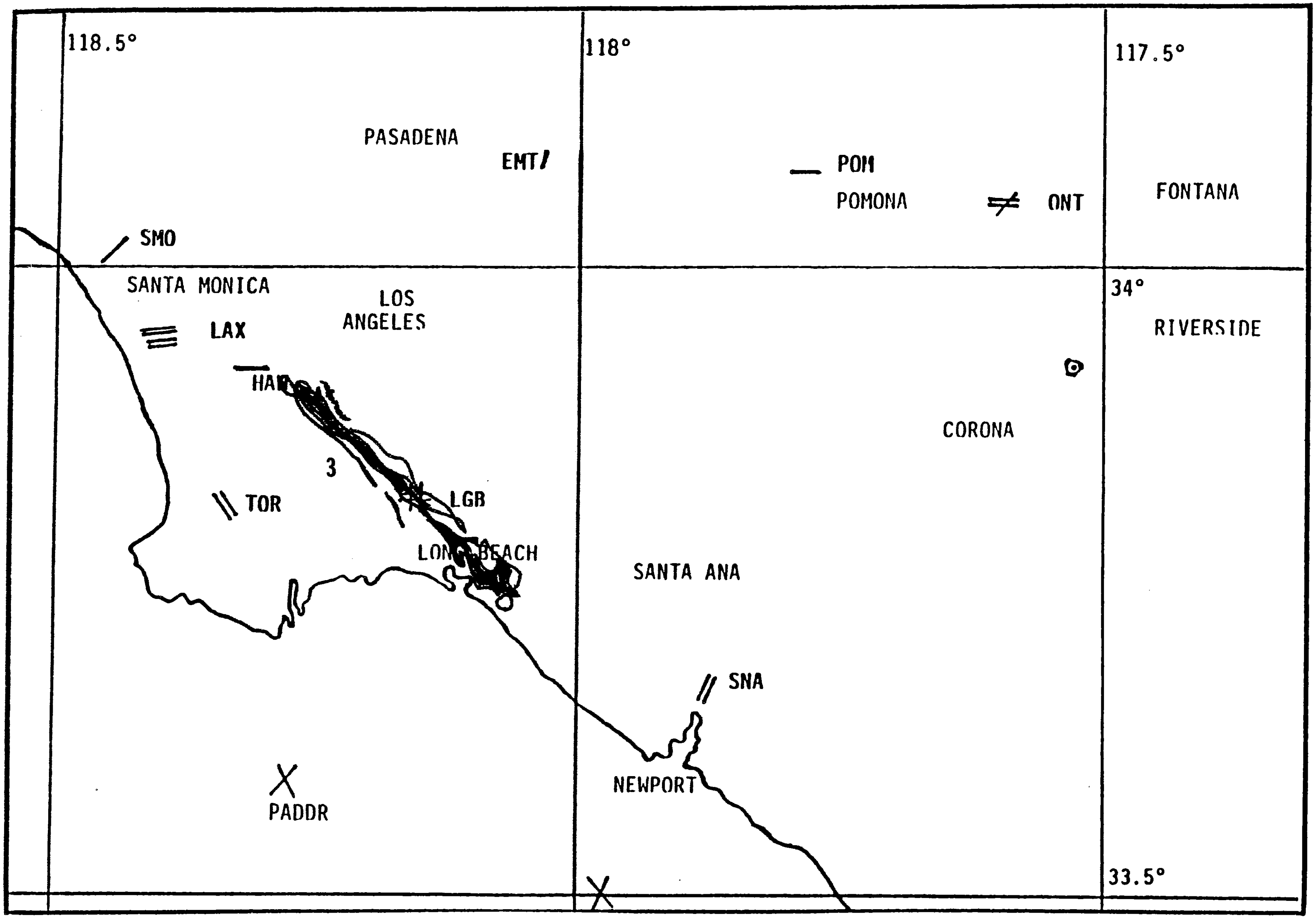
Flight Number: 432

							Grab Sample Codes							
		Time (PDT)		Altitude (ft msl)						Cloud water			Bubblers	
Pass	Type	Start	End	Start	End	Length (min)	HC Can	Filter Set	Total Sample Collector	Unstabilized	H_2O_2	S(IV)	Carbonyl	Pan
1	Spiral	0224	0231	750	3000	6.72								
2	Orbit	0240	0321	2000	2000	40.03		1	1	U1,U2	P1	S1	1	PK1,PW1
between										U9				
3	Orbit	0339	0439	2500	2500	59.98	TV 675	2	2	U3,U4	P3	S3	2	PK2,PW2
4	Orbit	0447	0529	2700	2700	41.87		3	3	U5	P5	S5	↓	↓
5	Orbit	0538	0616	3000	3000	37.78		4	4	U6	P6	S6	↓	↓
6	Zero spiral	0618	0638	3000	0985	19.78								
blanks								5	5					

