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AIRBORNE MEASUREMENTS OF AIR POLLUTION
CHEMISTRY AND TRANSPORT

I. INITIAL SURVEY OF MAJOR AIR BASINS
IN CALIFORNIA

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SAPRC REPORT NO. 1

Airborne Measurements of Air Pollution Chemistry and Transport

I. Initial Survey of Major Air Basins in California

by

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ABSTRACT

An instrumented aircraft has been used to study photochemical air pollution in the State of California. Simultaneous measurements of the most important chemical constituents (ozone, total oxidant, hydrocarbons, and nitrogen oxides, as well as several meteorological variables) were made. State-of-the-art measurement techniques and sampling procedures are discussed. Data from flights over the South Coast Air Basin, the San Francisco Bay Area, the San Joaquin Valley, the Santa Clara and Salinas Valleys, and the Pacific Ocean within 200 miles of the California coast are presented. Pollutants were found to be concentrated in distinct layers up to at least 18,000 feet. In many of these layers, the pollutant concentrations were much higher than at ground level. These findings bring into serious question the validity of the present practice of depending solely on data from ground-based monitoring stations for predictive models.

INTRODUCTION

An instrumented aircraft offers the potential for solution of a crucial problem: how to effectively supplement a ground-based, two-dimensional data collection network to sample what is really a three-dimensional chemical reactor--the polluted atmosphere. Although present sampling networks provide vitally needed measurements for health-warning systems, a particular problem of present monitoring networks has been the geographic, political or economic constraints that limit stations in either number, density or area coverage. Furthermore, effective public health policies ultimately require an accurate understanding of the detailed chemistry and transport of air pollution in our atmosphere. This understanding has been limited both by inconsistencies in the data from smog chamber experimental results and by insufficient ambient air quality data.

In most previous studies, aircraft equipped with meteorological and pollution instrumentation have been used to survey selected aspects of the pollution problem in a given region. For example, Ahlquist and Charlson (1968) have presented vertical sounding data of aerosol concentrations in urban air. McCaldin and Johnson (1969) and Stephens and McCaldin (1971) have described a single-engine aircraft which was used to study sulfur dioxide in coal-fired power plant plumes. Adams and Koppe (1969) have described an elaborately instrumented twin-engine aircraft for air pollution measurements. Lovill and Miller (1968) and Miller and Ahrens (1970) have found high levels of oxidant formed from photochemical smog over the San Francisco Bay area. Oxidant data obtained by Miller, McCutchan, and Milligan (1972) have furnished evidence that photochemical oxidant from population centers in the San Joaquin Valley of California is transported westward to the higher elevation valleys in the Sierra Nevada.

Early studies in the Los Angeles area by Neiburger et al. (1955) have indicated that maximum above-ground oxidant concentrations were attained at the base of the inversion, while the oxidant levels decreased above this altitude. On the other hand, Lea (1968) found from chemiluminescent ozone-sonde data that there was a tendency for the ozone maximum to occur above the base of the inversion. This last observation was supported by Edinger, McCutchan, Miller, Schroeder, Ryan, and Behar (1970), who used a single-

engined aircraft to measure the three-dimensional variation of total oxidants in the eastern South Coast Air Basin of California. Their data show that the oxidant formed beneath the inversion in the South Coast Air Basin exited up the slopes of the San Bernardino Mountains and that layers of high oxidant content were contained within the inversion layer. Edinger, McCutchan, et al. (1972) and Edinger (1973) further conclude that some of the oxidant exiting up the mountain slopes during the daylight hours can be injected into the middle of the inversion layer, where it will remain unmixed within a layer of equal kinetic energy. This inversion-bound pollution can be returned to lower altitudes by drainage winds at night or by fumigation during the day resulting from erosion of the inversion layer from below by convection.

The principal intent of the present project was to study in detail the two major urban centers in California--the Los Angeles Area and the San Francisco Bay Area. The Los Angeles basin is a classic example of photochemical air pollution in an urban center, with extremely severe episodes throughout most of the year. The San Francisco Bay region is one where significant changes in pollution levels are now being observed. Both areas are preferred study regions because of extensive ground monitoring networks which will supplement the data gathered by aircraft survey. This study was intended to serve as a proving ground for eventual global surveys of air quality as a part of NASA's Earth Resource Technology Satellite Program and was one of the first intensive uses of an aircraft over an extended time period during which an attempt has been made to elucidate several aspects of photochemical air pollution. Vertical soundings have been conducted over much of California, including the San Joaquin Valley, Santa Clara Valley, and Salinas Valley, as well as the South Coast Air Basin and the San Francisco Bay Area.

METHODS

A. Aircraft

For this study a Cessna 401-A, twin-engine aircraft (shown in Figure 1) was modified for air pollution sampling. Typical performance characteristics for this aircraft are given in Table I.

Aircraft modifications for air pollution survey included the addition of a sampling train and an inverter (Topaz Corp., Model 500 GWD) to supply 60 Hz, 120 VAC power for the instrumentation. The general arrangement of the modifications and instrumentation is shown in Figure 2, and a close-up of the sampling Pitot tubes is shown in Figure 3. Three sampling Pitot tubes were fabricated from 0.75-inch-OD stainless steel tubing, and were mounted to extend 6 inches in front of the nose of the aircraft 4 feet ahead of the propeller plane. The two outside tubes were lined with teflon and were connected to 0.75-inch-ID teflon tubing, extending 20 feet back into the aircraft for sampling. The Pitot tubes were operated using only ram air, and the dwell time for parcels of air in the sample lines was calculated to be less than 0.1 second from flow rate measurements at a sampling flight speed of 180 mph. Each instrument sampled the air stream using its own internal sampling pumps. The third sampling tube was reserved for future use in particulate sampling.

A total instrument package weight of 440 lbs. was flown during the initial phases of our study. Each package was configured to mount on racks riding on the seat tracks of the aircraft for easy removal and movement, and each was designed to provide a safe mounting for all instruments for an acceleration of up to 4.5 g. For these flights, analog recording equipment and voice tape recorders were used for data logging.

B. Instrumentation

Ozone Measurements. Measurements were made with an ozone photometer (Model 1003A, DASIBI Corporation, Inc., Glendale, California). This instrument is a self-contained unit whose operation (see Bowman and Horak, 1972) is based upon the physical measurement of the absorption by ozone of ultraviolet light at 2537A in an absorption chamber 14 inches long. Measurements are updated every 11 seconds and are based on two half-cycle integration periods. During the first half-cycle, atmospheric air is first passed through a catalytic scrubber to remove ozone and to establish a digital reference light measurement over the total integration period of approximately one second. During the second half-cycle the ozone is not scrubbed, and the digital light intensity measurement is integrated over precisely the same time period as the reference measurement. The differ-

ence between the two measurements is then related to the ozone concentration via Beer's Law.

At a nominal sampling speed of 180 mph, the ozone sample was collected over a spatial distance of less than 0.05 mile, with instrument readings updated every 0.5 mile. The ozone concentrations were either recorded on chart paper or observed on the digital readout.

Under the operating environment of the aircraft, this instrument has proved itself to be both reliable and rugged, with no apparent interferences due to nitrogen dioxide, hydrocarbons or sulfur dioxide. Its accuracy has been verified as being within ± 0.02 ppm by calibration against the standard potassium iodide technique described below, while the measurement precision was ± 0.005 ppm.

Total Oxidant Measurements. A total oxidant analyzer (Model 724-2, Mast Development Company, Davenport, Iowa) was used for measurements at ambient concentrations. This instrument used the potassium iodide technique and was modified for mounting on a standard electronics rack. To prevent repeated siphoning of the potassium iodide solution through the analyzer section, it was necessary to avoid the full ram pressure at the Mast inlet port. This was accomplished by inserting the instrument sampling line perpendicular to the arms of the air sampling manifold to act as a static probe. The calibration accuracy of this instrument was ± 0.02 ppm, while the measurement precision was ± 0.01 ppm.

Because the Mast analyzer responds to several oxidants, it was calibrated for response to ozone, nitrogen dioxide, and sulfur dioxide. In the case of nitrogen dioxide, the response was 16% of the total response for equal concentrations of ozone. The instrument response for sulfur dioxide was negative relative to the response for ozone and had a 1:1 correlation with it. All three calibration curves were linear. During level flight, this instrument was not susceptible to normal vibrational problems, although too-sudden altitude changes or steep aircraft turns would induce a noise excursion in the output current readings. We have found that optimal performance of the Mast oxidant analyzer in the aircraft requires a regular schedule of inspection and maintenance.

Oxides of Nitrogen. An airborne monitor (Model Au-400, Theta Sensors, Inc., Orange, California) was used for total oxides of nitrogen measure-

ments at ambient levels. The proprietary process employed in this unit includes a semipermeable membrane, a redox cell using controlled aqueous reactions to measure both nitric oxide and nitrogen oxide, and chemical suppressants to inhibit interference by sulfur dioxide. The response time of this unit is dependent on sample concentration due to the time required to establish equilibrium across the membrane and in the cell. At ambient concentrations (0.5 ppm or less), a typical response time is 20 seconds. Proper operation of this instrument requires a sample flow rate of 50 to 200 cc/min. Therefore, a teflon constant-volume displacement pump was added to insure that the flow through the instrument would be maintained at 176 cc/min.

Hydrocarbon Analyses. Air samples for hydrocarbon analyses were initially collected in one-liter borosilicate gas sampling tubes, sealed at either end with stopcocks using Dow Corning High Vacuum Silicone Stopcock grease. Aromatic hydrocarbon (C_6-C_9) and oxygenates could not be analyzed in these tubes, as these species are trapped in the grease. An improved sample tube was constructed, using teflon vacuum stopcocks with Viton O-rings, which minimized the absorption of the hydrocarbons and oxygenates. Baking out and nitrogen flushing of the sample tubes is necessary to reduce the background hydrocarbon levels. The samples were stored at room temperature ($24 \pm 1^\circ C$) and analyzed in the laboratory for C_1 through C_6 paraffins, olefins, and acetylenes, using a Series 600 Varian Aerograph gas chromatograph equipped with a flame ionization detector (see Stephens and Burleson, 1967, 1969, for a description of the analytical procedure).

