

# **AIR QUALITY IN SAN ANTONIO - 1999**

**Findings for the 1999 Ozone Season**

**from the**

**University of Texas**

## **FINAL REPORT**

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## SUMMARY

Air quality monitoring was performed by the University of Texas at a new site (Somerset) southwest of San Antonio, during the 1999 ozone season. Meteorological data, ozone concentrations, and concentrations of oxides of nitrogen were collected continuously throughout the period. Hydrocarbon sampling was done episodically.

Ozone concentrations at the Somerset site exceeded 100 ppb on three days in 1999. NO, NO<sub>2</sub>, and NO<sub>x</sub> levels measured at Somerset during 1999 were generally low. Average concentrations of NO<sub>2</sub> and NO<sub>x</sub> were typically 0-10 ppbv with occasional levels between 40 and 100 ppbv. NO levels were typically 0-5 ppbv occasionally reaching 10-20 ppbv. The highest concentrations of nitrogen oxides were observed when winds were out of the south to the west.

VOC concentrations were usually in the range of 50 to 400 ppbC, with average concentrations of approximately 140 ppbC. Compounds commonly detected at high concentrations included paraffins and biogenics. The bulk of the compounds detected were, in general, relatively unreactive.

For many of the days with high ozone concentrations, backward trajectories indicate that the air parcels traveled through the Corpus Christi area before entering the San Antonio region. The trajectories also indicate transport from other areas with moderate to high ozone levels such as East Texas, Dallas-Fort Worth, Houston-Beaumont, and various parts of Louisiana.

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## **I. INTRODUCTION**

Air quality in San Antonio is generally good, however, when temperatures are high, cloud cover is negligible, and winds are light or reverse directions, air pollutant levels can approach unhealthful levels. The air pollutant that approaches unhealthful levels over the widest area with the greatest frequency is ozone. Ozone (O<sub>3</sub>) formed in the lower atmosphere is a concern because it can damage the respiratory system. In addition, as a strong oxidant it can damage materials and harm crops. In order to preserve public health and welfare, the U.S. Environmental Protection Agency sets standards for the maximum allowable concentrations of air pollutants, such as ozone, in ambient air. From 1979 until 1997, the National Ambient Air Quality Standard (NAAQS) for ozone was 0.12 parts per million (ppm). If ozone concentrations, averaged over an hour, exceeded 0.12 ppm (or 125 parts per billion) more than three times over a three year period, then regulations designed to reduce ozone levels would be imposed.

In 1997, the U.S. Environmental Protection Agency developed a new National Ambient Air Quality Standard for ozone. The new NAAQS, which is currently under legal challenges, is based on 8-hour averages of ozone concentration. To determine whether a region attains the new standard, daily maxima of 8-hour averaged ozone concentrations are determined. The fourth highest daily maximum during each of three consecutive years is identified, and these values are averaged. This yields a rolling, three-year average of the 4<sup>th</sup> highest daily maximum. This value is compared to the standard of 0.08 ppm. If the rolling-three-year average is 0.085 ppm (85 ppbv) or higher, the standard is violated. Table I-1 reports the fourth highest daily maximum ozone concentrations (8-hour average) and rolling three-year averages recorded in San Antonio since 1980.

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Table I-1. Fourth highest daily maximum ozone concentrations in San Antonio (8-hour average)

(calculation from TNRCC, 1999)

<i>Year</i>	<i>Fourth highest daily maximum ozone concentration (8 hr. Average) (ppb)</i>	<i>Rolling three year average (ppb)</i>
1980	93	87
1981	96	90
1982	91	93
1983	91	92
1984	89	90
1985	85	88
1986	87	87
1987	89	87
1988	88	88
1989	81	86
1990	90	86
1991	82	84
1992	78	83
1993	84	81
1994	92	85
1995	96	88
1996	82	88
1997	84	87
1998	90	85
1999	91	88