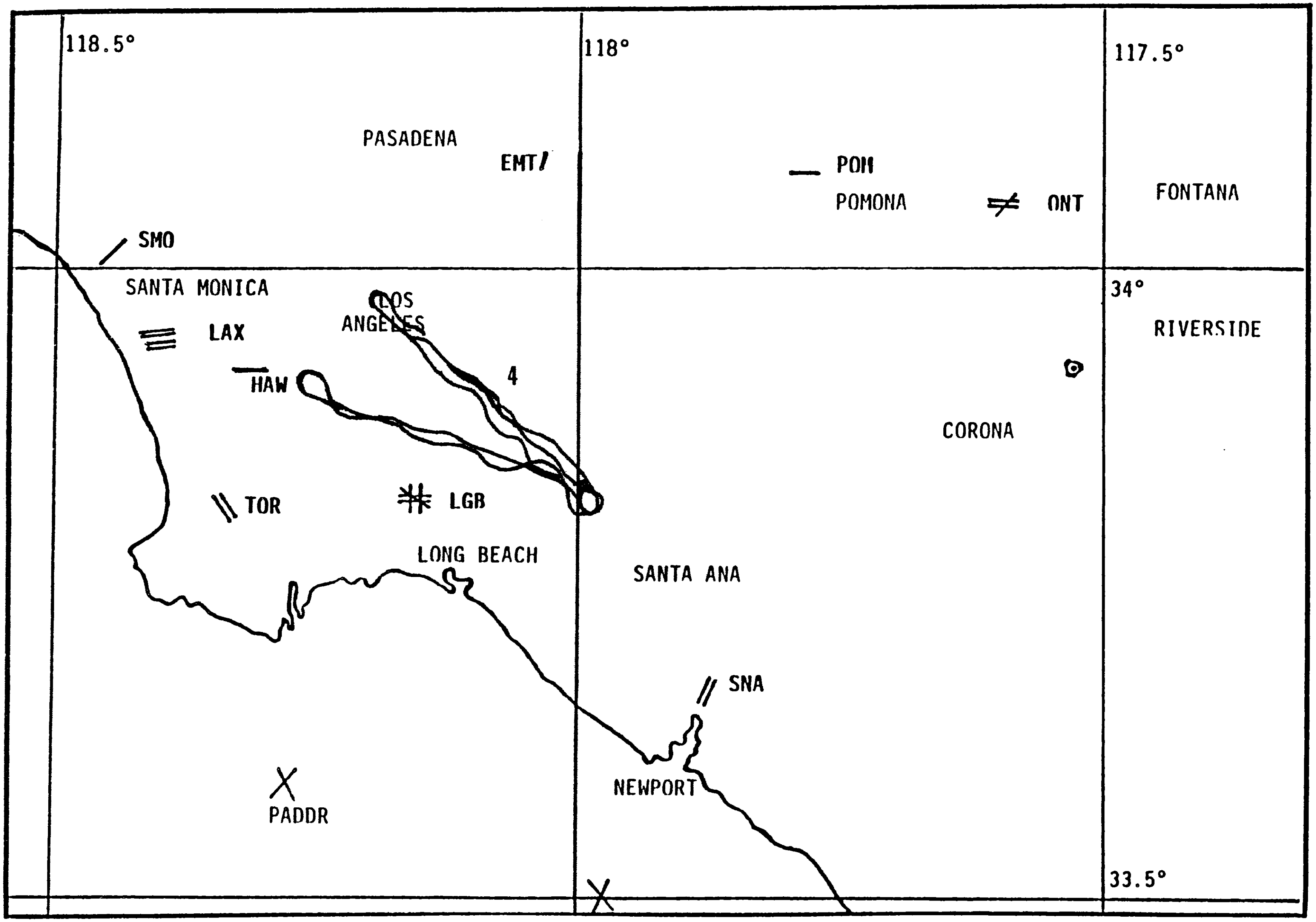
pH inop entire flight



Flight 432 Sampling Locations 21 May 1985



Flight 432 Sampling Locations 21 May 1985



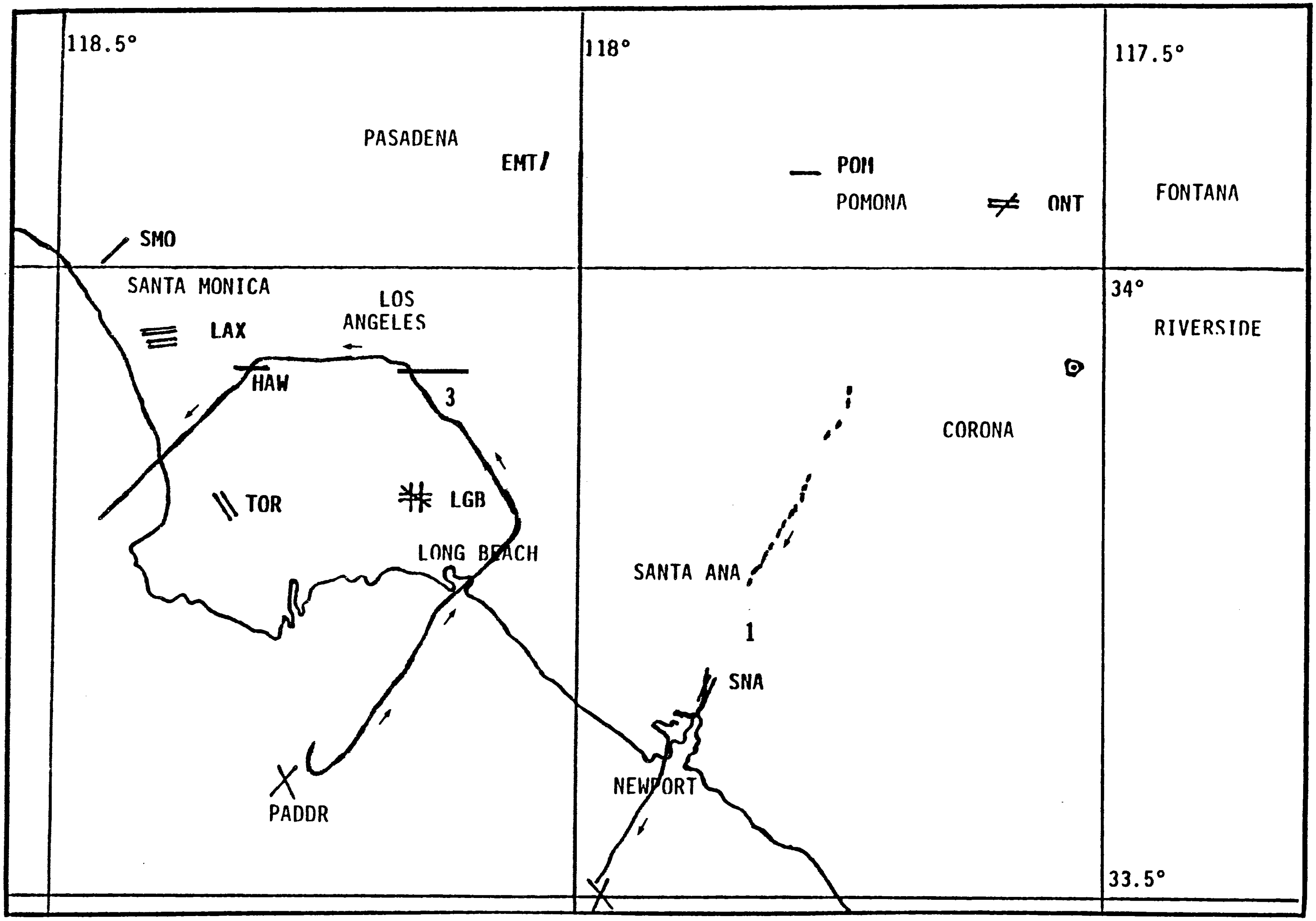
Flight 432 Sampling Locations 21 May 1985

Flight Summary
CARB Cloud Sampling
Date: 24 May 1985

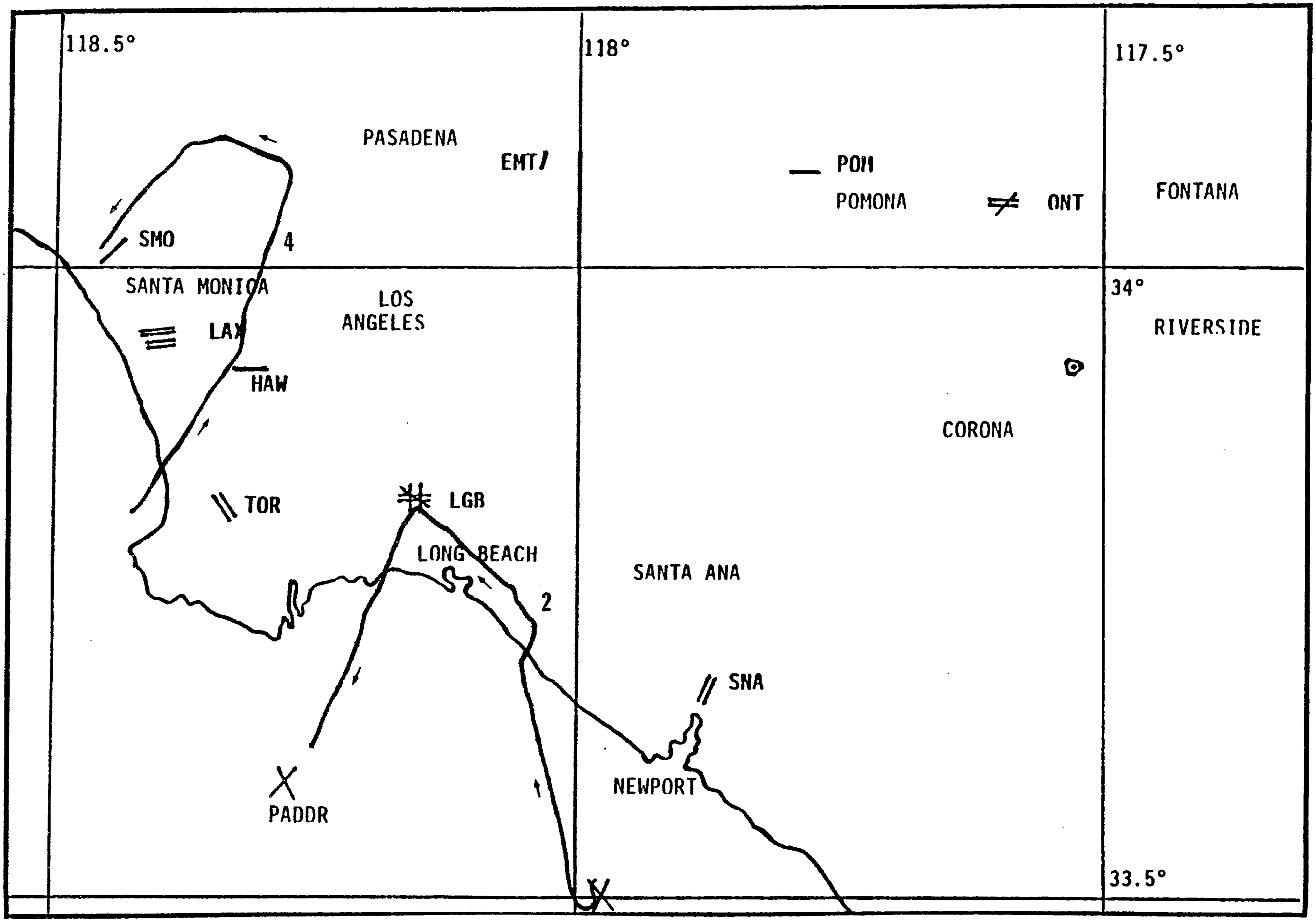
Flight Number: 433

							Grab Sample Codes							
									Total	Cloud water			Bubblers	
		Time (PDT)		Altitude (ft msl)		Length	HC	Filter	Sample	Unsta-			Car-	Pan
Pass	Type	Start	End	Start	End	(min)	Can	Set	Collector	bilized	H_2O_2	S(IV)	bonyl	
1	Missed appr.	0107	0119	3000	3000	12.13		10	10	U10	P10	S10		
2	Missed appr.	0119	0139	1600	2400	19.23		↓	↓	↓	↓	↓		10
3	Missed appr.	0139	0202	2400	2400	23.53		↓	↓	U11	↓	↓		↓
4	Missed appr.	0210	0257	2700	2700	46.43		11	11	U12,U13	P11	S11		↓
blanks								12 18 (also flown on flight 434) 25 (also flown on flight 434 & 435)	12,13,14					↓

Aliquot removed from: U13
Aliquot sample code: D1
Analized for: Carbonyl



Flight 433 Sampling Locations 24 May 1985



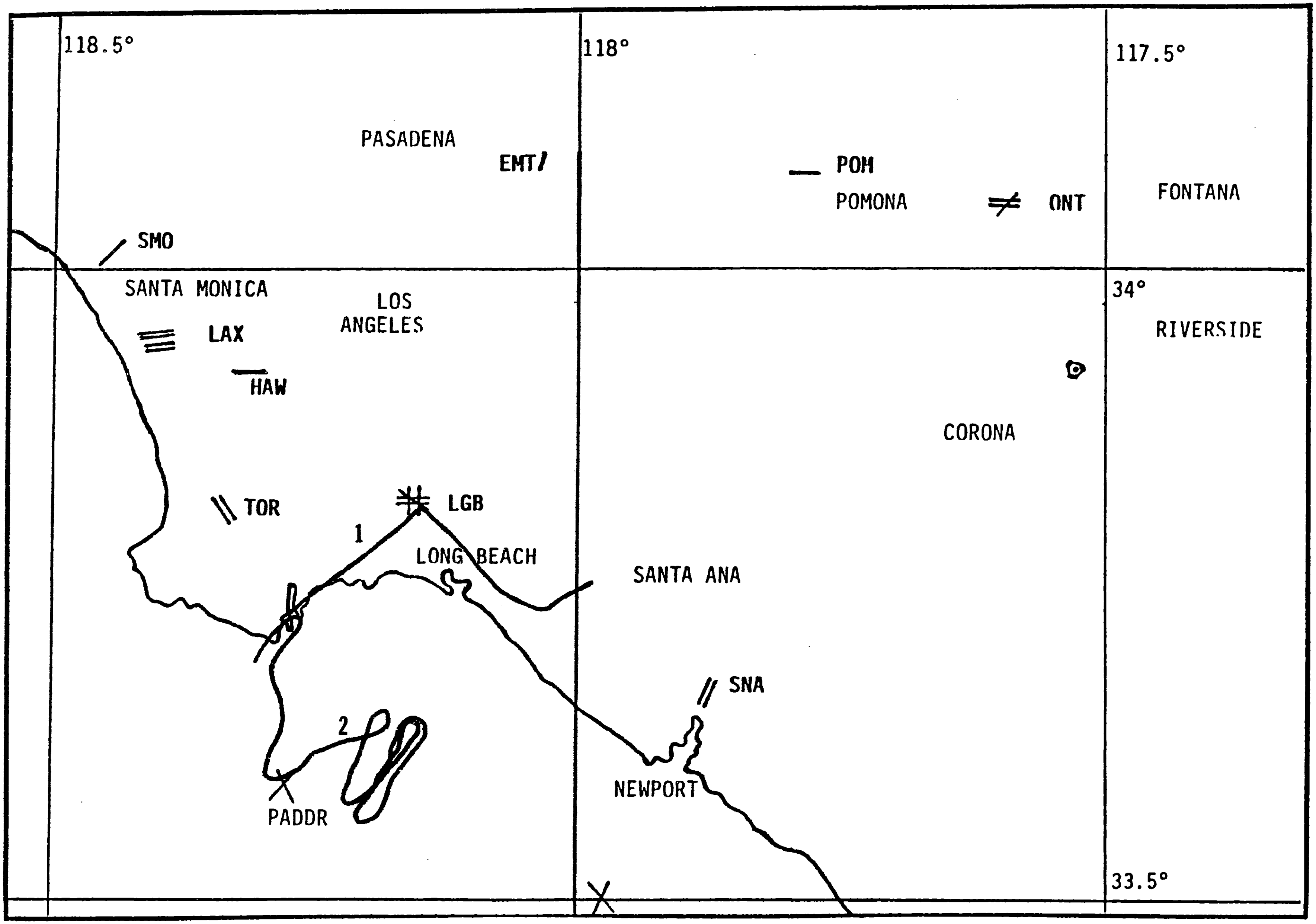
Flight 433 Sampling Locations 24 May 1985