Dew Point. A dew point hygrometer (Model 707, Technology Versatronics, Inc., Yellow Springs, Ohio) was used to measure the water content of the atmosphere. The instrument had a dew point range of $-40^\circ F$ to $+100^\circ F$ with an accuracy of $\pm 2^\circ F$. Under most circumstances, the response time of $4-5^\circ F$ per second was adequate for measurements.

Temperature. A thermistor bridge digital thermometer (Digitemp; Instrulab, Inc., Dayton, Ohio) was used to measure air temperature during flight. This instrument had an accuracy of $\pm 0.1^\circ F$ and a response time of less than one second.

C. Calibration Techniques

Several methods of instrument calibration were employed, and these procedures are summarized below.

The neutral buffered-potassium iodide colorimetric method (Public Health Service Publ. No. 999-AP-11, 1965) was used for ozone source calibrations. A 0.0025N I_2 in 0.1N potassium iodide solution, standardized against standard potassium thiosulfate, was used to calibrate the response of a spectrophotometer (Spectronic 20, Bausch and Lomb, Inc., Rochester, N.Y.). The absorbance of 10^{-4} N to 10^{-3} N I_2 solutions was measured at 352 nm. Several ozone source concentrations (0.05 to 1.0 ppm) were used to calibrate the Mast and DASIBI instruments. Calibrations by the potassium iodide method made before each flight were estimated to be accurate to ± 0.02 ppm.

Nitrogen dioxide source calibrations were determined by the Saltzman method (Public Health Service Publ. No. 999-AP-11, 1965). A fritted bubbler containing 5cc of Saltzman reagent was operated at a sample flow rate of 0.2 liters/minute. The color change of the reagent was usually complete after 15 minutes, whereupon the reagent's absorbance at 550 nm was determined in a spectrophotometer. Unreacted Saltzman reagent was used to zero the spectrophotometer. A known nitrogen dioxide concentration was prepared by injecting a specific volume of nitrogen dioxide gas (The Matheson Corporation) into a 23-liter stainless steel vessel which had been aged in the presence of nitrogen dioxide. The tank was pressurized to 75 pounds, and the concentration was determined by infrared absorption (1640 cm^{-1}) in a 40 meter pathlength cell. Other NO_2 concentrations were prepared by diluting this sample in a stream of filtered air. Dynamic calibrations using nitrogen dioxide permeation tubes (Metronics Corp., Palo Alto, California) were compared to the Saltzman method. The estimated accuracy of the calibration was ± 0.05 ppm.

Gas chromatographic hydrocarbon calibrations were made by injecting the pure hydrocarbons into a 2-liter calibrated volume containing nitrogen gas. Subsequent dilution and measurements to concentration levels as low as 1 ppb indicated a linear concentration vs. peak height relationship for the hydrocarbon flame ionization detector with a response proportional to the number of carbons in the hydrocarbon. Periodic recalibrations with

methane established the instrument response factor to within 3%.

D. Flight Patterns

Various flight patterns used to sample the atmosphere were designed to provide appropriate data for the determination of both horizontal and vertical pollutant profiles. Horizontal flight paths were used primarily for broad surveys, while vertical sawtooth patterns were used in the Los Angeles area to provide three-dimensional coverage. This latter pattern, when combined with touch-and-go landings, yielded data on the vertical distributions of pollutants to ground level. Flying a tight spiral ascent or descent with a diameter of 1 to 2 miles over a fixed area was designed to simplify computer analysis of the vertical distributions of pollutant species by reducing the number of spatial variables. However, experimental results obtained from the use of such patterns have indicated that care must be taken in designing the flight path, otherwise the aircraft's exhaust products are collected in the hydrocarbon sample bottles. Therefore, the diameter of the flight path as well as the rate of climb were increased.

E. Sample Technique Validation

The effect of the teflon sample line on pollutant concentrations was tested in the laboratory by using a length and size of line comparable to that in the aircraft. These tests were performed at a flow rate of 1.25 cfm, which is approximately one-third of the actual flow rate during flight. Concentrations of ozone, nitric oxide, and nitrogen dioxide comparable to ambient levels were measured individually before and after passage through the sample line. The results indicated that the teflon tubing had no effect on either the nitric oxide or the nitrogen dioxide concentration, and that $95 \pm 3\%$ of the ozone remained undecomposed as the gas traversed the length of the tubing. Further testing at a flow rate of 3 cfm indicated that at least 97% of the ozone did not decompose.

During one flight, a second Mast total oxidant meter was set up on the control tower at Riverside Municipal Airport, Riverside, California, and the aircraft passed within 100 yards of the tower at tower altitude (60 feet above the runway). Both the oxidant meter in the aircraft and that on the tower provided essentially identical readings.

RESULTS AND DISCUSSION

A. Regional Surveys

Ocean. Two surveys were made over the Pacific Ocean in order to estimate both the extent of pollutant advection to sea and the lower limit of detectable oxidant and ozone background. One flight generally paralleled the coast about 200 miles offshore from Santa Barbara north to Monterey, while the second flight was an out-and-back flight to a point 280 miles offshore southwest of Santa Monica.

The results of the flight northward along the California coast are given in Figure 4. These measurements were recorded while climbing from Los Angeles on a heading of 231° off the Santa Barbara coast for a distance of 225 miles and swinging northward on a flight path generally paralleling the California coast at a distance of 200 miles. The temperature data show a nearly dry adiabatic lapse rate at all levels, except for a surface-based inversion with the top at 2,000 feet off the Monterey coast. The oxidant profile exhibits some unexplained discontinuities during the climb to 18,000 feet off the Santa Barbara coast, as oxidant maxima of 0.06, 0.14, and 0.16 ppm were observed in layers at 14,900 feet, 16,300 feet and 17,300 feet, respectively. On the northward leg of the flight toward Monterey, a gradual descent from 18,300 feet to 10,500 feet showed no such maxima, although a maximum of 0.06 ppm was observed at 10,300 feet simultaneously with observation of a haze layer.

The presence of layers of oxidant and the absence of a correlation of oxidant data with lapse rate indicates that the parcels of air samples were not well mixed. These phenomena have previously been observed within the inversion layer for oxidants generated by photochemical air pollution (see Miller and Ahrens, 1970, and Edinger et al., 1970). The origin of the oxidant layers above 10,000 feet observed here may be the intrusion of ozone from the stratosphere. Recent NASA flights over the Eastern Atlantic Ocean near Africa have corroborated the presence of these layers (Gloria, 1972).

The data for the late afternoon, offshore survey which extended 280 miles southwest of Los Angeles on an approximate heading of 210° is given in Figure 5. A peak in all pollutant levels (i.e., ozone, total oxidant,

acetylene, and 1-butene) was noted at about 50 miles on the outbound leg, and haze was present throughout the flight. The higher ozone level relative to the total oxidant level observed at the distance of 50 miles was due to instantaneous maxima indicating the presence of pockets of high ozone concentrations. About 90 miles from Los Angeles on the return leg (2 hours later), a similar total oxidant peak was encountered, apparently due to air parcel movement at a windspeed of 20 mph in the two hours that had elapsed between these points. No comparable ozone peak was observable on the return journey since the ozone level had fallen to near zero shortly after sunset, although the ozone level did increase from a background of 0.01 ppm to 0.04 ppm simultaneously with the increase in total oxidant to 0.12 ppm.

The contaminant levels measured indicate that this flight occurred within the plume from the Los Angeles Basin. The Los Angeles Basin was experiencing Santa Ana winds sweeping seaward as a result of a high pressure zone located over the Great Basin area of Utah. Under these conditions, the L.A. Basin is generally well ventilated, with almost all airborne pollution carried out to sea. Therefore, the presence of the high oxidant levels to a distance of 280 miles is not surprising, although the dramatic decrease in ozone at sunset was not expected under these conditions. The occurrence of a smaller ozone peak of 0.04 ppm during the return flight does indicate that the ozone will persist in the atmosphere after sunset, and, therefore, that ozone is stable in the atmosphere barring the presence of either physical, photolytic, or chemical decomposition processes. The source of the higher total oxidant measurements after sunset is uncertain at this time. Later ozone measurements over the ocean to an altitude of 10,000 feet have shown that ozone levels at midday will be less than 0.01 ppm in the absence of pollutants.

San Joaquin Valley. A flight along the more populous eastern edge of the 400-mile length of the San Joaquin Valley provided data on pollution levels in relation to cities located in the valley. Figure 6 shows the detailed ozone, temperature and dew point profiles which were measured over Bakersfield, Fresno, Sacramento, and Redding. The dew point profiles are very similar, in that the dew point at the ground remained at 43°F in each

case, except at Redding, and decreased only slightly up to an altitude of 5000 to 6000 ft., after which it decreased more rapidly. The temperature profiles also showed similar lapse rates throughout the valley, although convective heating from the ground increased as the day progressed. It should be noted that the maximum ozone levels were often observed below the altitude at which there was a sudden decrease in the dew point readings, thereby indicating that the maximum ozone level had been reached within a moisture-laden air layer and that mixing may not have been complete. This phenomenon was usually noted on each of the flights throughout the State of California and particularly over the Southwest Coastal Air Basin, which includes the Los Angeles area.

Note that the ozone concentration over Sacramento remained almost constant from ground level to 3500 feet. This concentration most probably resulted from local pollution sources. In contrast, over the Bakersfield-Fresno area the ozone concentration appeared to be present in an upper air layer. It is not certain from our data whether the ozone at 5000 to 6000 ft. was produced from pollution transported from distant sources or by pollutants of local origin. Other isolated pockets of high pollutants have been routinely observed during our flights.