As shown in Table I-1, the ozone concentrations observed in 1999 put the TNRCC's San Antonio monitoring region in violation of the pending 8-hour ozone standard. Ozone data alone, however, do not provide much insight into the reasons for the high ozone concentrations observed in 1999. Understanding the reasons for the high ozone concentrations requires detailed data on emissions, meteorology and concentrations of ozone precursors. This report presents data on ozone and ozone precursor concentrations, collected by the Texas Natural Resource Conservation Commission and the University of Texas, at Calaveras Lake site and Somerset site, respectively, during the summer of 1999. Other reports prepared for the Alamo Area Council of Governments, by a variety of contractors and government agencies, provide data on emissions, meteorology and ozone reductions that can be expected from emission reductions. The data on ozone and ozone precursor concentrations presented in this report can be used to evaluate the performance of emission inventories and regional air quality models.

## **II. SCOPE AND OBJECTIVES**

The objective of this monitoring study was to determine concentrations of ozone, NO<sub>x</sub>, and of volatile organic compounds (VOCs) at the Somerset site, which was located southwest of San Antonio. The data will be compared to similar data collected at the CAMS 59 site at Calaveras Lake and can be used in evaluating the performance of emission inventories and photochemical grid modeling of the San Antonio region.

Data collection took place during the summer of 1999 at the University of Texas' Somerset site and at CAMS 59. The University of Texas was responsible for determining ambient concentrations of precursors to ozone formation, namely NO<sub>x</sub> and VOCs, as well as ambient ozone concentrations and meteorological data at the Somerset site. The TNRCC measured ozone and NO<sub>x</sub> concentrations and collected meteorological data at CAMS 59, and these data are also presented in this report.

### **III. SAMPLING LOCATION AND METHODS**

#### ***III.1 Sampling Location***

The Somerset sampling location selected for this study was chosen to complement existing air quality monitoring done by the TNRCC. The TNRCC installed San Antonio's Continuous Air Monitoring station (CAMS 59) at Calaveras Lake in 1998. The location of CAMS 59 is shown in Figures III-1 and III-2. The TNRCC reports the daily maximum concentrations from this CAM site to the U.S. Environmental Protection Agency (EPA). The EPA uses the data from this official site and three other official sites in and around San Antonio, shown in Figure III-2, to determine whether the San Antonio region is in attainment of the NAAQS for ozone. Since the function of the CAM sites is to determine the maximum ozone concentration for San Antonio, the locations for the monitors were chosen to be generally downwind of emissions sources, where the maximum ozone concentrations were anticipated to occur. The site at Somerset was chosen based on different reasoning. The Somerset site was selected to provide concentrations of ozone and ozone precursors entering the San Antonio region. CAMS 59 may play a similar role, but because CAMS 59 is located near a large point source of emissions of nitrogen oxides, there was some concern that CAMS 59 data might not represent true background levels. Thus, a major goal of this sampling program was to compare data collected at CAMS 59 and Somerset.

Monitoring at CAMS 59 was performed throughout the 1999 ozone season by the TNRCC. Since CAMS 59 is operated year round by the TNRCC, ozone, NO<sub>x</sub>, and meteorological data were continuously available. The data collection and archiving system at CAMS 59, known as LEADS (Lockheed Environmental Analysis and Display System) controls all routine measurement functions, including calibrations and the archived data become available at the TNRCC's web site. Hourly averages of ozone, NO, NO<sub>2</sub>, NO<sub>x</sub>, resultant wind speed, and wind direction were downloaded daily over the internet and were stored on a personal computer hard drive. The files were backed-up to disk once a week.