Flight Summary
CARB Cloud Sampling
Date: 25 May 1985

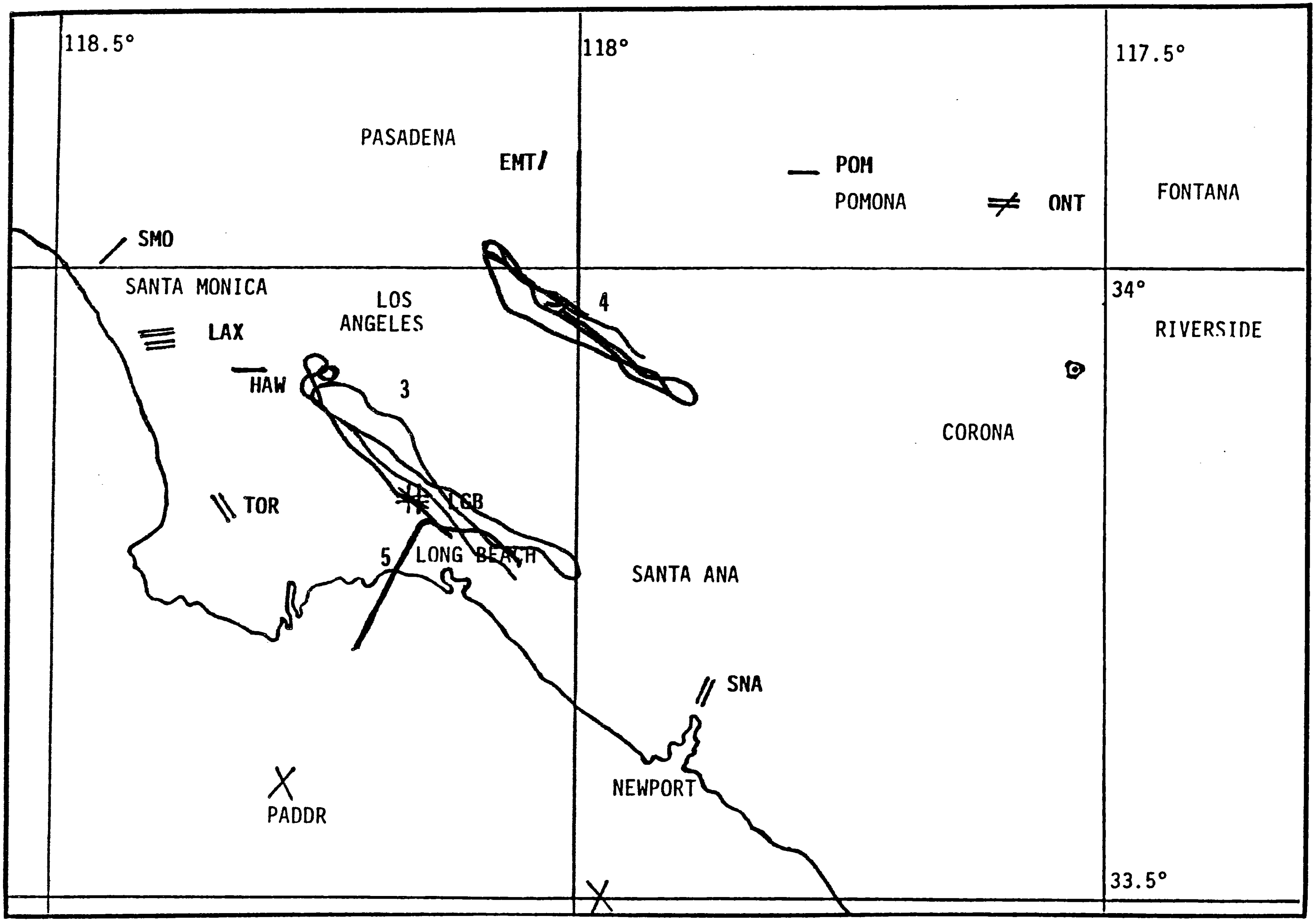
Flight Number: 434

							Grab Sample Codes							
		Time (PDT)		Altitude (ft msl)					Total	Cloud water			Bubblers	
Pass	Type	Start	End	Start	End	Length (min)	HC Can	Filter Set	Sample Collector	Unsta- bilized	H_2O_2	Car- bonyl	Car- bonyl	Pan
1	Missed appr.	0033	0042	2400	2600	9.57				A				
2	Orbit	0047	0112	2000	2000	25.35		15	15	U15,U16	P15	D15		
between										B				
3	Orbit	0125	0202	2000	2000	37.47	TV 250	16	16	U17,U18,C	P16,P17	D16,D17	3	PK15,PW15
between										D			↓	↓
4	Orbit	0211	0244	2500	2300	32.15		17	17	U19,U20	P18,P19	D18,D19	↓	↓
5	Spiral	0300	0305	1000	3000	4.78				E				
landing										F				
blanks								18 (also flown on flight 433) 25 (also flown on flight 433 & 435)	18,25 (also flown on flight 435)					

Aliquot removed from:	U16	U17	U20	U17	U20	U15	U17	U19
Aliquot sample code:	PU16	PU17	PU20	PU17 blank	PU20 blank	SU15	SU17	SU19
Analized for:	H_2O_2	H_2O_2	H_2O_2	H_2O_2	H_2O_2	S(IV)	S(IV)	S(IV)



Flight 434 Sampling Locations 25 May 1985



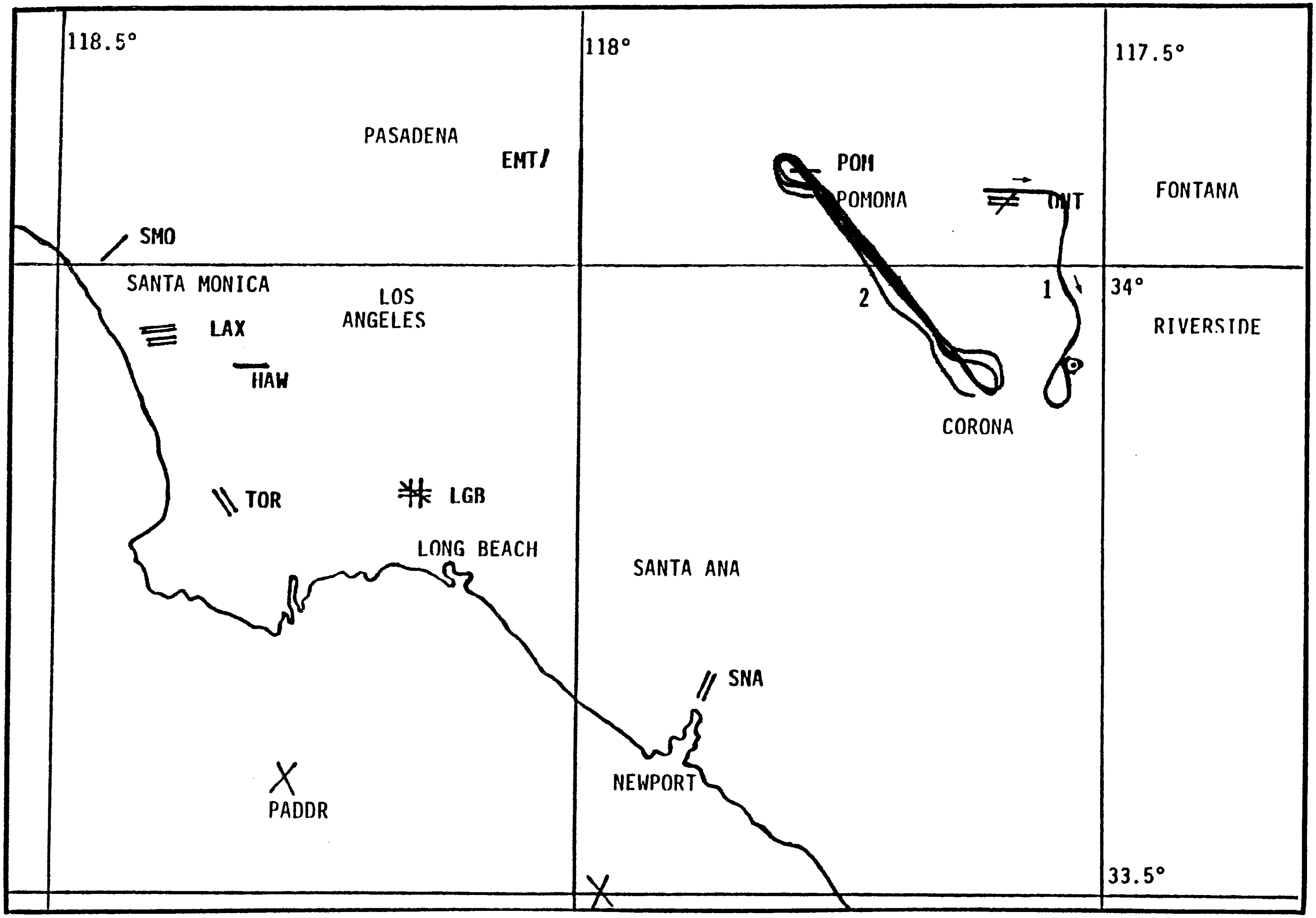
Flight 434 Sampling Locations 25 May 1985