Monterey Bay Area. Three flights were made in the Monterey Bay area and the Salinas Valley. On the first flight, Sept. 10, 1971, a distinct plume containing nitrogen dioxide was visually observed near the large power plant at Moss Landing. The lower plume boundary was very distinct visually, as it extended down the Salinas Valley an estimated 55 miles, ascending from an altitude of 1300 feet over Salinas to an altitude of 6000 feet over King City. The nitrogen dioxide was identified by its characteristic red-brown color, as well as by the positive response of the total oxidant meter which was off-scale several times both at 2800 feet over Moss Landing and at an altitude of 1300 to 1700 feet over Salinas, a distance of 13 miles from the power plant. Typically, the full-scale deflection of the oxidant meter corresponds to a nitrogen dioxide level of 6 ppm when no ozone is present. The specific ozone meter remained at a significantly lower level (typically less than 0.12 ppm) throughout the flight.

On the following day, the meteorological conditions were stable and similar to those of the previous day (Read, 1971) and the plume over Moss Landing was clearly visible. The measured temperature profile indicated the presence of an inversion with its base at 1000 feet, its top at 2000 feet, and an isothermal layer extending from 2100 to 4100 feet. High concentration zones of oxidants--levels up to 1 ppm (full-scale deflection)--were again observed several miles from the power plant at Moss Landing, and these measurements generally extended to 4100 feet. The fact that most of the high oxidant levels were recorded between 2000 and 4100 feet suggests that the isothermal layer acted very efficiently to retard mixing and dilution.

Figure 7 shows a second survey of the total NO_x levels in the Salinas Valley. On this date (November 19, 1971), a mild offshore wind (Read, 1971) was present, and the meteorological conditions were less stable. Over Salinas, an almost isothermal layer of air extended to 2000 feet with a normal lapse rate above this altitude. The emissions from the Moss Landing power plant were measured at 1000 feet over Monterey Bay, and they extended inland toward Salinas. The measured NO_x concentrations above the power plant approached 2.0 ppm at an altitude of 1000 feet, while the NO_x concentrations at 150 feet were on the order of 0.2 ppm. On this occasion, the NO_x levels were lower than those calculated from data taken September 10 and 11. The recurring presence of the isothermal layer suggests that this atmospheric condition may account for frequent visual observation of the plume by residents of the area (Quarnstrom, 1972).

B. Basin Surveys

1. Los Angeles

A series of flights covering the California South Coast Air Basin (see map in Figure 8) were made from July 1971 to May 1972. These flights included general surveys of a large area, as well as detailed profiles of pollution concentrations over smaller areas. Figure 8 is an outline map of the area floor and shows the basic flight path which begins in Riverside, extends northward to Rialto, and then westward to El Monte and Santa Monica. The return flight to Riverside usually included passes over Long Beach, and data to ground level were collected by touching down at each airport.

The results shown in Figure 9 and Table II are of two general survey flights along a flight path paralleling the east-west axis of the basin. The flights occurred during typical summer meteorological conditions characterized by a day-time onshore breeze over much of the Los Angeles coastal plain (DeMarrais, et al., 1965).

The three hydrocarbons listed in Table II (acetylene, n-butane, and n-pentane) are among the less reactive products of automobile exhaust. Olefinic hydrocarbons were only found in the samples collected near the ground. For example, near the ground level over El Monte, a propylene concentration of 4.6 ppb was observed, whereas above the ground the levels were below the reliable detectable limit of 1 ppb. This observation of olefin depletion with increased altitude is an example of air mass aging due to chemical reaction. The ratio of acetylene:n-butane:n-pentane was about 2:4:2 over the area from the coastline to a point east of downtown Los Angeles. From El Monte eastward, the same ratio changed to 2:2:1 due either to the aging of the latter air mass while it was advected downwind or to the increased contribution of unburned gasoline vapors in the more heavily traveled Los Angeles area. The data over Banning show hydrocarbon levels higher at 6500 feet than at 4850 feet. This reversal in the hydrocarbon concentration gradient undoubtedly represents pollutant transport to this point via the basin plume, since no local pollution sources exist on the ground. These data also show the air mass dilution that occurs with altitude. For example, if we assume that the ground source strengths in this area are comparable, the hydrocarbon data over El Monte established that a dilution factor of at least twenty occurs over an altitude increase of 3500 feet, whereas the ozone levels tend to be higher at the higher altitude. We anticipate that all ground elevation emissions will behave in this more classic manner unless, as is the case for ozone, they can be photochemically regenerated above ground level.

Figure 9 indicates the results of a flight which began at 11:00 A.M. PST (August 11, 1971) and extended from Rialto to beyond the Santa Monica Coast. The data show that an inversion was present (dotted line) which inhibited the rate of atmospheric mixing and caused the buildup of significant ozone concentrations, particularly near the ground. On the return

journey, maxima in the ozone profiles of 0.21 ppm and 0.16 ppm were recorded at an altitude of 2800 feet and 1700 feet, respectively, over Riverside, which is south of Rialto, while the ground level concentration of ozone at Riverside Municipal Airport was 0.04 ppm. These high levels of ozone appeared to be contained in strata as previously reported by Edinger et al. (1970). Subsequent flights have shown that these strata may extend for many miles and that within these strata pockets of higher ozone levels might exist.

Figure 10 shows the ozone profile over Riverside, California, on three successive days (August 10, 11 and 12, 1971). The data clearly show the presence of ozone layering in the atmosphere, although it cannot be determined from the data just what combination of actinic light, nitrogen oxides and meteorological advection would lead to this profile. The temperature profiles on the right-hand side of the figure indicate a very stable condition which would inhibit vertical mixing below the effective mixing height. Additional data on one of the days (August 10, 1971) show that a definite inversion was present to the west toward the coast, whereas the higher temperatures during the afternoon tended to break the inversion inland.

Vertical isopleths of pollutant concentrations are often drawn by taking ground-level data and assuming complete mixing below the inversion layer. This procedure is questionable at best since this work shows that frequently a deep isothermal region exists within which little or no mixing occurs. This is particularly emphasized by visual and instrumental evidence of extensive layering, as also observed by Edinger et al. (1970). Such stratification can occur anywhere within the basin under a variety of weather conditions and during different seasons.

The data in Figure 11 show an ozone and oxidant profile obtained in the Santa Catalina Channel off of Los Angeles, which is representative of earlier data taken in the Monterey Bay area. Near sea level on the Catalina Channel flight, both the ozone and oxidant readings were in agreement. By 2000 feet, however, the ozone decreased to a level of 0.03 ppm and the oxidant increased to a maximum of 0.08 ppm. At 4000 feet, where the isothermal layer ends and there is better mixing with the air above, the oxidant level rapidly decreased to a value in agreement with the ozone level.

This discrepancy between the ozone and total oxidant readings had earlier been attributed to the presence of nitrogen dioxide from power plant emissions. In this case, however, there was no visual evidence of the characteristic red-brown color, and none would be expected unless the total optical path length were sufficiently large. In the same area, approximately one hour earlier at 2700 feet, a high oxidant concentration of 0.17 ppm and ozone concentration of 0.03 were observed. If the difference of 0.14 ppm is attributed to the presence of nitrogen dioxide, then, by applying the calibration factor of 0.16 for the response of the Mast oxidant meter to nitrogen dioxide, the nitrogen dioxide level was calculated to be 0.88 ppm at this altitude. This phenomenon was again observed on later flights in the same channel and elsewhere.

Low altitude local flights in the Long Beach area resulted in the data of Tables III and IV. Each flight consisted of an approach to the Long Beach Airport, and the flight path crossed over a complex of power plants in this area. On each flight, a well-defined plume was visually and instrumentally observed. From the calculated nitrogen dioxide levels of Table III, the data show that the plume was localized over land near the power plant-airport complex, as well as near the refineries on Signal Hill, where a calculated nitrogen dioxide concentration of 1.5 ppm was observed. This same cloud also extended out over Long Beach Harbor toward Santa Catalina Island at 2600 feet. As already mentioned, additional high calculated NO_2 levels have been found over the Catalina Channel. On the second survey (Table IV), the measured NO_x concentrations clearly indicated the plume presence near the airport-power plant complex. On this day, the plume was visible only in the near vicinity of the power plant.

2. San Francisco Bay Area

Flights in the San Francisco Bay area are complicated by low inversion levels usually caused by radiation inversion conditions. Oxidant and ozone pollutant concentrations are often much lower than in Los Angeles. Our data show that higher concentrations of pollutants are usually found in the eastern side of the bay due to prevailing winds and to industrial congestion. The Bay Area seems to show a higher level of total oxidant relative to ozone than does the Los Angeles area.

A total oxidants profile (Figure 12) of the East Bay region and of the eastern Santa Clara Valley area was taken on September 15, 1971, during the first smog alert ever called in the Bay area. The higher total oxidants levels in Figure 12 provide a contrast to the more typical ozone values observed in the Southern Santa Clara Valley (Figure 13). These values are lower than those recorded in Southern California. Layering similar to the Los Angeles area was observed in the nearly isothermal, and therefore, unmixed layers. These layers remained in approximately the same area until late afternoon winds dissipated and mixed them. Two flights were undertaken in January 1972, on the west side of the bay on a relatively clean day, with mild winds and no inversion. Levels of NO_x , total oxidant, and ozone remained very low, although NO_x peaks were observed in the San Leandro area of the East Bay. The peak levels were 0.2 ppm, with typical readings of 0.08 ppm or less for that day.

SUMMARY

The utility of an airplane for intensive air pollution monitoring has been demonstrated. The data obtained over many different areas under a variety of conditions can be summarized as follows.

1. We have observed distinct sets of pollutant layers at altitudes up to 18,000 feet under a variety of meteorological conditions. The occurrence of ozone and total oxidant layers below 10,000 feet appear to be the result of urban air pollutant emissions and their subsequent photochemistry, as well as the meteorological structure of the atmosphere. On the other hand, the total oxidant layers above 15,000 feet may possibly result from stratospheric intrusion of ozone into the troposphere.