At the Somerset site, a sampling shed was equipped by the University of Texas with monitors for ozone and NO<sub>x</sub>. The location of the Somerset site is shown in Figure III-3. A tower was mounted next to the trailer. A Young meteorological instrument mounted on the top of the 3-meter tower provided continuous measurements of wind speed and

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wind direction. The raw voltage outputs from the meteorological instruments were fed into a Campbell 21X datalogger, which converted the wind speed and direction signals to miles per hour and degrees, respectively. The continuous data from the ozone, chemiluminescent NO<sub>x</sub>, and wind instrumentation were also stored in the Campbell datalogger and downloaded by telephone through a modem. The datalogger was programmed to record 5 minute and hourly averages of ozone, NO, NO<sub>2</sub>, NO<sub>x</sub>, mean wind speed, resultant wind speed, wind direction, and the standard deviation of the wind direction. Data files were downloaded daily and were stored on a personal computer hard drive. The files were backed-up to disk once a week. The sampling shed was air-conditioned to provide a stable environment for the instruments and the temperature in the trailer was controlled to 78° F.

Data collection at the Somerset site began on April 9, 1999 (when the site was made available) and ended on October 26, 1999. Meteorological data and ozone concentrations are collected at CAMS 59 throughout the calendar year.

Table III-1 presents a summary of the technologies that were used to make the measurements at both the CAMS 59 and Somerset sites (the University of Texas designs its samplers to the same standards used by the TNRCC at CAM sites). Sample periods for each measurement are also indicated in Table III-1. Quantitative objectives for data quality are listed in Table III-2.

Table III-1. DATA MEASUREMENT METHODS

<i>Compound</i>	<i>Method</i>	<i>Sampling Time</i>	<i>Frequency</i>
Hydrocarbons	Canister sampling and GC/FID or GC/MS analysis	1 hour	episodic
Ozone	UV Photometry	5 min	Continuous
Nitrogen oxide	Chemiluminescence	5 min	Continuous
Nitrogen dioxide	Chemiluminescence	5 min	Continuous
Total oxides of nitrogen	Chemiluminescence	5 min	Continuous
Wind direction	Vane	5 min	Continuous
Wind speed	cup anemometer	5 min	Continuous

Table III-2. DATA QUALITY OBJECTIVES

Measurement	Method Detection Limit	Accuracy	Precision
O <sub>3</sub>	1.0 ppbv	90 to 110 %	± 10%
NO and NO <sub>x</sub>	1.0 ppbv	80 to 120%	± 20%
Hydrocarbons	2.5 ppbc (1)	75 to 125%	± 25%
Wind Speed	1.0 m/s	± 1 m/s (2)	± 2 m/s (3)
Wind Direction	not applicable	± 10 °	± 20 °

(1) hydrocarbons with 9 or more carbons per molecule may not meet this criterion.

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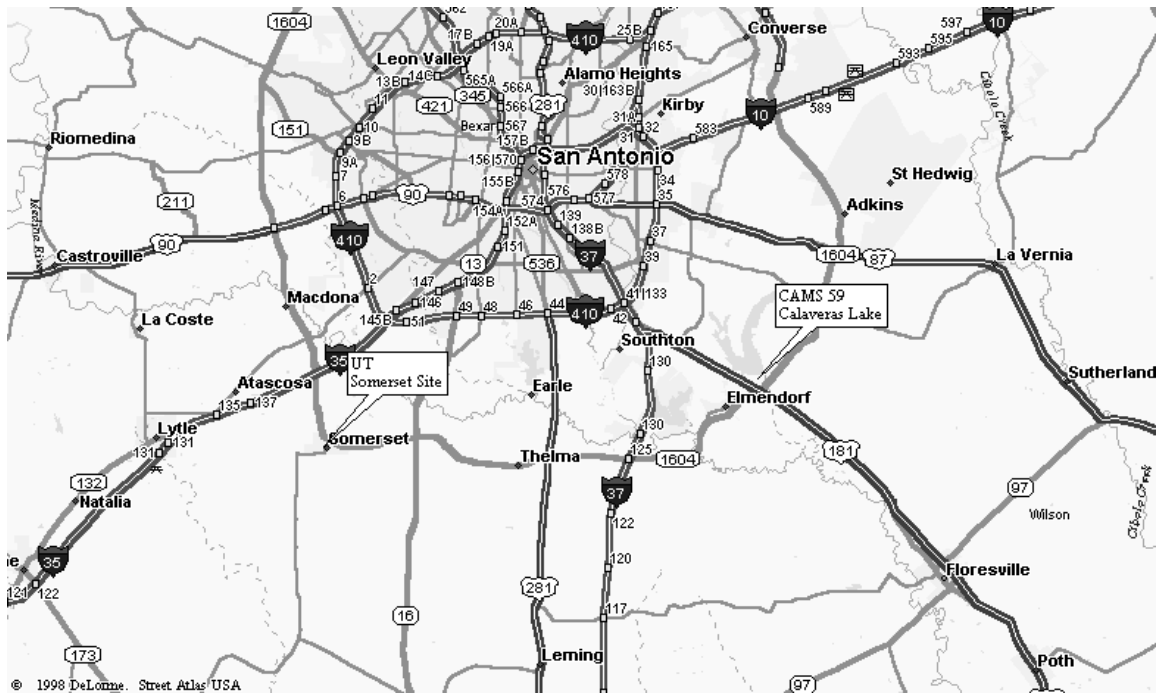