Flight Summary
CARB Cloud Sampling
Date: 26 May 1985

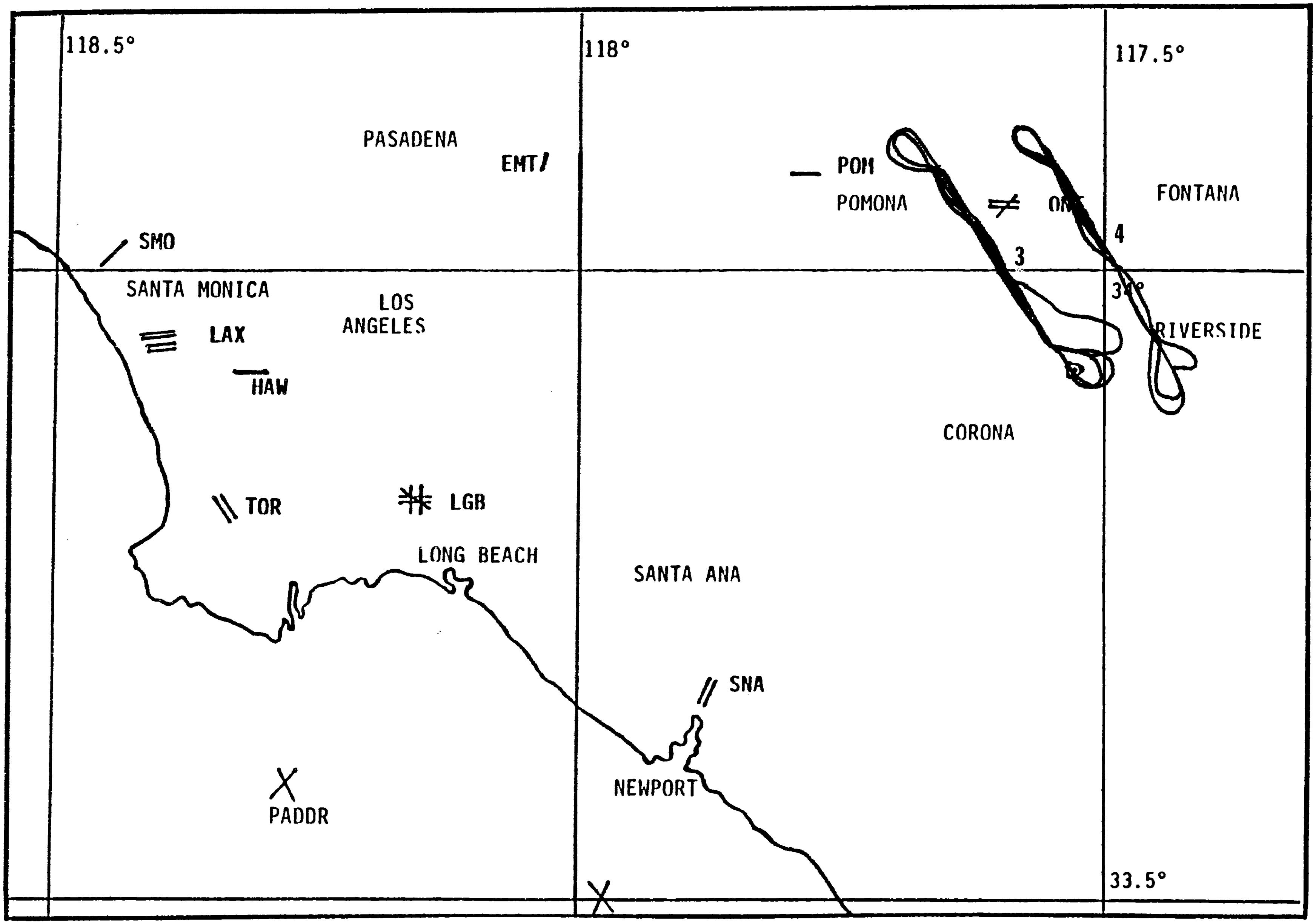
Flight Number: 435

							Grab Sample Codes							
		Time (PDT)		Altitude (ft msl)						Cloud water			Bubblers	
pass	Type	Start	End	Start	End	Length (min)	HC Can	Filter Set	Total Sample Collector	Unsta-bilized	H_2O_2	Car-bonyl	Car-bonyl	Pan
1	Spiral	2357	0005	985	4000	8.07								
2	Orbit	0012	0055	3200	3200	42.83	TV 667	21	21	U21,U22,U23	P21,P22	D21	4	PK21,PW21
between										H			↓	↓
3	Orbit	0113	0150	3300	3300	36.70		22	22	U24,U25	P26	D22	↓	↓
between										K			↓	↓
4	Orbit	0213	0253	3300	3300	40.02		23	23	U26,M	P24,P25	D23,L	↓	↓
5	Spiral	0300	0311	5000	985	11.08								
blanks								24,25 (also flown on flight 433 & 434)	24,25 (also flown on flight 434)					

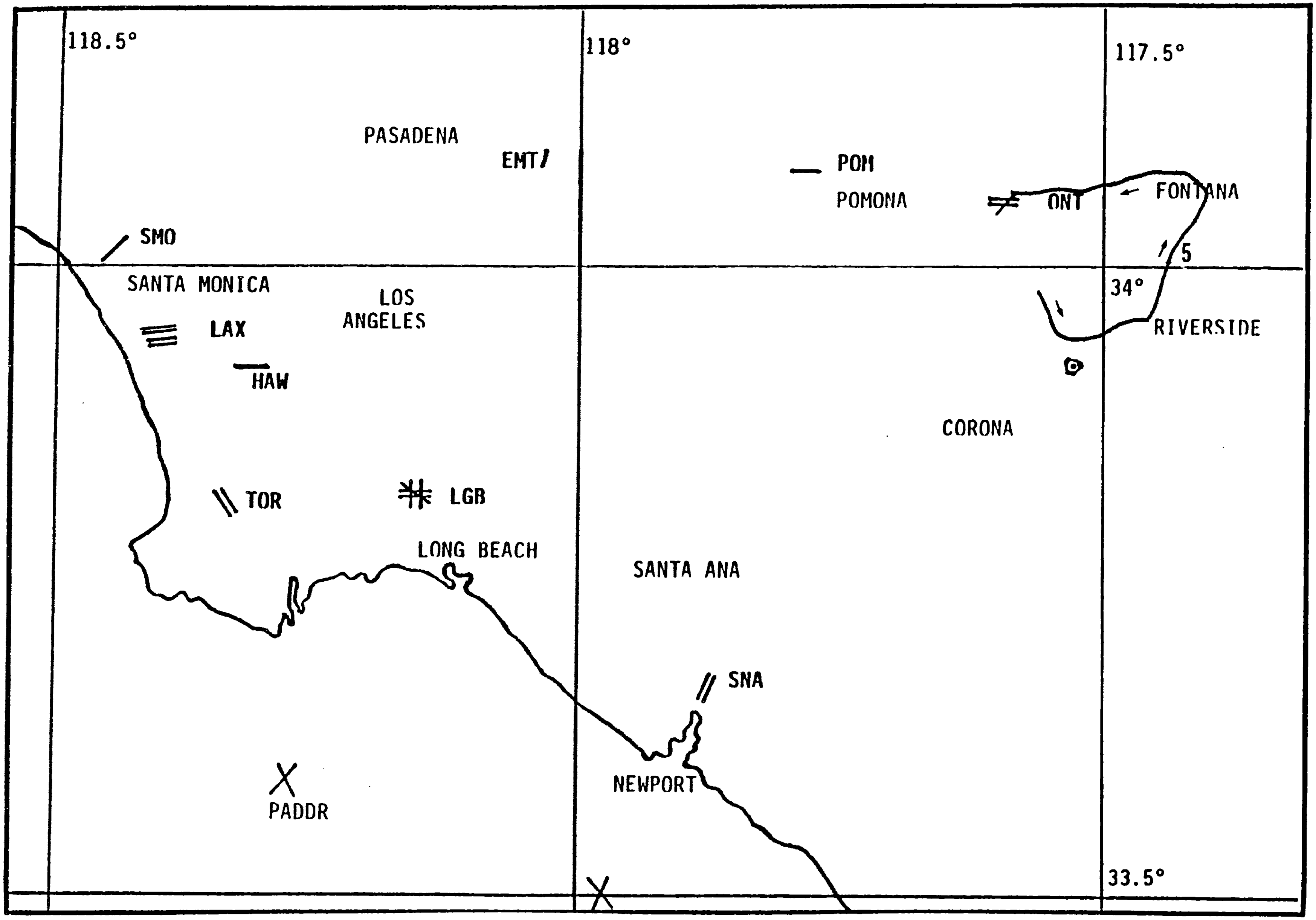
Aliquot removed from:	U23	U23	U25	M	M	U23	U25	M
Aliquot sample code:	PU23	PU23 blank	PU25	PM	PM blank	SU23	SU25	SM
Analized for:	H_2O_2	H_2O_2	H_2O_2	H_2O_2	H_2O_2	S(IV)	S(IV)	S(IV)