2. Although oxidant and ozone levels may be low at ground level, they often increase by factors of from two to ten at the higher altitudes within the mixing layer (1000 to 4000 feet above the ground), whereas ground level emissions such as hydrocarbons and nitrogen oxides tend to dilute as the air mass mixes and rises to higher altitudes. These results suggest that the ozone buildup that occurs in advected air masses is primarily the result of a continuous photochemical aging of the air mass. The smaller ground-level ozone measurements are probably decreased by two processes: physical

quenching on surfaces and/or chemical quenching by nitric oxide and olefinic hydrocarbons. In the absence of these quenching processes the half-life for ozone decomposition appears to be relatively long.

3. An isothermal temperature profile in the Los Angeles Basin was common during the periods when smog episodes occurred. This isothermal air mass often extended up to the so-called "mixing" height and appeared to restrict vertical mixing.

4. High total oxidants levels relative to lower ozone measurements can result from oxidation reactions resulting from nitric oxide emissions by fossil-fuel power plants. The reaction of nitric oxide with ozone tends to retard ozone buildup and leads to high levels of nitrogen dioxide. Under stable atmospheric conditions, the nitrogen dioxide plume can be detected at least 30 miles away.

These results suggest that meteorological transport mechanisms are better portrayed by vertical pollutant profiles. Moreover, horizontal ground data are insufficient to provide a complete understanding of the photochemistry and the transport mechanism and, therefore, air pollution control decisions or models developed exclusively by using ground-based data may prove inadequate. These data also show that a true measure of the physical and chemical interactions occurring within the atmosphere will depend heavily on airborne measurements.

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TABLE I

Performance characteristics for the Cessna 401-A

Gross weight	6400 lbs
Pay load with full fuel	1000 lbs
Cruise speed	240 mph
Sampling speed range	120-200 mph
Minimum speed	110 mph
Maximum rate of climb	1600 fpm
Range	1100 miles
Service ceiling	26,000 ft

TABLE II
Survey of the Los Angeles Air Basin^a

Location	Temp (°F)	Altitude MSL (ft)	Ozone (ppm)	Oxidant (ppm)	Acetylene (ppb)	n-butane (ppb)	n-pentane (ppb)
Ocean, 18 miles west of L.A.	76.0	1000	0.01	0.02	0.8	1.1	0.6
Santa Monica	75.5	1100	0.05	0.02	1.2	1.4	0.8
N. Los Angeles	76.0	2000	0.04	0.02	3.1	7.9	3.0
Alhambra	71.5	5500	0.02	0.02	0.8	0.6	0.5
El Monte	72.0	3900	0.05	0.03	0.8	0.6	0.5
El Monte	75.5	450	0.00	0.00	19.0	18.2	8.7
Pomona	69.9	6800	0.04	0.04	1.1	1.0	0.5
Rialto	75.0	1400	0.00	0.00	9.3	10.9	5.5
San Bernardino	73.0	4000	0.04	0.05	5.2	6.4	2.9
Banning	70.0	4850	0.04	0.05	1.0	0.8	0.6
Banning	68.5	6500	0.06	0.05	2.6	2.1	0.9

^aFlight occurred 12 August 1971 from 4:30 to 8:30 PM, PST. The measurements over Banning were recorded at 8:10 PM, PST, at dusk when the photochemical potential for the generation of ozone was low compared to midday flights.

TABLE III

Ozone-oxidant survey over the Long Beach Power Plant Complex

Location	Altitude MSL (ft.)	O ₃ (ppm)	Oxidant (ppm)	Calculated NO ₂ (ppm)
Seal Beach	2600	.04	.05	--
Belmont Shores	2400	.08	.09	--
Long Beach State University	1600	.13	.13	--
Power Plant Complex	500	.15	.21	.30
Long Beach Airport	700	.15	.21	.36
Douglas Plant	1000	.19	.24	.30
Signal Hill	1300	.21	.70	1.51
Long Beach	1800	.19	.24	.42
Inner Harbor	2200	.06	.08	--
Outer Harbor	2600	.03	.28	1.21

TABLE IV

Ozone-nitrogen oxides survey over the Long Beach Power Plant Complex

Location	Altitude MSL (ft)	O ₃ (ppm)	NO _x (ppm)
<u>Pass No. 1</u>			
Sunset Beach	2400	.05	.30
Seal Beach	1500	.04	.21
Belmont Shores	1200	.03	.36
Long Beach State University	800	.01	.38
Airport	500	.002	.90 and rising
Long Beach	1900	.01	.06
Long Beach Harbor	2700	.04	.02
<u>Pass No. 2</u>			
Belmont Shores	1500	.03	.21
Long Beach State University	1200	.02	.60
Airport	800	.02	1.20
<u>Pass No. 3</u>			
Belmont Shores	1500	.04	.21
Long Beach State University	1400	.04	.30
Airport	500	.01	1.8

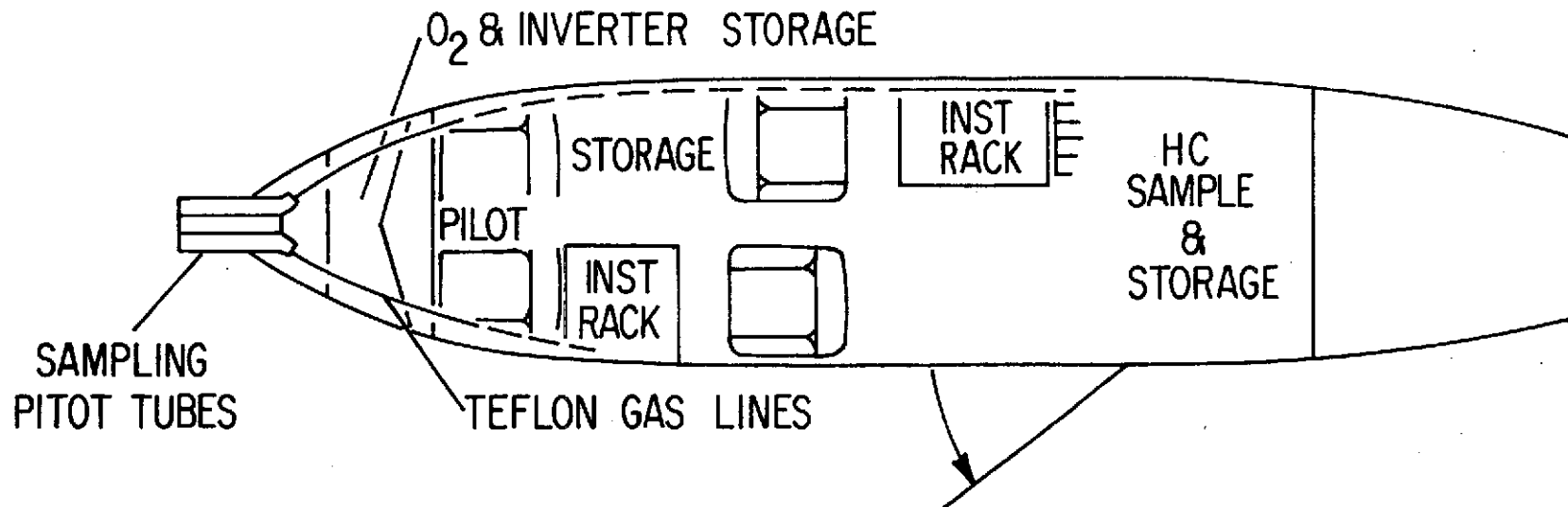


Figure 1. Cessna 401-A, twin-engine aircraft modified for air pollution sampling

CESSNA 401-A CONFIGURATION

FALL 1971 FLIGHTS

EQUIPMENT WEIGHT - 440 lbs
 GROSS WEIGHT - 6400 lbs



INSTRUMENTATION: CO	TEMPERATURE	HYDROCARBON SAMPLES
NO _x	DEW POINT	NEPHELOMETER
O ₃		RECORDERS

Figure 2. General arrangement of modifications and instrumentation installed on Cessna 401-A

