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

Executive Summary

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Prepared for:

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EXECUTIVE SUMMARY

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.

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.

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. On 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.

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.

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 and 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 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.

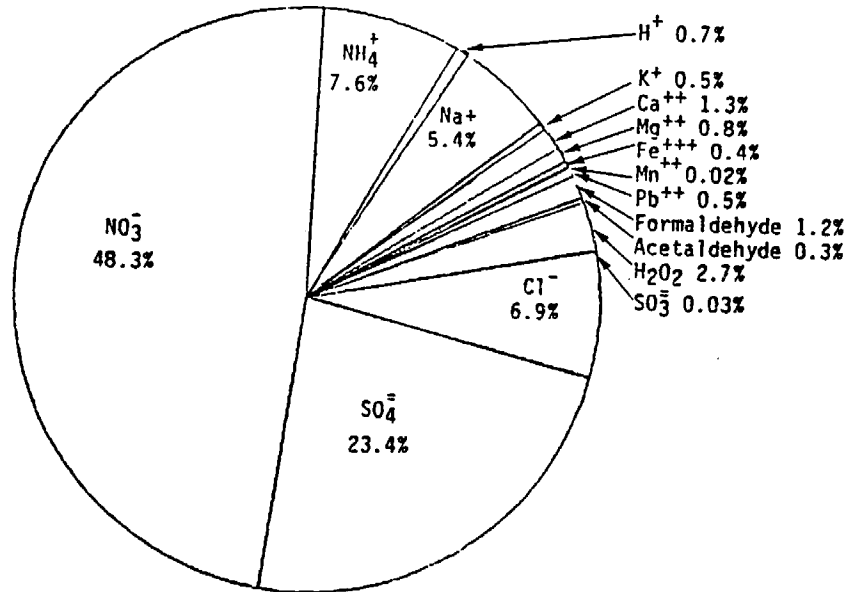


Figure 1. May-June 1985 average cloud water composition by mass. Only species determined are included.

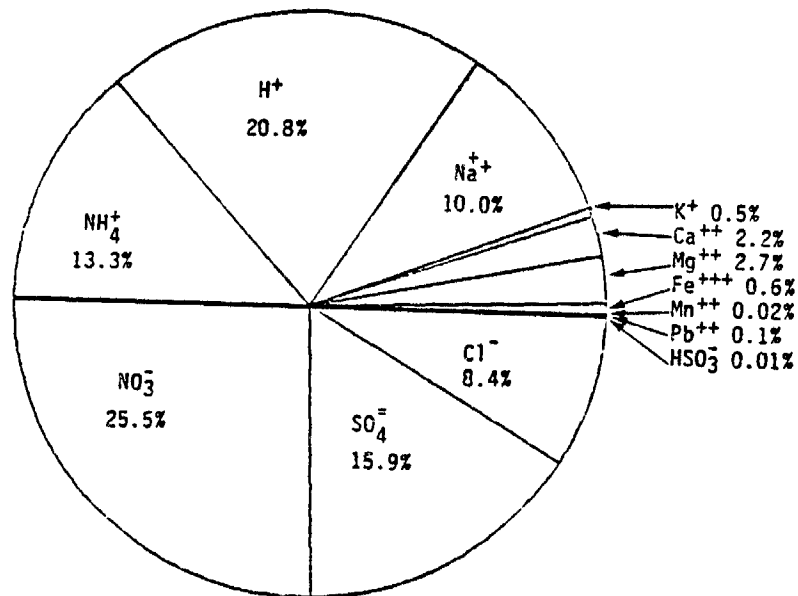


Figure 2. May-June 1985 average cloud water composition by equivalents. Only ionic species determined are included.

Table 1. Summary of cloud water concentrations

Analyte	Time Period	Mean	Maximum	Minimum
Ambient concentrations of water species in $\mu\text{g}/\text{m}^3$				
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				
H ₂ O ₂	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

2. The species of second importance is sulfate. On a mass basis, the 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.

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.

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 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 ($\mu\text{g}/\text{m}^3$), so they are unaffected by cloud evaporation and cloud condensation. Note the logarithmic scale and the small distance in the plot for a 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 4 shows on a logarithmic scale the ambient concentrations ($\mu\text{g}/\text{m}^3$) 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.