Flight 435 Sampling Locations 26 May 1985



Flight 435 Sampling Locations 26 May 1985



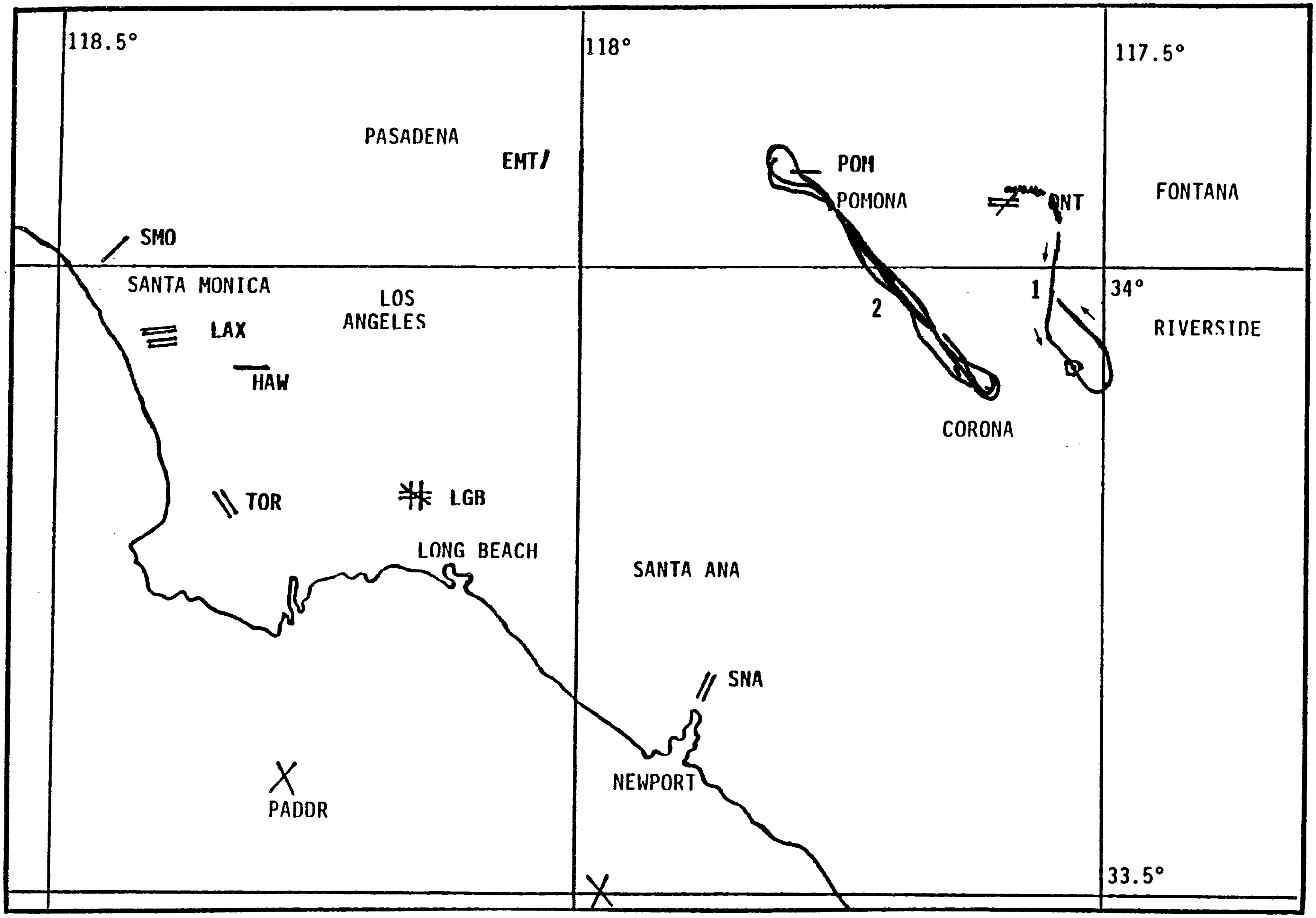
Flight 435 Sampling Locations 26 May 1985

Flight Summary
CARB Cloud Sampling
Date: 27 May 1985

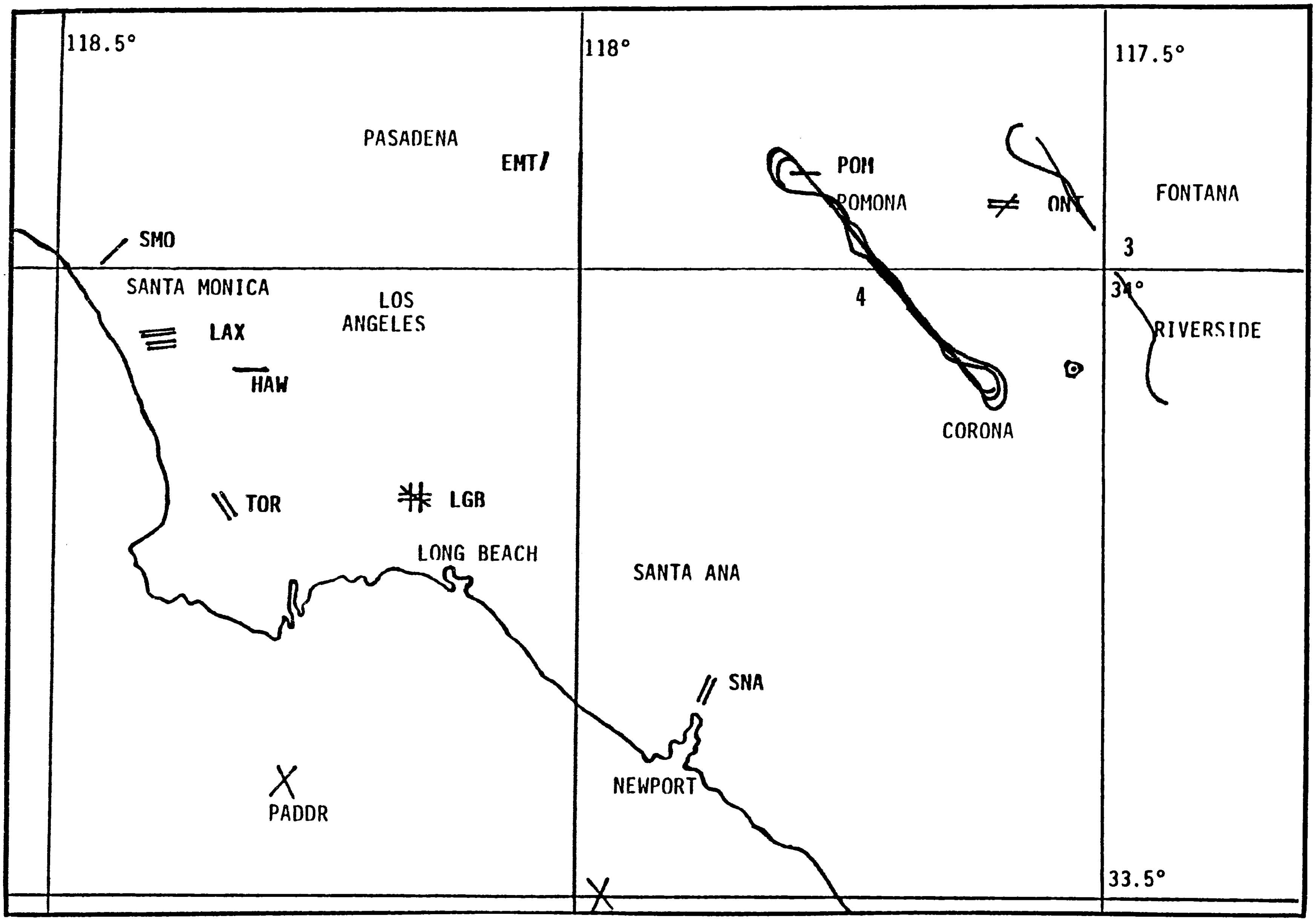
Flight Number: 436

							Grab Sample Codes							
		Time (PDT)		Altitude (ft msl)					Total	Cloud water			Bubblers	
Pass	Type	Start	End	Start	End	Length (min)	HC Can	Filter Set	Sample Collector	Unsta-bilized	H_2O_2	Car-bonyl	Car-bonyl	Pan
1	Spiral	0057	0107	985	5000	9.33								
2	Orbit	0114	0159	4000	3500	44.57	TV 659	31	31	U31,U32,A31	P31	D31	5	PK31
3	Orbit	0213	0258	3500	3500	45.00		32	32	U33	P32	D32	↓	↓
4	Orbit	0316	0401	3600	3600	45.00		33	33	U34	P33	D33	↓	↓
5	Spiral	0411	0421	5000	985	10.07				U35				
blanks								34,45	34,45					

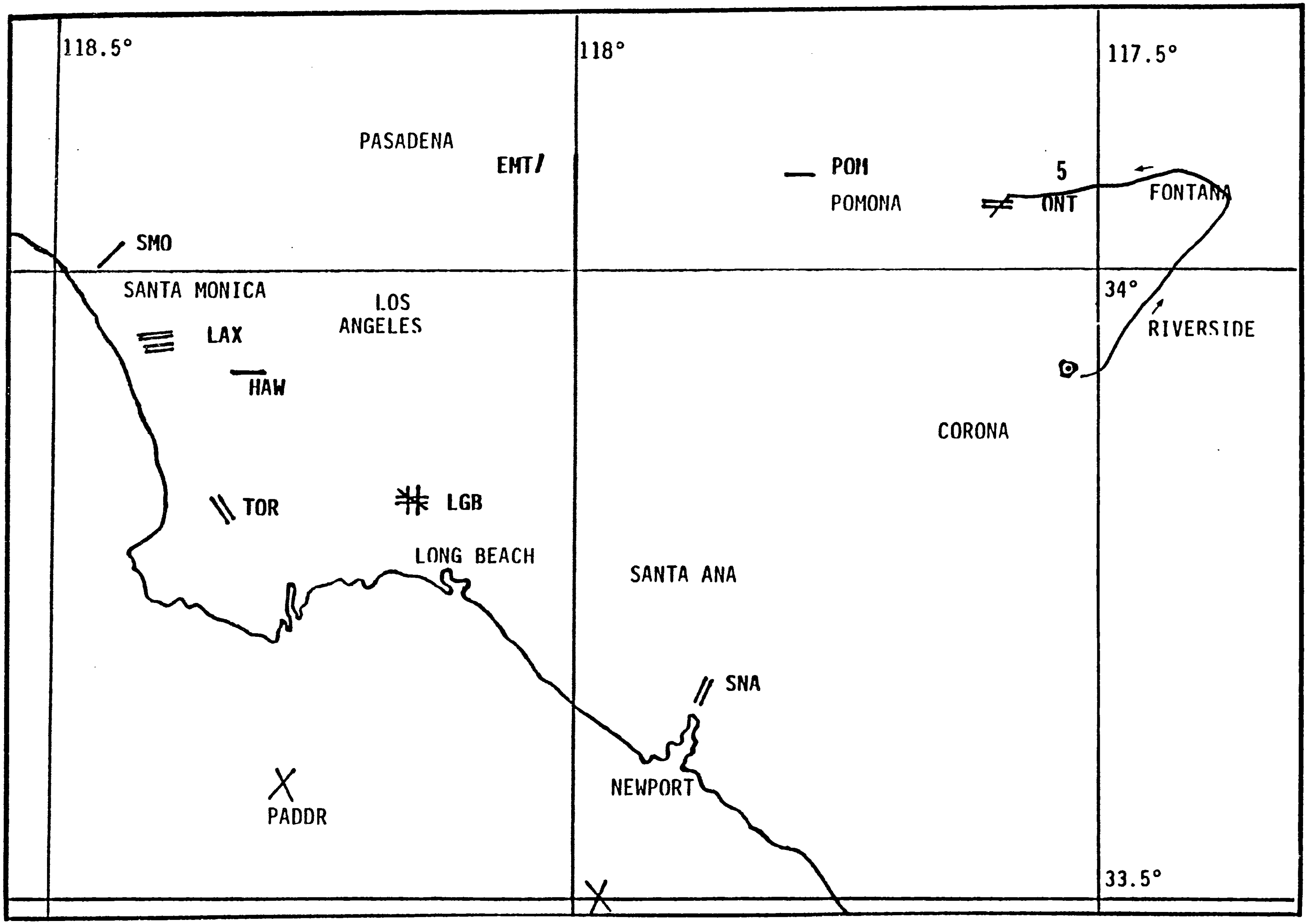
Aliquot removed from:	U31	U31	U33	U34
Aliquot sample code:	PU31	PU31 blank	PU33	PU34
Analized for:	H_2O_2	H_2O_2	H_2O_2	H_2O_2



