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LIBRARY-AIR RESOURCES BOARD

## CHARACTERIZATION OF THE COMPOSITION AND THREE DIMENSIONAL DISTRIBUTION OF ACIDITY IN SOUTHERN CALIFORNIA CLOUDS

EXECUTIVE SUMMARY

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Prepared for:

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## EXECUTIVE SUMMARY

### 1. INTRODUCTION

Sonoma Technology, Inc. (STI) conducted a study in 1983 and 1984 for the California Air Resources Board in which an aircraft was used to collect cloud water samples, filter samples of submicron aerosol, 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 by STI in 1982.

### 2. OBJECTIVES

The objectives of the study were to:

- a. Determine under a limited set of conditions the spatial distribution of acidity in clouds in and upwind of the Los Angeles Basin and the spatial relationship of acidity to sources.
- b. Determine the distribution of sulfur, nitrogen, and carbonyl compounds between the gas, aerosol, and droplet phases for pre-cloud formation conditions, in-cloud conditions, and post evaporation conditions to better understand the chemical species and reaction pathways important in the formation of acidity and aerosol precursors in clouds and the fate of these species when the clouds evaporate. The investigation of the chemistry of sulfur (IV) and carbonyl compounds was emphasized.

### 3. EXPERIMENTAL

Three short aircraft flights were made on 30 October and on 11 and 14 November 1983, but satisfactory clouds did not form during this period. Three complete cloud sampling flights were made 3, 4, and 5 June 1984. One November and two June flights began shortly after midnight, and the remaining flights began later in the night and ended at about 7:30 A.M.

New methods were developed and used to determine the concentrations of reactive chemical species in the cloud water. Cloud water was simultaneously collected in three bottles, two of which contained stabilizing solutions for reactive species. At any one time, two of the following three species were stabilized continuously during the collection process: hydrogen peroxide, carbonyl compounds (formaldehyde and acetaldehyde), and sulfur (IV). (Sulfur (IV) is used to designate sulfur compounds in the plus four oxidation state, such as sulfur dioxide and sulfite.)

New sampling equipment added to the aircraft for the 1983-84 study included a second cloud water collector, a probe to continuously measure the pH of the cloud water entering the sample bottle, and a LORAN C navigation system. Work was begun on the development and evaluation of "total sample collectors," which are designed to collect all the sulfate and nitrate in an air sample regardless of the particle size or the distribution of the nitrate between the gas and particle phases. Such a collector is needed to obtain the accurate total nitrate and sulfate concentrations to determine the formation rates of these species.

Airborne cloud sampling in Los Angeles is a highly intense activity. For example, in June about 9 hours of flight time resulted in 5.72 hours during which grab samples were collected and data were recorded for later processing. During this time, 224 grab samples (or about 25 samples per hour) were collected and the associated sample flow rates and sampling times recorded. A total of 437 analytical determinations were made on these samples. The flight patterns were designed to extend throughout the Los Angeles Basin. Because the flights were necessarily made under instrument flying conditions, detailed coordination with air traffic control was required.

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.

The cloud conditions in October and November 1983 were generally unsatisfactory, so few conclusions in this report are based on those data. The June 1984 cloud conditions were more favorable, and were typical for that time of year. If anything, there was more tendency toward drizzle and rain than normal. The June sampling ended when a storm produced relatively clean and deeply mixed conditions.

Complete experimental details are given in the body of the report.

#### 4. RESULTS AND CONCLUSIONS

The results and conclusions from this study are presented in the form of a few general statements. These statements are followed by lists of observations which support or qualify the statement.

The statements are primarily based on the observations made while flying in stratus clouds on three consecutive days in June 1984. These clouds were found in a narrow range of altitudes near 3000 ft msl. Stratus clouds frequently form in May and June in the Los Angeles Basin, and the conditions at the time the samples were collected are believed to be representative of such cloudy nights. However, it is not possible to know how closely this small data set represents the current average conditions existing in the stratus clouds which form in the late spring.

#### 4.1 Extent of Oxidation of Sulfur and Nitrogen Species

The oxidation of sulfur dioxide to sulfate had typically gone to completion in the sampled clouds, and the cloud water contained an oxidant which would very rapidly oxidize any additional sulfur dioxide mixed into the clouds.