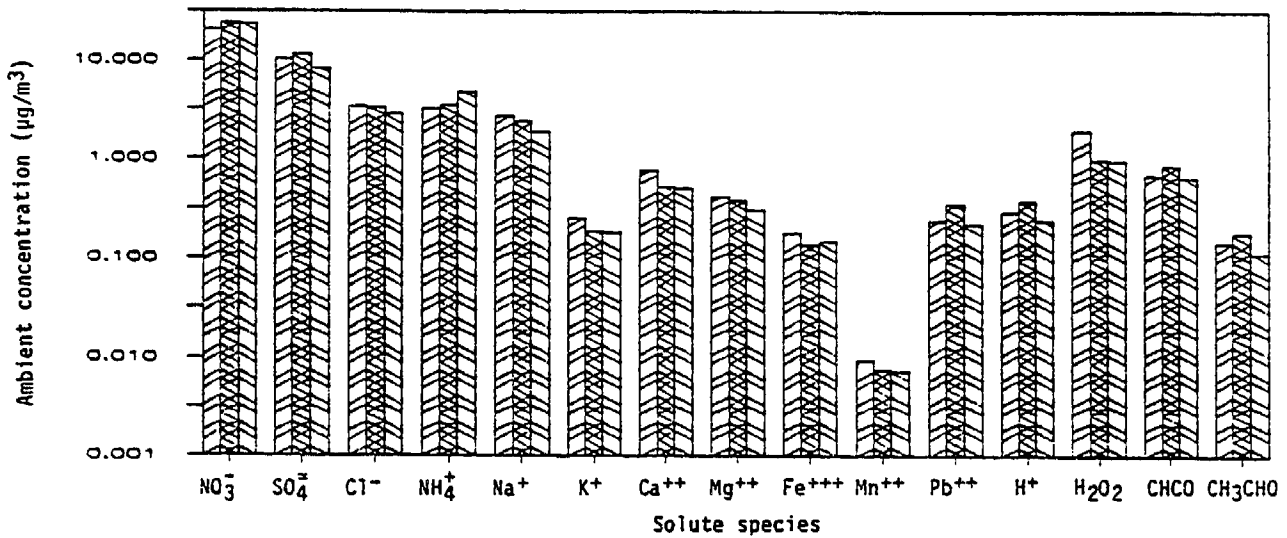


Figure 3. Trends with time in the average ambient concentrations of cloud water species measured in flights in which air parcels were approximately followed. Note the logarithmic concentration scale. The three bars for each species show average concentrations measured at approximately one hour intervals.