Flight 436 Sampling Locations 27 May 1985



Flight 436 Sampling Locations 27 May 1985

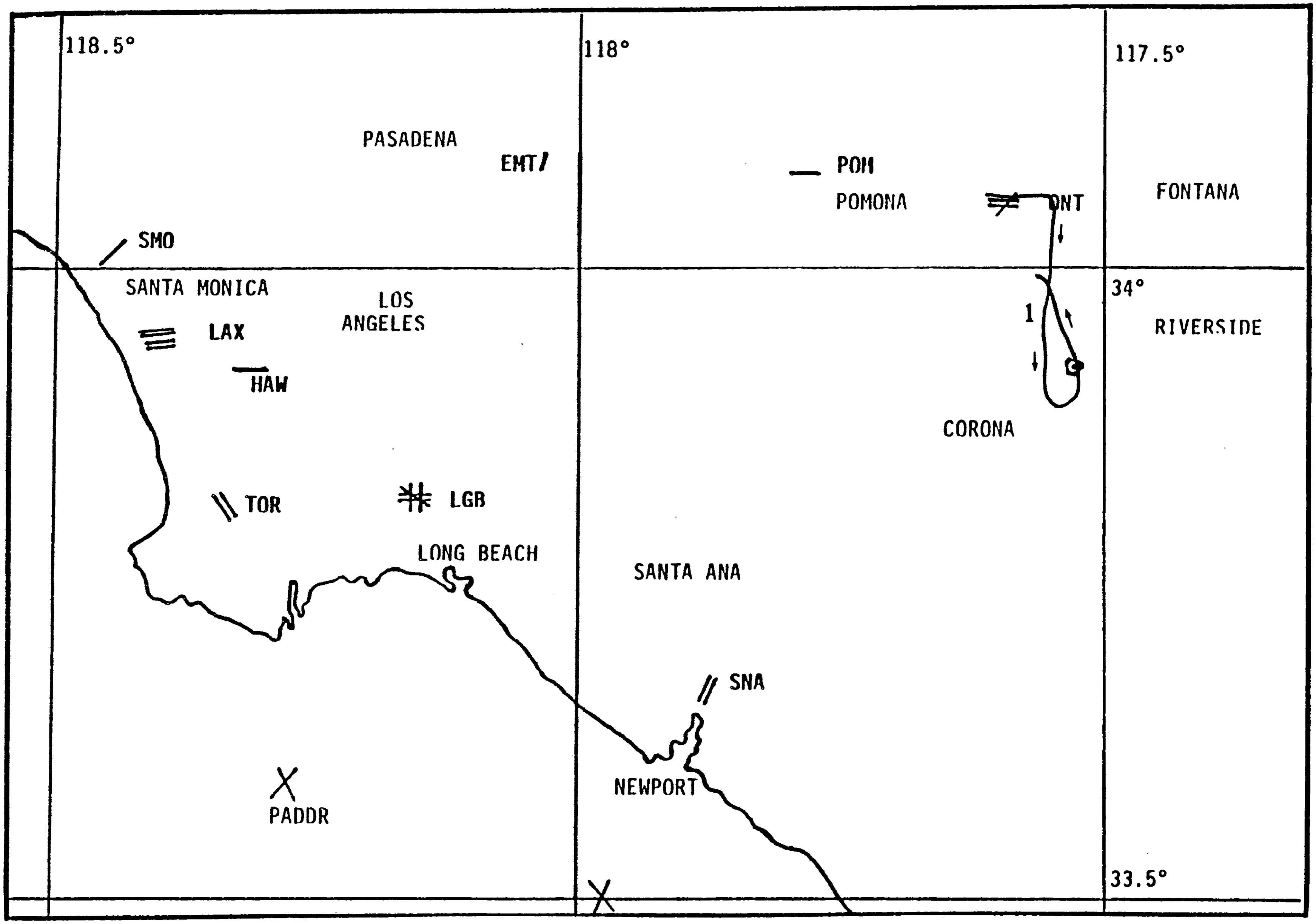


Flight 436 Sampling Locationa 27 May 1985

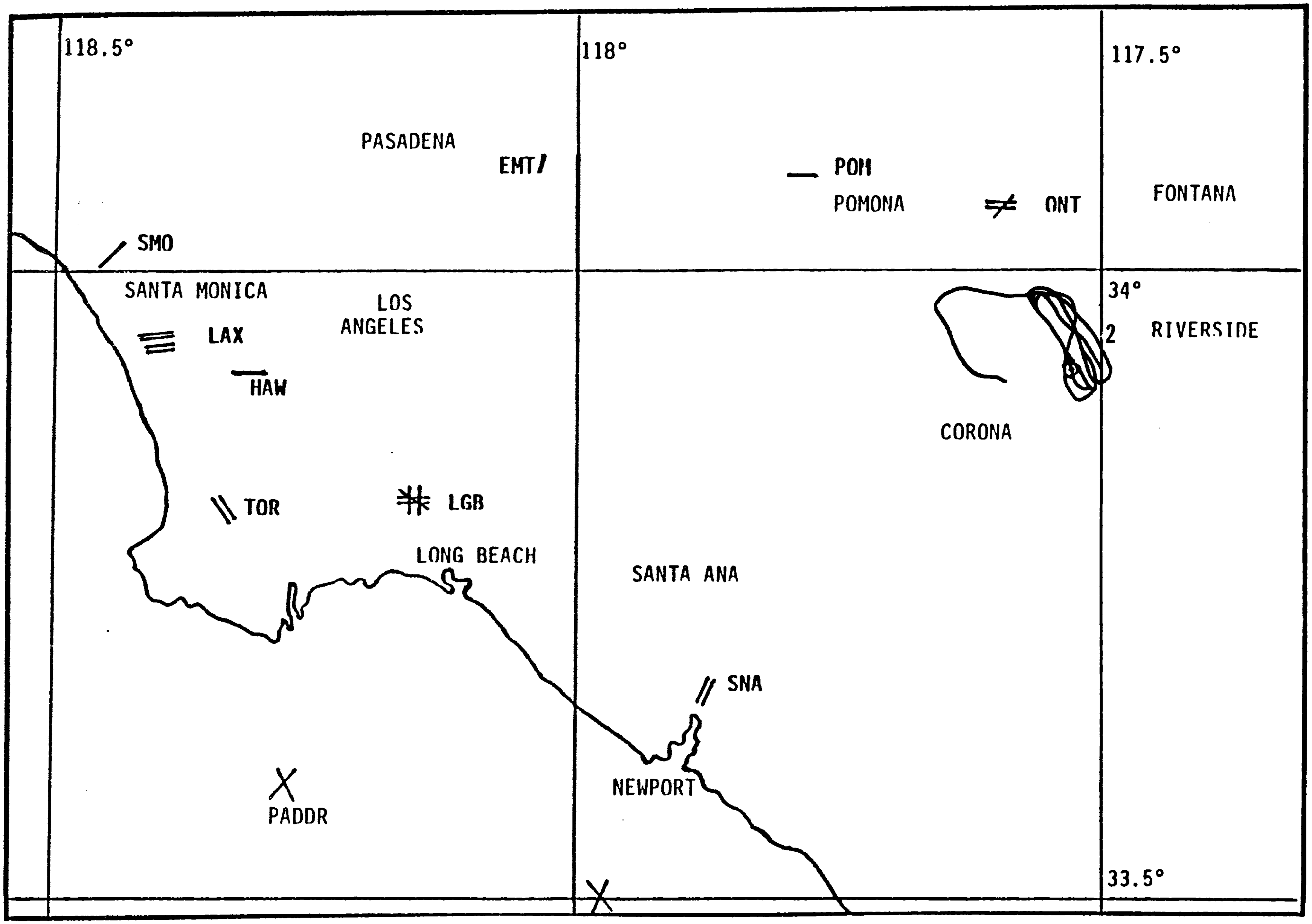
Flight Summary
CARB Cloud Sampling
Date: 1 June 1985

Flight Number: 438

							Grab Sample Codes							
		Time (PDT)		Altitude (ft msl)						Cloud water			Bubblers	
Pass	Type	Start	End	Start	End	Length (min)	HC Can	Filter Set	Total Sample Collector	Unstabilized	H_2O_2	Carbonyl	Carbonyl	Pan
1	Spiral	0248	0258	985	5500	10.02								
2	Orbit	0307	0334	4800	4800	26.63		41	41	U41	P41		6	PK41,PW41
blanks									42,43,44,45,46					