- a. Gas phase sulfur dioxide concentrations were below the limit of detection (about 1 ppb) during all sampling in clouds except for two isolated plumes near the coast.
- b. The combined sulfate concentrations in the cloud water and in the aerosol particles ranged from  $6 \mu\text{g}/\text{m}^3$  to  $27 \mu\text{g}/\text{m}^3$  and averaged  $14 \mu\text{g}/\text{m}^3$ .
- c. No sulfur (IV) was found in the aerosol, and sulfur (IV) concentrations in the cloud water were a few thousand times smaller than the sulfate concentrations.
- d. The observed sulfate concentrations were enough larger than the upper limit of the gas phase sulfur dioxide concentrations as well as the cloud water and aerosol sulfur (IV) concentrations that the oxidation of sulfur species had effectively gone to completion.
- e. Hydrogen peroxide was found in all cloud water samples which were analyzed for this species. Available rate data indicate that hydrogen peroxide in clouds oxidizes sulfur dioxide to sulfate at ambient concentrations in times of a few tens of minutes. Therefore, finding hydrogen peroxide indicates that any additional sulfur dioxide mixed into the clouds would have been very rapidly oxidized to sulfate.
- f. The gas phase hydrogen peroxide concentration was estimated from the observed liquid phase concentration assuming the two concentrations were in equilibrium. It was calculated that the clouds contained enough hydrogen peroxide to form an additional  $1 \mu\text{g}/\text{m}^3$  to  $6 \mu\text{g}/\text{m}^3$  of sulfate. This would have increased the sulfate in the cloud water by 6% to 30%, and the combined cloud water plus aerosol sulfate concentrations by about half those percentages.
- g. Measured concentrations of iron and manganese in the cloud water were used to estimate the relative importance of the iron-manganese catalyzed oxidation of sulfur dioxide. Calculations based on laboratory-measured rate constants indicate that this oxidation pathway is 100 to 500 times slower than the oxidation by hydrogen peroxide. Thus, when hydrogen peroxide concentrations in cloud water are in the range of those observed in this study, the oxidation of sulfur dioxide by the iron-manganese catalyzed reaction is unimportant.

The oxidation of nitrogen oxides to nitrate was half to three quarters complete. Ozone was always present in the clouds, and the oxidation of NO to NO<sub>2</sub> had always gone to completion. It is likely that the ozone in the clouds was oxidizing the NO<sub>2</sub> to nitrate at night.

1. Less complete oxidation of NO<sub>x</sub> to nitrate was observed in the inland part of the basin at 7:30 A.M. one morning when unstable conditions improved the vertical mixing and likely brought fresh rush-hour emissions to the sampling altitude.
2. The average NO<sub>x</sub> concentrations ranged from 3 to 10 ppb and the combined cloud water plus filter nitrate concentrations ranged from 10 to 30 µg/m<sup>3</sup>. (The filters were designed to collect fine-particle nitrate and nitric acid gas.)

#### 4.2 Spatial Distributions

Ozone was always observed all night at all sampling locations aloft in this and in the prior study. In June 1984, the ozone concentrations in the clouds ranged from 50 ppb to 80 ppb and were higher above the clouds.

- a. There is a significant difference between ozone concentrations aloft and at ground level in the Los Angeles Basin at night. Surface emissions of NO and other sinks destroy ozone at ground level at night.
- b. The lack of ozone and presence of NO at night at ground level prevents oxidation reactions from taking place at ground level which may occur all night aloft. An example is the reaction of NO<sub>2</sub> with ozone to form species which are readily hydrolyzed to form nitric acid.

No strong horizontal spatial gradients were observed in the Los Angeles Basin. The pH of the cloud water showed little variation with location. Sulfate and nitrate concentrations were high in the clouds along the coast as well as inland.

1. The pH of the cloud water samples was typically close to 3.0. The probe which continuously read the pH of the cloud water entering the collection bottle showed little pH variability within each sample.
2. Sulfate concentrations were as high along the coast as inland, which is consistent with the location of sulfur dioxide sources near the coast and very rapid oxidation of sulfur dioxide in clouds.
3. Lead was found in cloud water samples collected over land near the coast as well as inland, indicating that all samples collected over land contained urban air pollution.

4. One sample was collected over the ocean off Newport Beach in November (when there were no clouds over land) in which the chloride and trace metal concentrations showed that essentially all sulfate in the cloud water came from sea salt.
5. Nitrate concentrations showed no marked spatial variability in the samples collected over land, but were significantly smaller in the sea salt sample collected off Newport Beach.

#### 4.3 Cloud Water and Aerosol Compositions

In general, the cloud water compositions were those which would be obtained by mixing 50 to 60 equivalents of nitric acid, 20 to 30 equivalents of ammonium sulfate, 10 to 20 equivalents of sodium chloride, and a few equivalents of calcium, magnesium and iron salts.

- a. The cloud water samples typically contained about twice as many equivalents of hydrogen ion as sulfate, so sulfur chemistry cannot entirely account for the observed acidity.
- b. Nitric acid is the dominant source of cloud water acidity.
- c. The fact that ammonium and sulfate concentrations are similar does not indicate they have a common source. The above recipe is only a simple way to summarize the observed concentration ratios.
- d. Preliminary data from the total sample collector suggest that the true gas plus particle nitrate concentrations are larger than those reported here, which were obtained by combining the nitrate collected in the cloud water samples and on the filter samples. If this is the case, some nitrate eludes the cloud water and aerosol samplers.