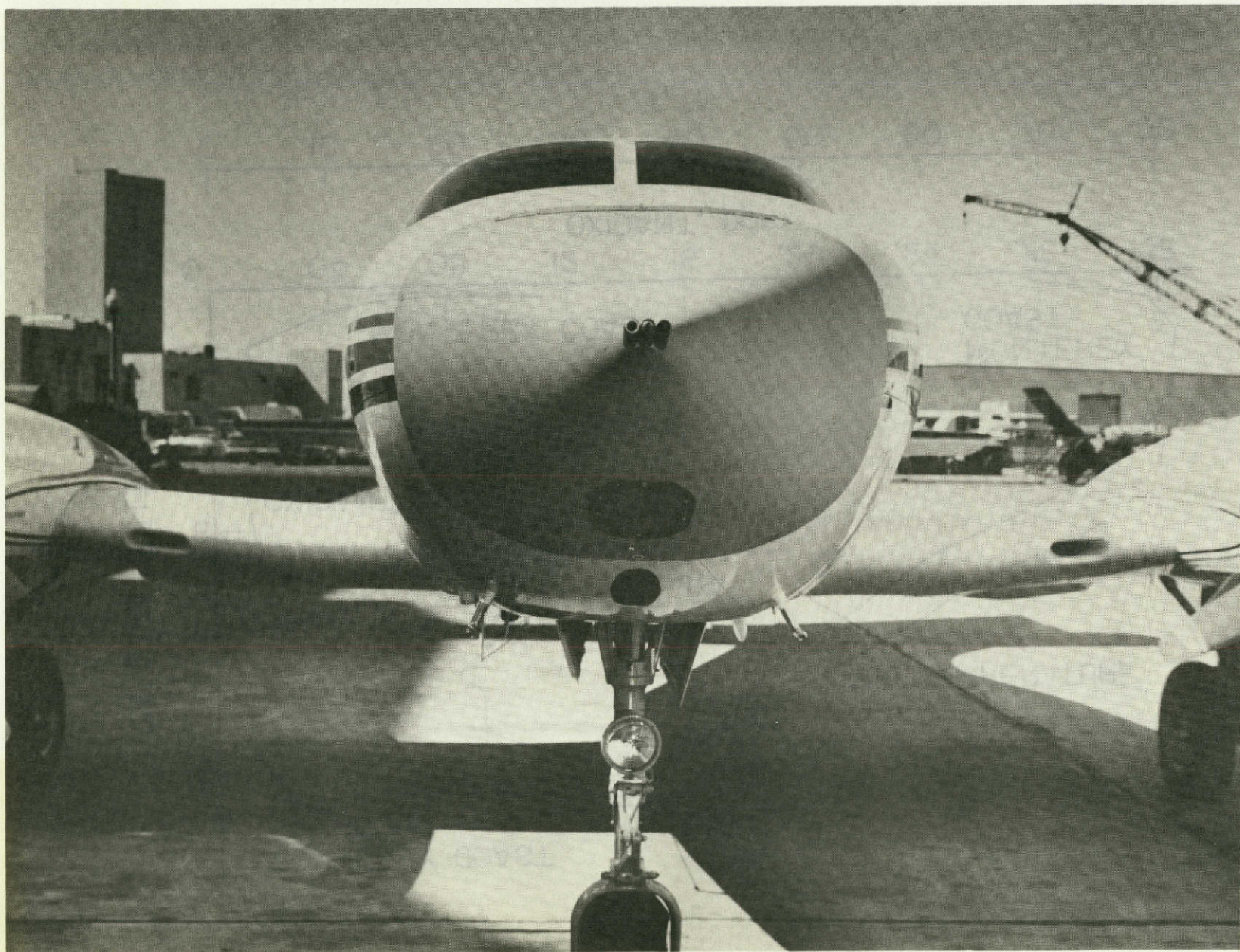


Figure 3. Detailed close-up of sampling Pitot tubes installed on Cessna 401-A

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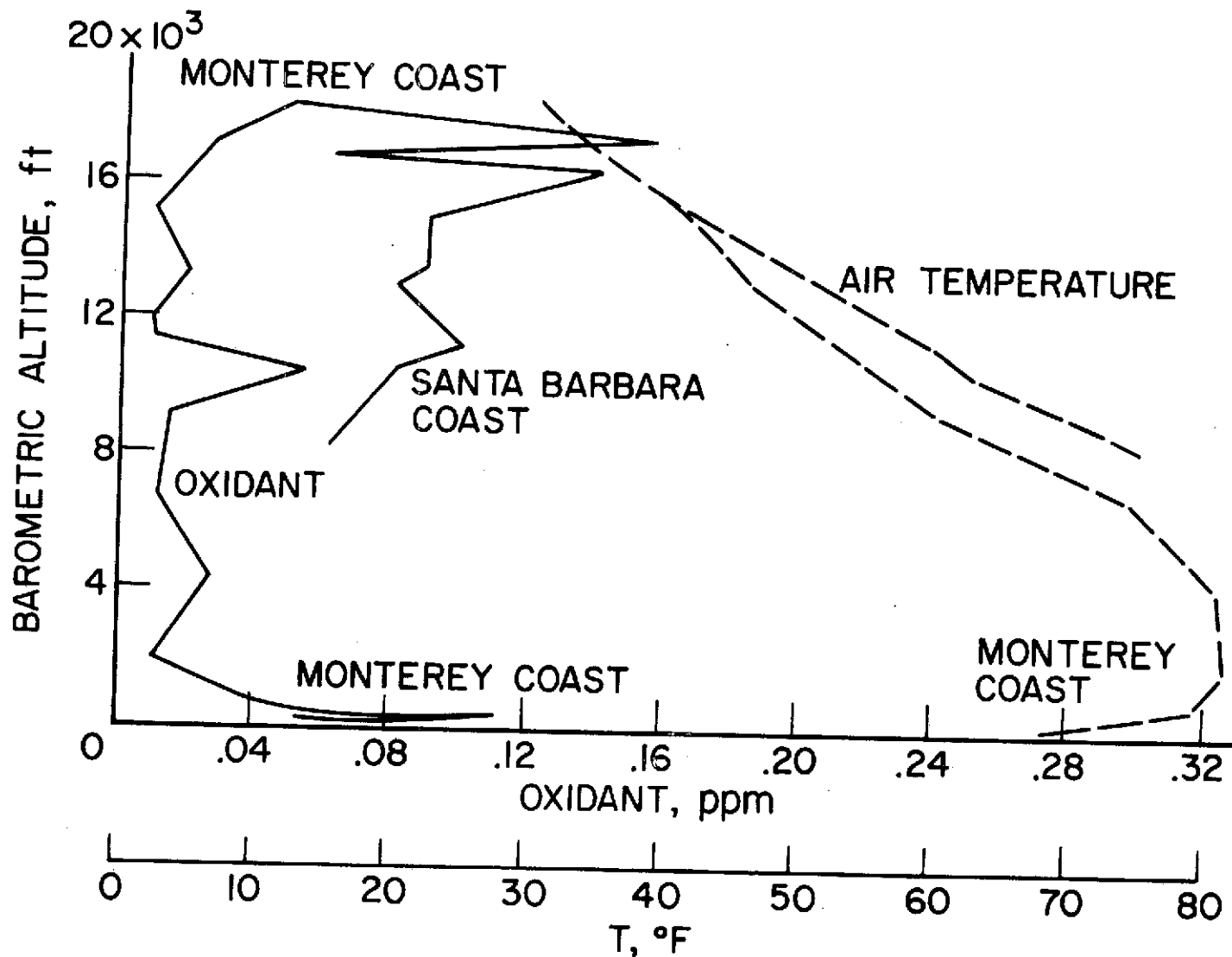


Figure 4. Ocean Background Oxidant Survey, September 11, 1971. (This flight started at the Santa Barbara, California coastal area, paralleled the California coastline at a distance of 200 NM, and was completed at Monterey, California.)

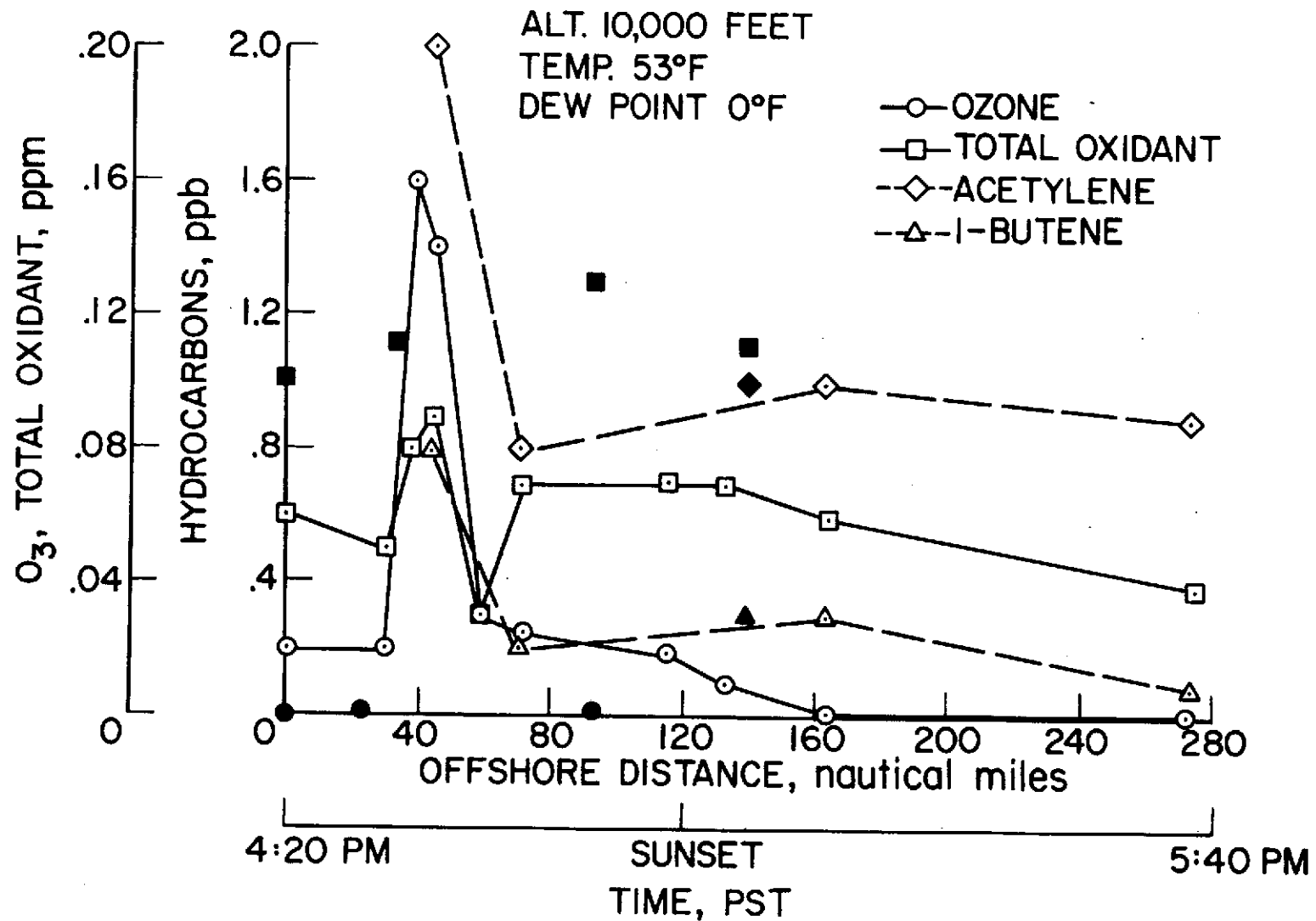


Figure 5. Los Angeles Offshore Survey, November 3, 1971. The open points indicate data collected during the flight from the coastline, while the filled data points indicate data collected on the return flight.