Flight 438 Sampling Locations 1 June 1985

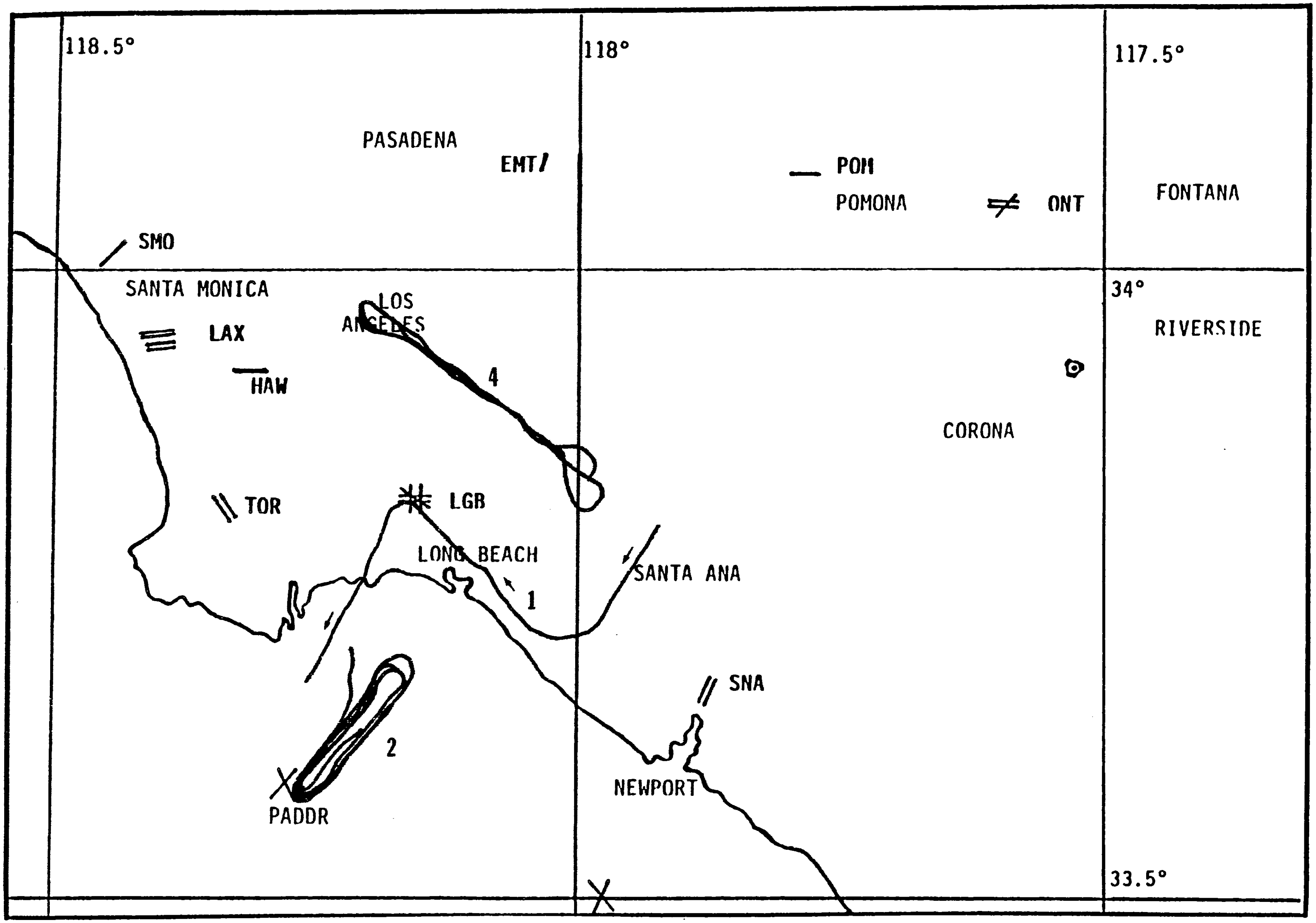


Flight 438 Sampling Locations 1 June 1985

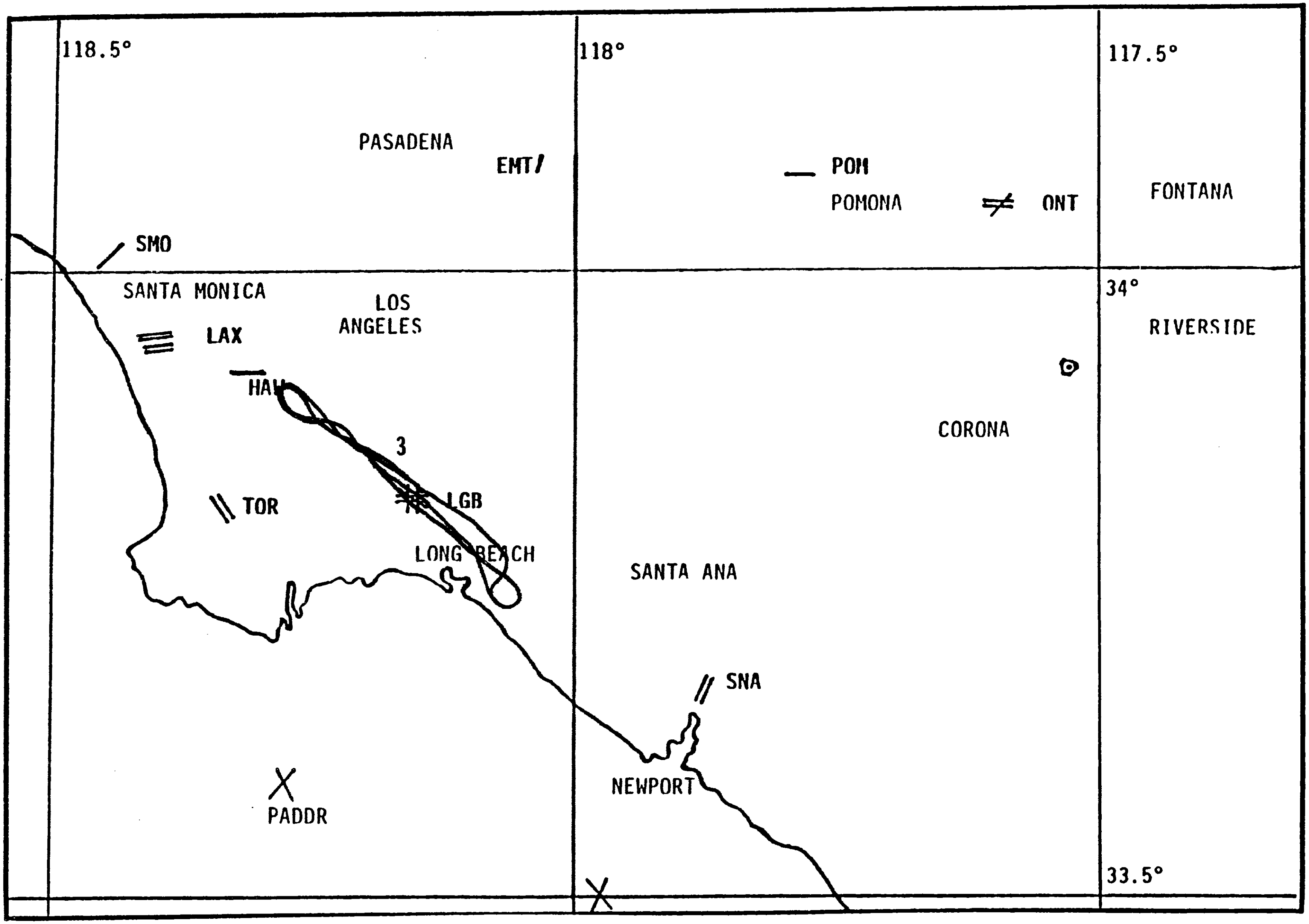
Flight Summary
CARB Cloud Sampling
Date: 10 June 1985

Flight Number: 440

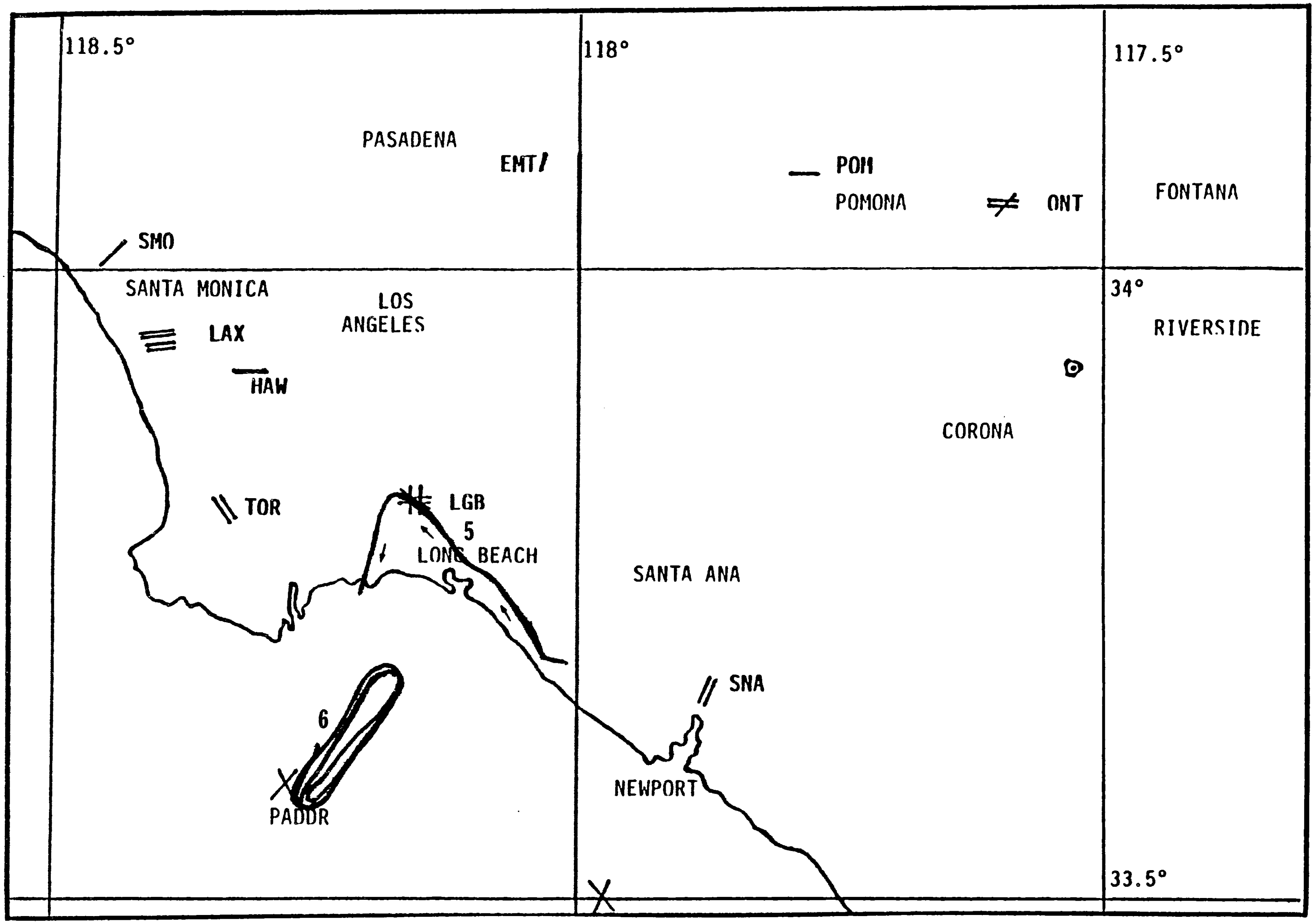
										Grab Sample Codes				
									Total	Cloud water			Bubblers	
		Time (PDT)		Altitude (ft msl)		Length	HC	Filter	Sample	Unsta-		Car-	Car-	Pan
Pass	Type	Start	End	Start	End	(min)	Can	Set	Collector	bilized	H_2O_2	bonyl	bonyl	
1	Missed appr.	0112	0127	2000	720	14.55				U51	P51			
2	Orbit	0133	0203	1600	1600	30.00		51	51	U52,U53	P52			
3	Orbit	0209	0239	1600	1600	30.00	TV 264	52	52	U54	P53	D51	51	PK51,PW51
4	Orbit	0246	0316	1750	1750	30.00		53	53	U55	P54	D52	↓	↓
5	Missed appr.	0330	0338	1900	1900	8.07				U56	P55	D53		
6	Orbit	0342	0412	1600	1600	30.05		54	54	U56,A52	↓	↓	↓	↓
7	Orbit	0422	0452	1600	1600	30.00		55		A53	A54 $\overset{?}{\longleftrightarrow}$	A55		
8	Zero spiral	0503	0517	5000	985	13.72								