Figure III-1. Sampling locations in San Antonio.

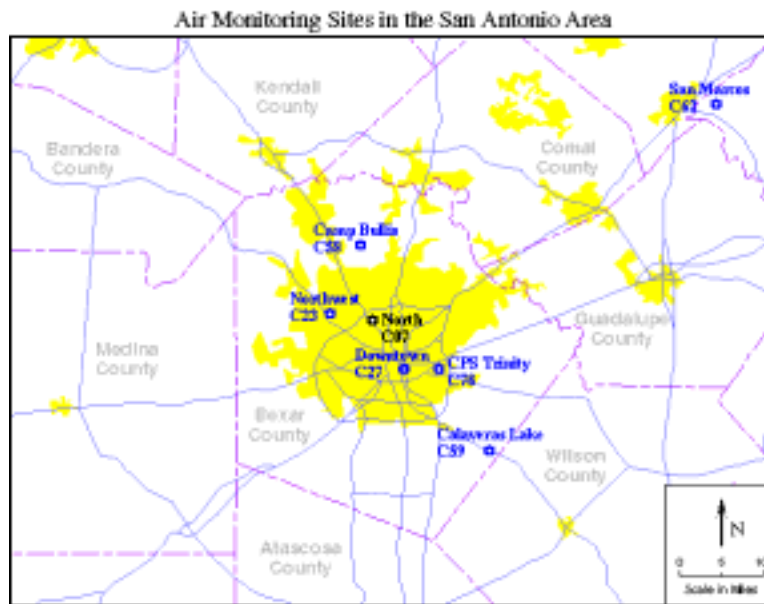


Figure III-2. TNRCC sampling locations in San Antonio.

## ***III.2 Sampling Methods***

### ***III.2.1 Ozone (O<sub>3</sub>) and Nitrogen Oxides (NO<sub>x</sub>) for Somerset Site***

O<sub>3</sub> measurements were made using a Dasibi ultraviolet absorption analyzer (Model 1008AH) operating in the range of 0 to 200 ppbv. Instruments had a minimum detectable sensitivity of 1 ppbv. All connections to the ozone photometric analyzer that contacted the ambient sample were constructed of teflon, glass, or other inert materials. The air sampling line was equipped with a 0.5 µm teflon filter placed near the instrument inlet.

Nitric oxide concentrations were measured by O<sub>3</sub> chemiluminescence. The Monitor Laboratories instrument (Model 9841A) operated within the dynamic range of 0 to 200 ppbv. Operation in this range allowed the instrument to achieve a detection limit of 1.0 ppbv. All connections to the instrument that contacted the ambient air sample or the quality control standards were constructed of teflon, glass, or other inert materials. The air sampling line was equipped with a 5.0 µm teflon filter placed near the instrument inlet.