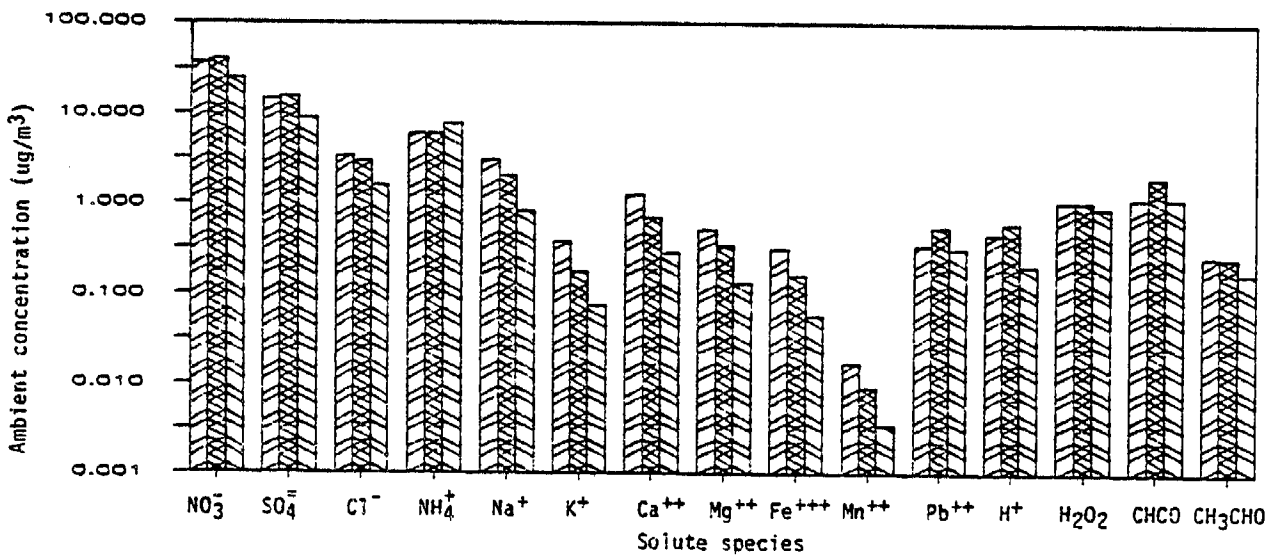


Figure 4. Ambient concentration by mass of species in the cloud water on a night when there was significant drizzle. The three bars for each species show concentrations measured at one hour intervals.

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 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.

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

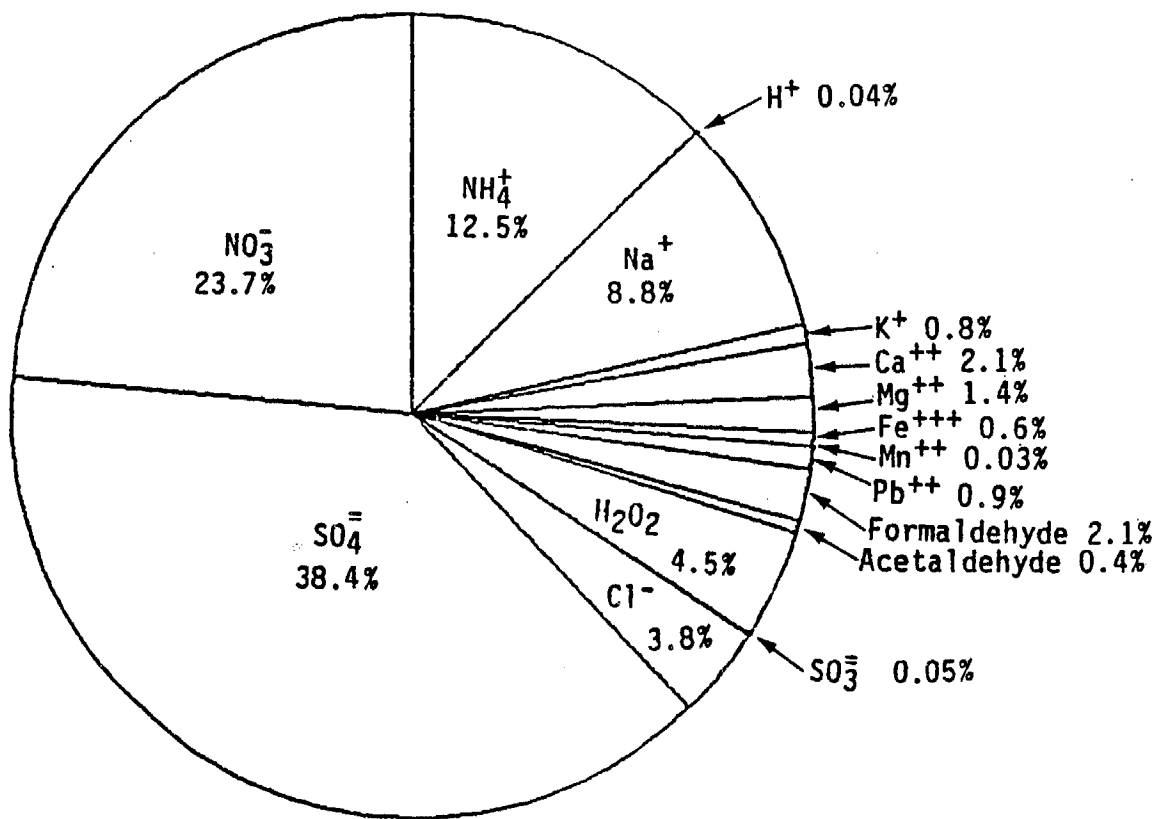


Figure 5. Calculated May-June 1985 average composition by mass of the aerosol remaining after cloud evaporation. Only species determined are included. Compare with Figure 1-1.

support this belief by showing that sulfur dioxide concentrations in clouds 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 $15 \mu\text{g}/\text{m}^3$ 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 $25 \mu\text{g}/\text{m}^3$.

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. 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.

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.

5. 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.