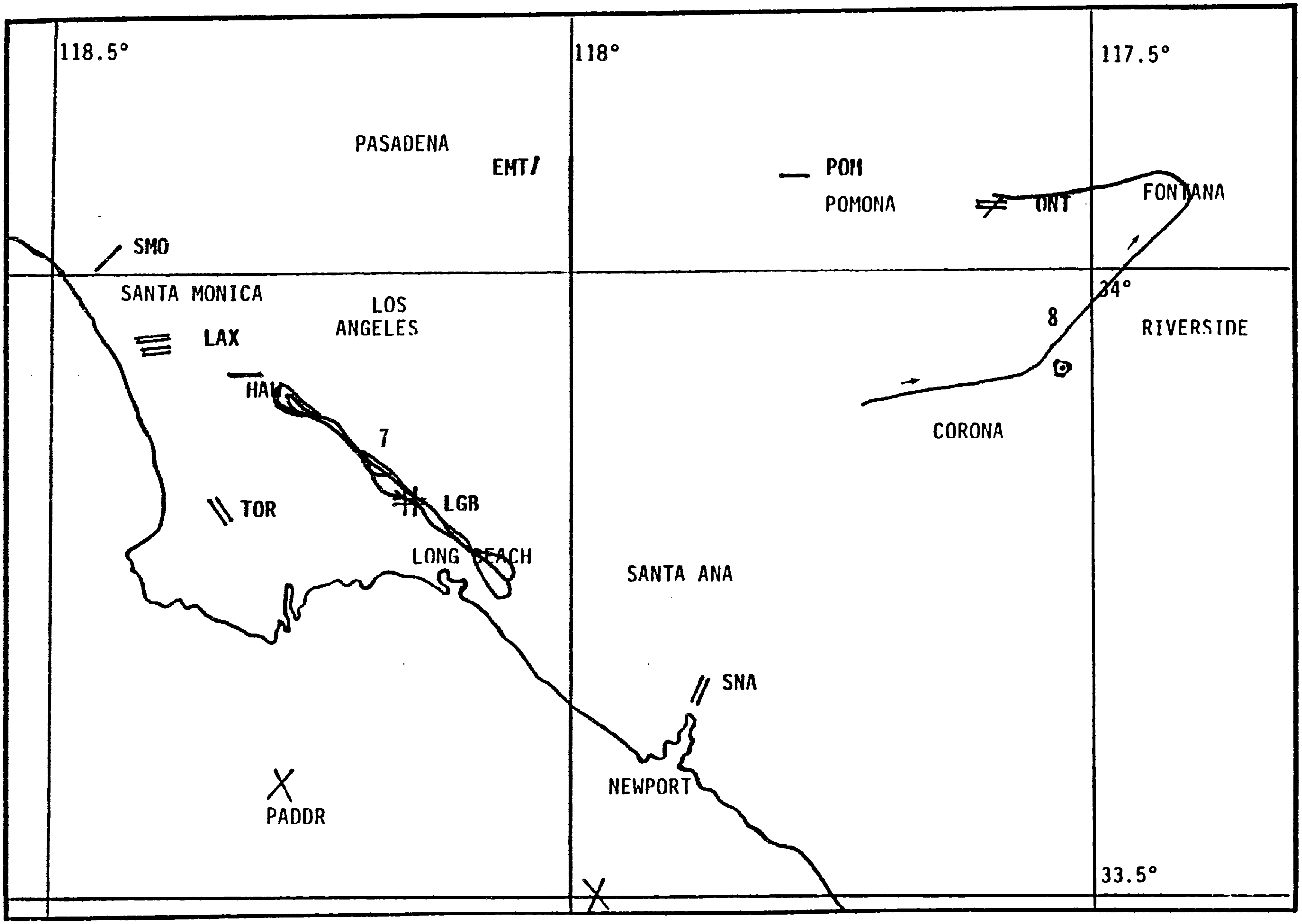
Flight 440 Sampling Locations 10 June 1985



Flight 440 Sampling Locations 10 June 1985



Flight 440 Sampling Locations 10 June 1985

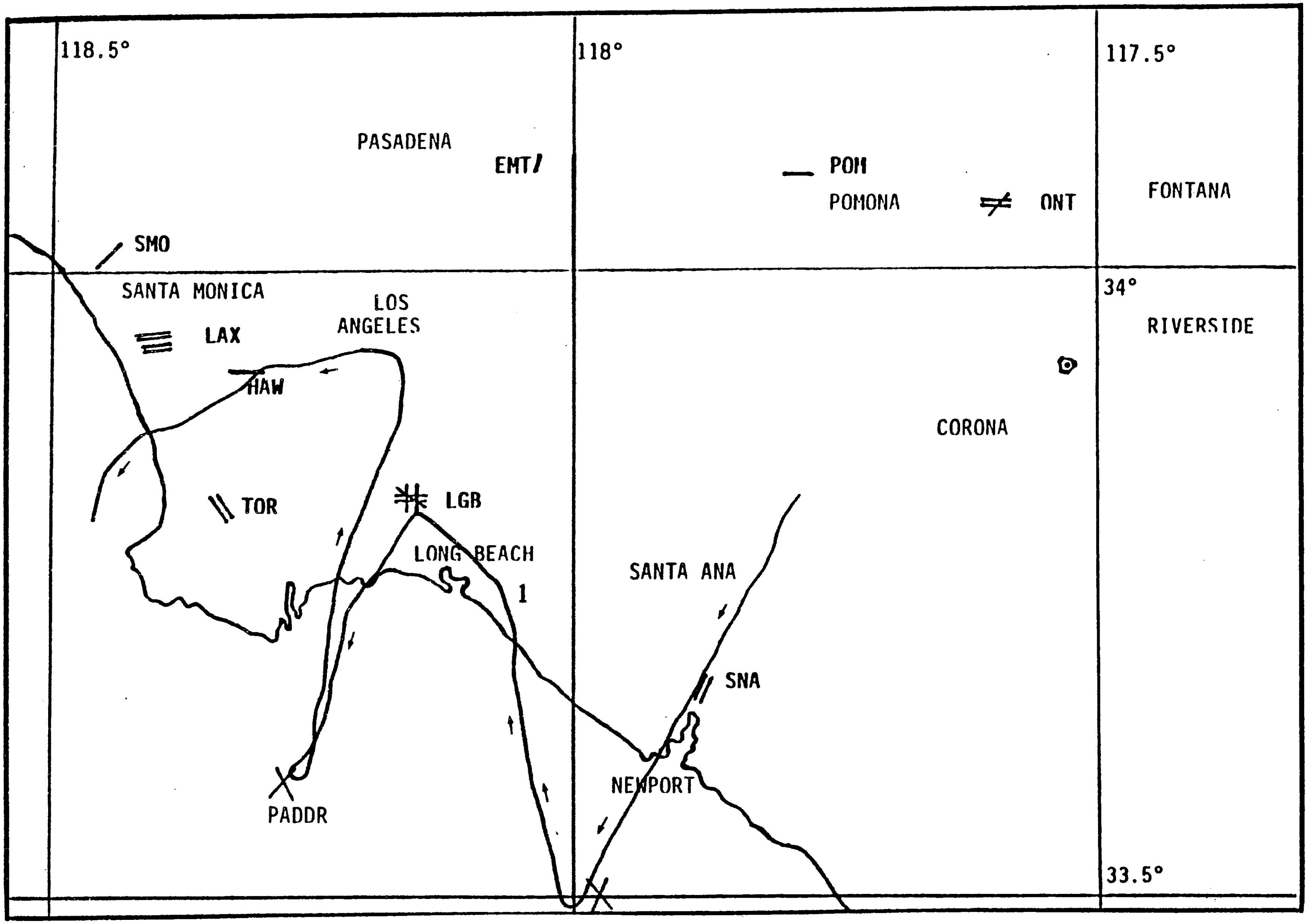


Flight 440 Sampling Locations 10 June 1985

Flight Summary
CARB Cloud Sampling
Date: 11 June 1985

Flight Number: 441

							Grab Sample Codes							
				Altitude (ft msl)					Total	Cloud water			Bubblers	
		Time (PDT)				Length	HC	Filter	Sample	Unsta-		Car-	Car-	Pan
Pass	Type	Start	End	Start	End	(min)	Can	Set	Collector	bilized	H_2O_2	bonyl	bonyl	
1	Missed appr.	0056	0148	2600	2600	51.92	TV 245	61		U61,U62, U63	P61, P62,P63	D61,D62	61	PK61,PW61
2		0154	ABORT					62		U64	P64	D63	↓	↓
blanks								63,64,65						



Flight 441 Sampling Locations 11 June 1985