All continuous gas monitoring equipment was calibrated at the beginning and end of the study period. In addition, calibration of a continuous gas monitor was performed after any equipment maintenance or repair that may have affected instrument response or if quality control standards were found to be outside the specific quality control limits. Prior to calibration, all in-service continuous gas monitors received an unadjusted or “as found” calibration to document instrument stability for the previous data. The calibration requires the analysis of four standard concentrations, not including zero, without adjustment of the instrument. Typical calibration curves are shown in Figures III-4 through III-6. All calibration gas standards were from a source of known and documentable concentration. Nitrogen oxide and nitrogen dioxide measurements were calibrated using an NO cylinder. NO calibration was done directly. NO<sub>2</sub> calibration was performed by titrating the NO with controlled amounts of ozone. Ozone used in the calibrations was from a Dasibi Model 5008 multi-gas calibrator. A minimum of five data points, including zero, spanning the working range of the instrument were used to conduct the calibrations. All calibrations were evaluated using a least squares fit.

### ***III.2.2 Ozone (O<sub>3</sub>) and Nitrogen Oxides (NO<sub>x</sub>) for TNRCC CAMS 59***

O<sub>3</sub> measurements were made by the TNRCC using an ultraviolet absorption analyzer operating in the range of 0 to 400 ppbv. Instruments had a minimum detectable

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sensitivity of 1 ppbv. All connections to the ozone photometric analyzer that contacted the ambient sample were constructed of teflon, glass, or other inert materials. The air sampling line was equipped with a 0.5  $\mu\text{m}$  teflon filter placed near the instrument inlet.

Nitric oxide concentrations were measured, by the TNRCC, using  $\text{O}_3$  chemiluminescence. The instrument operated within the dynamic range of 0 to 470 ppbv. Operation in this range allowed the instrument to achieve a detection limit of 1.0 ppbv. All connections to the instrument that contacted the ambient air sample or the quality control standards were constructed of teflon, glass, or other inert materials. The air sampling line was equipped with a 5.0  $\mu\text{m}$  teflon filter placed near the instrument inlet.

All continuous gas monitoring equipment was span checked twice a week throughout the study period. In addition, calibration of a continuous gas monitor was performed after any equipment maintenance or repair that may have affected instrument response or if quality control standards were found to be outside the specific quality control limits. The calibration requires the analysis of four standard concentrations, not including zero, without adjustment of the instrument.

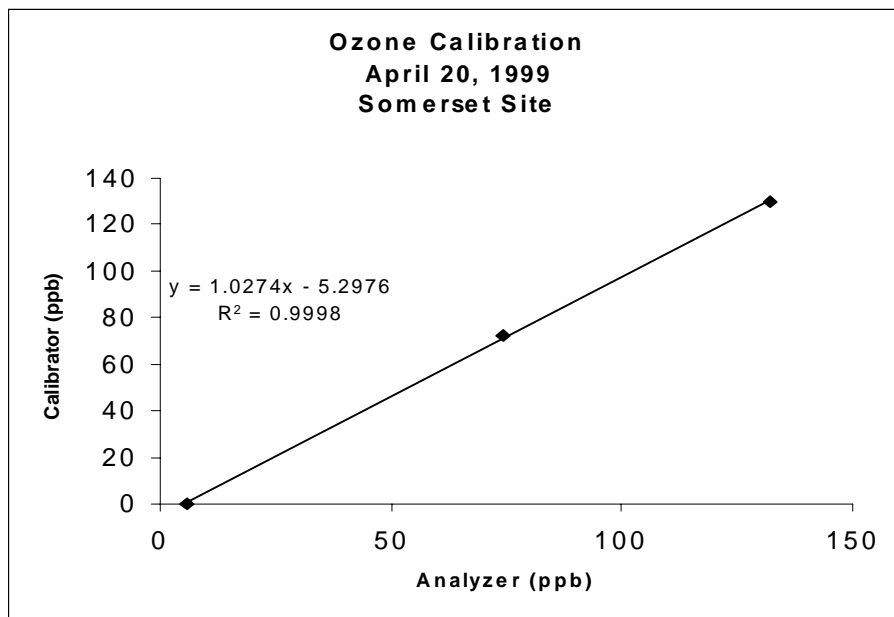


Figure III-3. Typical calibration curve for the ozone analyzer at Somerset.