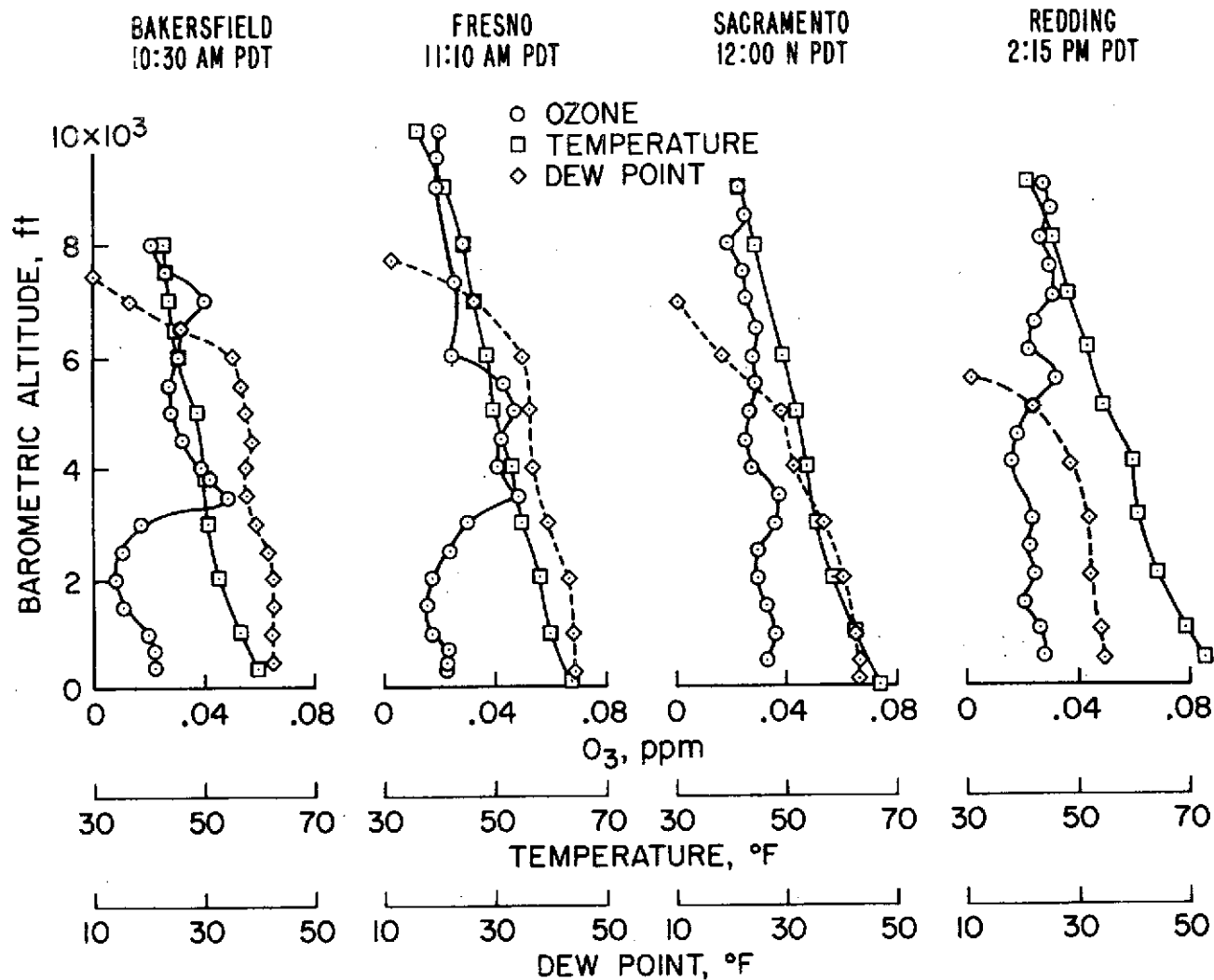


Figure 6. Ozone, Temperature and Dew Point Profiles in the San Joaquin Valley, May 9, 1972