When the clouds evaporate, it is expected that nitric and hydrochloric acids will also evaporate. It was calculated that 40 to 70% of the cloud water nitrate and chloride would volatilize when the clouds evaporate, and that the average loss was 57%.

1. On the average, nitrate was 56% and sulfate was 22% by weight of the inorganic materials whose concentrations were determined in the cloud water. However, nitrate was 37% and sulfate was 36% of the inorganic material estimated to remain in the aerosol resulting from the cloud evaporation.
2. The nitric and hydrochloric acids which were calculated to evaporate constitute an average of 37% of the inorganic species determined in the cloud water.

#### 4.4 Sulfur (IV) Compounds

Sulfur (IV) was determined in the aerosol and in the cloud water because of the relatively high concentrations reported in the previous cloud sampling study (Richards *et al.* 1983). The sulfur (IV) concentrations observed in this study were negligible.

- a. Sulfur (IV) concentrations in the cloud water were a few thousand times smaller than sulfate concentrations.
- b. Sulfur (IV) concentrations in the aerosol were below the limit of detection, which assures that they are also negligible.

#### 4.5 Carbonyl Compounds

The concentrations of formaldehyde and acetaldehyde were measured in cloud water and in the air because of the potential role of these species in influencing the chemistry of sulfur compounds. Significant concentrations were found.

- a. Concentrations of formaldehyde in the cloud water ranged from 20 to 70  $\mu\text{M}$ , and acetaldehyde concentrations ranged from 5 to 50  $\mu\text{M}$ . The ratio of the sum of the moles of formaldehyde and acetaldehyde to the number of moles of sulfate ranged from 10 to 45%.
- b. Gas phase concentrations were below the limit of detection, or below about 6 ppb for formaldehyde and 4 ppb for acetaldehyde.
- c. The calculated rate of reaction of sulfur (IV) with carbonyl compounds in the cloud water is about 1000 times slower than the calculated rate of oxidation of sulfur (IV) by the iron-manganese catalyzed reaction, which in turn is a few hundred times slower than the calculated rate of oxidation of sulfur (IV) by hydrogen peroxide. It is concluded that if sulfur (IV) were added to the cloud water sampled in this study, it would be oxidized much more rapidly than it would react to form an adduct with carbonyl compounds.
- d. The reported concentrations of acetaldehyde in the cloud water were about 100 times larger than expected from the measured upper limit to the gas phase concentrations and the equilibrium constants for the distribution between the gas and liquid phases and the formation of the gem diol in the liquid phase. This discrepancy has not been explained.

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Richards L. W., Anderson J. A., Blumenthal D. L., Duckhorn S. L. and McDonald J. A. (1983) Characterization of Reactants, Reaction Mechanisms, and Reaction Products Leading to Extreme Acid Rain and Acid Aerosol Conditions in Southern California. Final Report No. STI 83 FRD-200. Submitted to the California Air Resources Board, Contract No. A0-140-32, April 1983.

## 5. RECOMMENDATIONS

The first recommendation is a reminder derived from information which has been available for some time. The second is derived from new data presented in this report. The third recommendation has previously been made by others, but additional technical basis is provided by the results in this report.

1. When summarizing chemical properties of the air in the Los Angeles Basin or when designing control strategies, it is important to remember that at night the chemistry aloft is quite different from the chemistry at ground level.

Ozone persists aloft all night and is believed to cause some oxidation reactions to continue all night, especially in clouds. Ozone is destroyed at night at ground level by NO emissions and other sinks, and thus oxidation reactions caused by ozone cannot take place at ground level at night. Results from ground-level studies of air chemistry at night may not apply to the air aloft in the Los Angeles Basin.

2. It is recommended that the conditions described in the following paragraph be regarded as typical of stratus clouds in the Los Angeles Basin in the spring or summer as long as the sulfur dioxide emissions there remain near or below their present levels.

It was found that sulfur dioxide in the stratus clouds which commonly form at night in the late spring in the Los Angeles Basin had been completely oxidized to sulfate. All cloud water samples contained hydrogen peroxide, so it is believed that additional sulfur dioxide mixed into the clouds would be oxidized to sulfate as rapidly as the mixing takes place. Only a few isolated plumes contained enough sulfur dioxide to use up the hydrogen peroxide and leave un-oxidized sulfur dioxide. Under these conditions, additional sulfur dioxide mixed into the stratus clouds will rapidly cause corresponding increases in the sulfate concentrations.

3. It is recommended that more emphasis be given to reductions of sulfur emissions in the coastal portions of the Los Angeles Basin where stratus clouds most frequently occur than to reductions in areas where stratus clouds are less common.

Sulfur dioxide is oxidized to sulfate less rapidly in cloud-free air than in stratus clouds, so sulfur dioxide emissions in areas where stratus clouds are less common will less frequently undergo rapid conversion to sulfate.

No recommendations related to nitrate chemistry are made at this time; they will be formulated after the completion of the cloud sampling flights planned for May 1985.