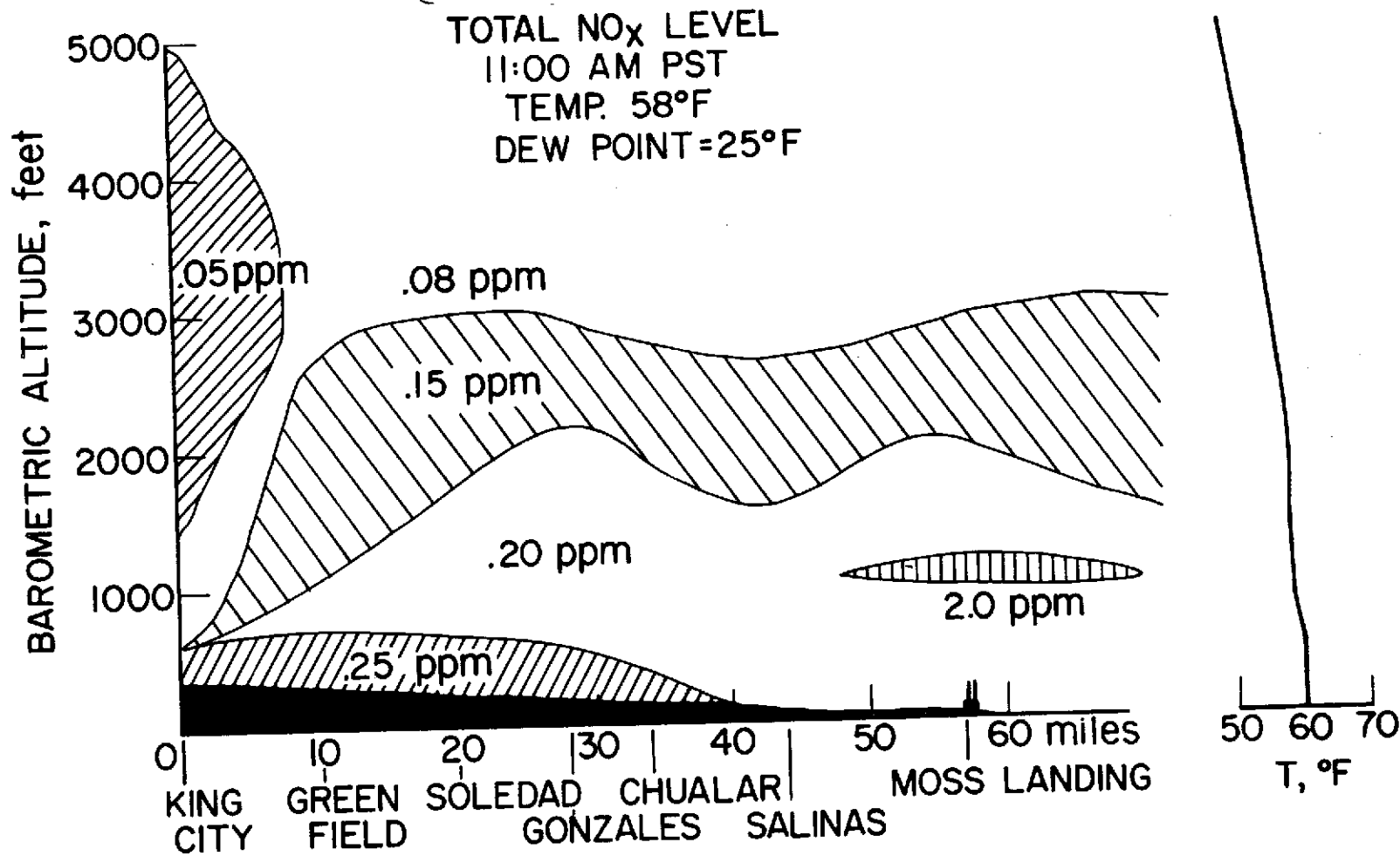


Figure 7. Salinas Valley NO_x Survey, November 19, 1971

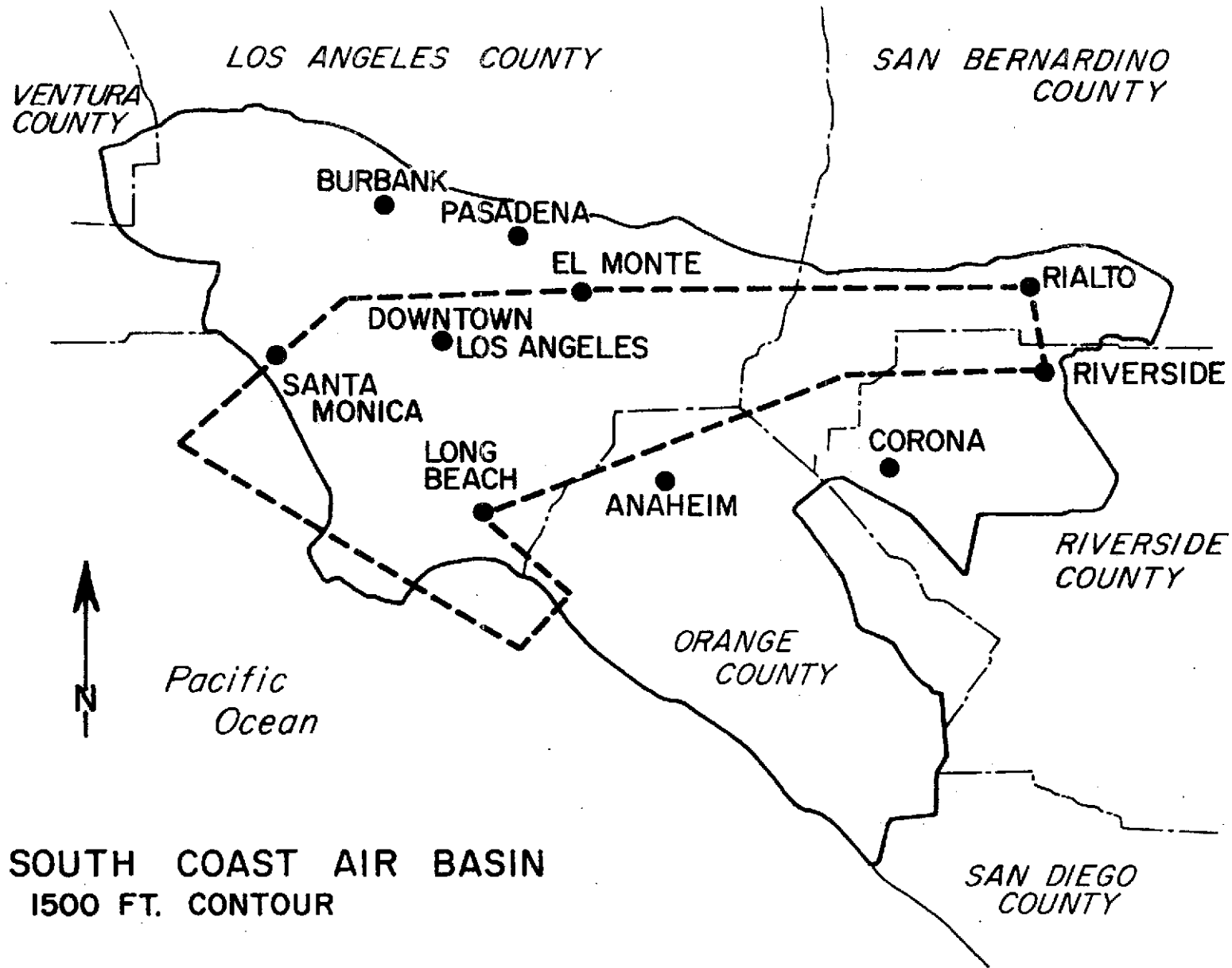


Figure 8. Outline Map of the Los Angeles Basin Area traversed during survey flights. General flight paths are indicated.

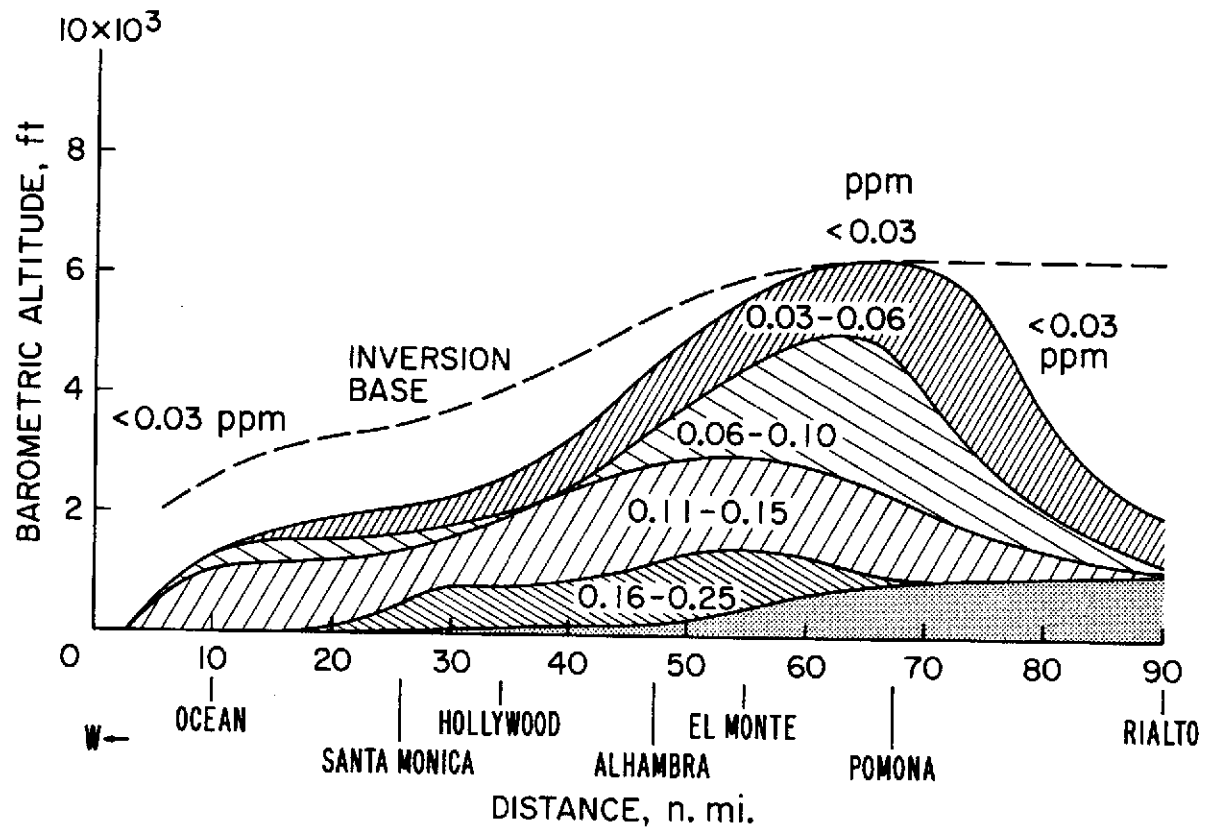


Figure 9. Ozone Isopleths (Vertical Cross Section) from South Coast Air Basin Survey, August 11, 1971

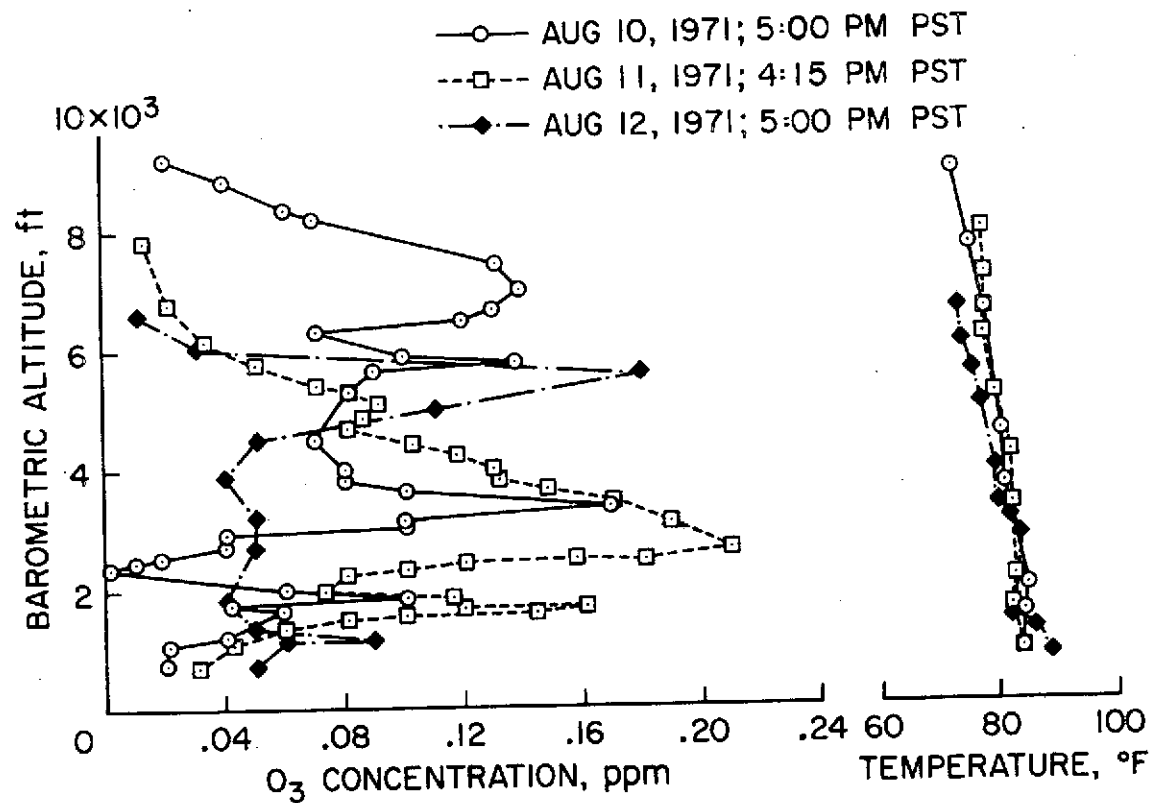


Figure 10. Ozone and Temperature Profiles, Riverside, California. August 10, 11, 12, 1971

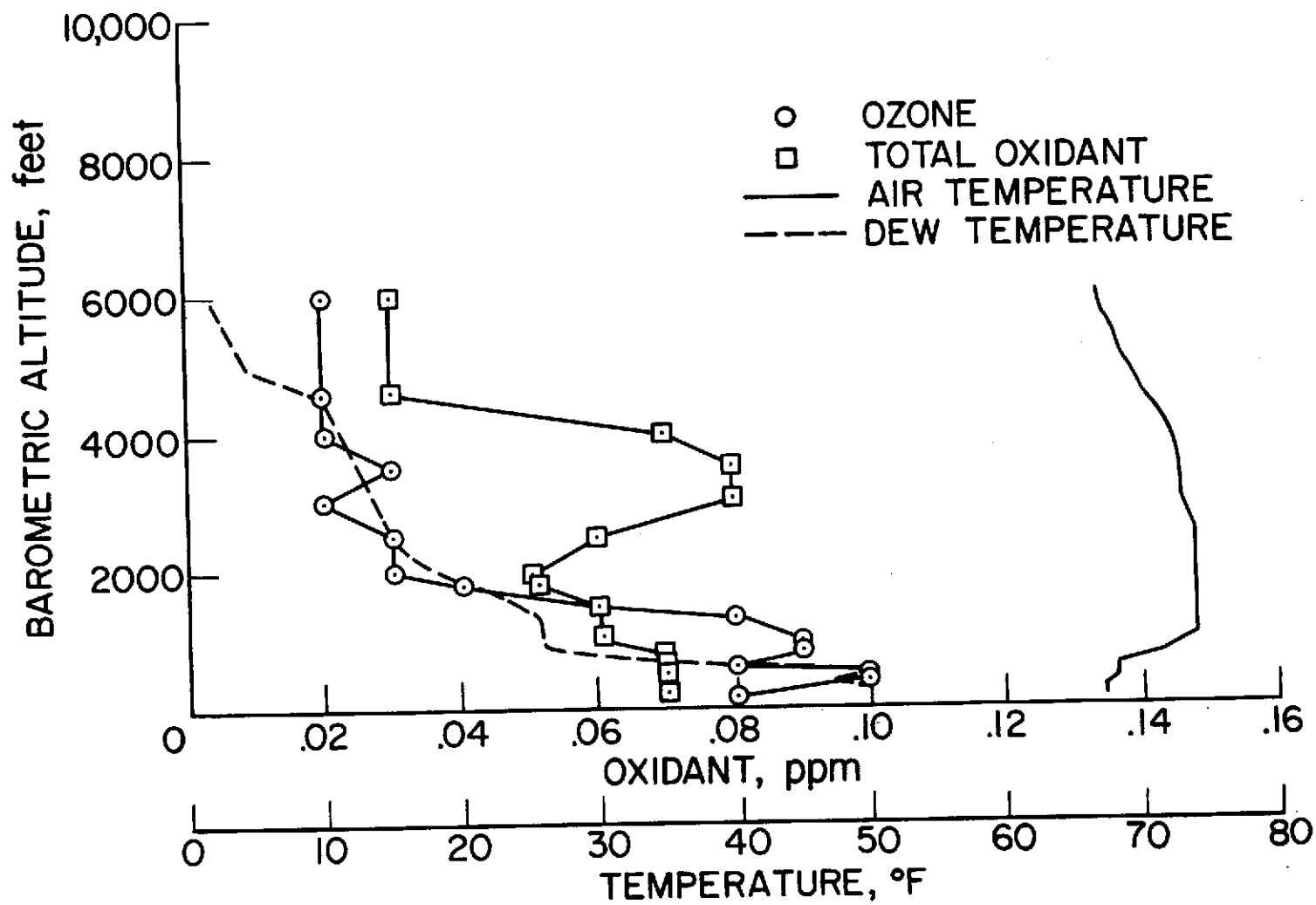


Figure 11. Catalina Island Channel Survey, November 4, 1971

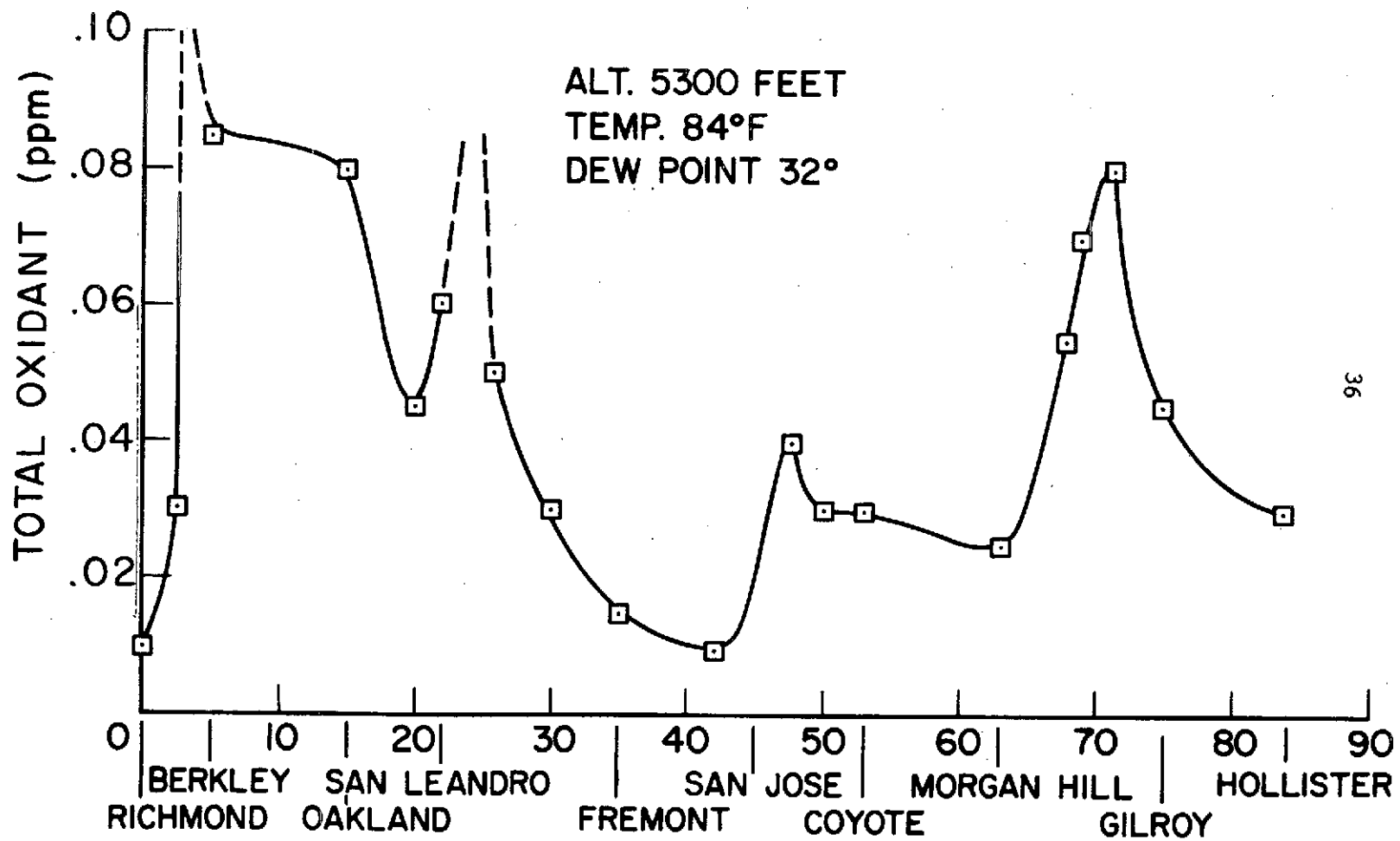


Figure 12. Total Oxidant Profile, East Bay--Santa Clara Valley, September 15, 1971

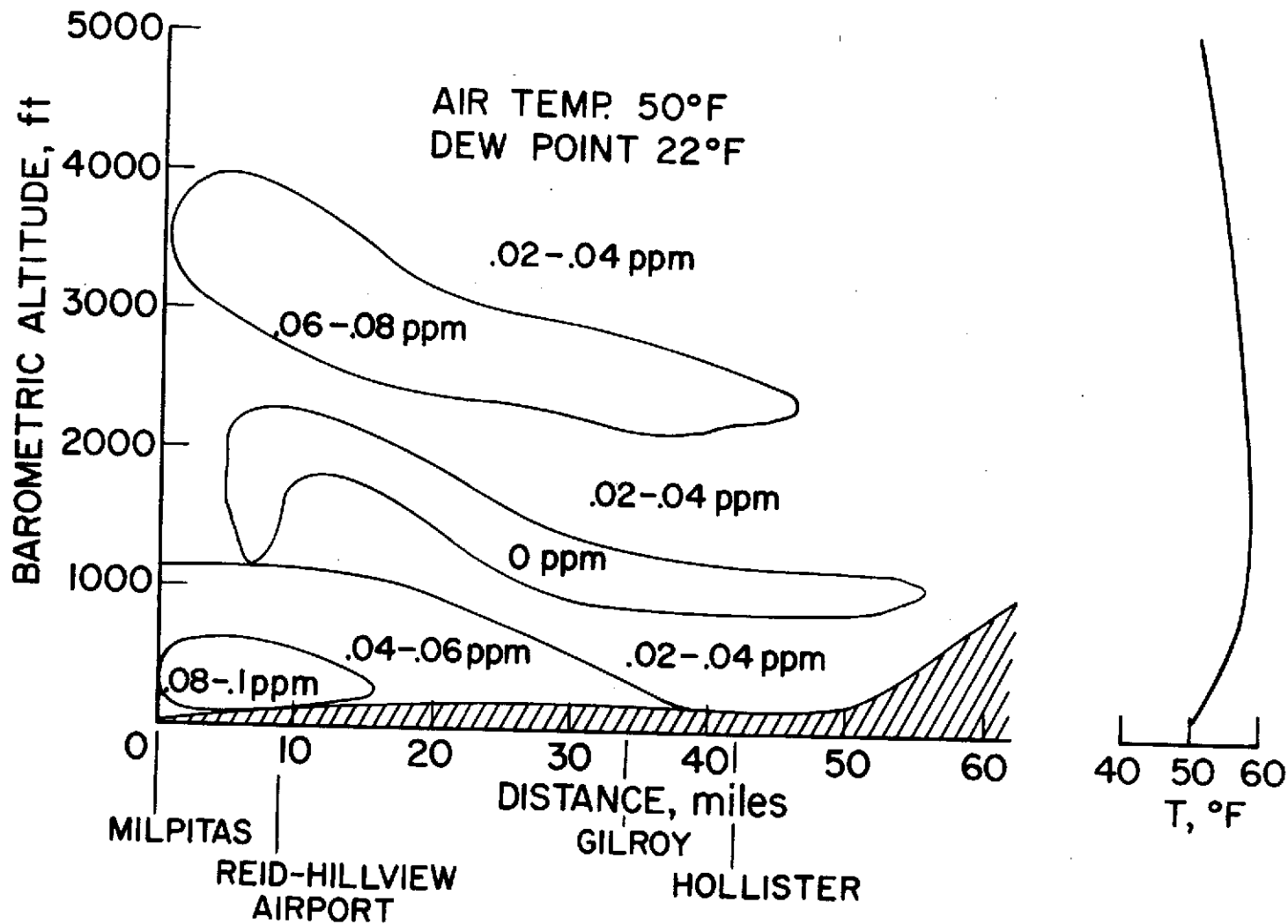


Figure 13. Ozone Isopleths, Southern Santa Clara Valley Survey, November 19, 1971