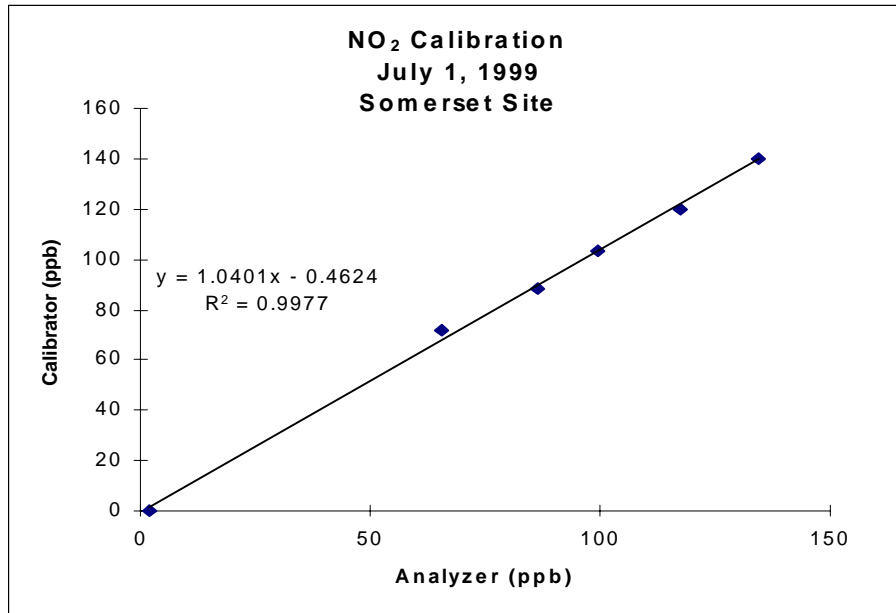


Figure III-4. Typical NO<sub>2</sub> calibration curve for the NO<sub>x</sub> analyzer at Somerset.

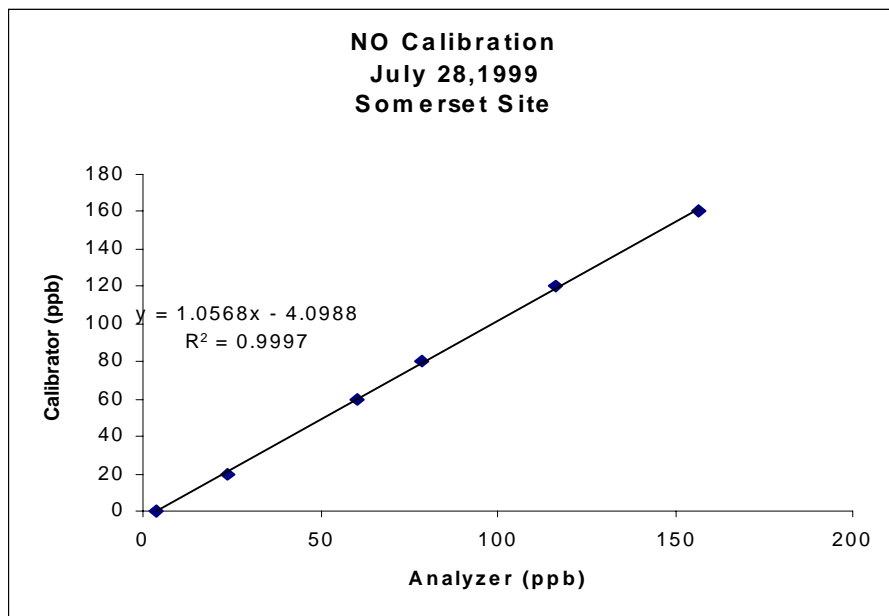


Figure III-5. Typical NO calibration curve for the NO<sub>x</sub> analyzer at Somerset.

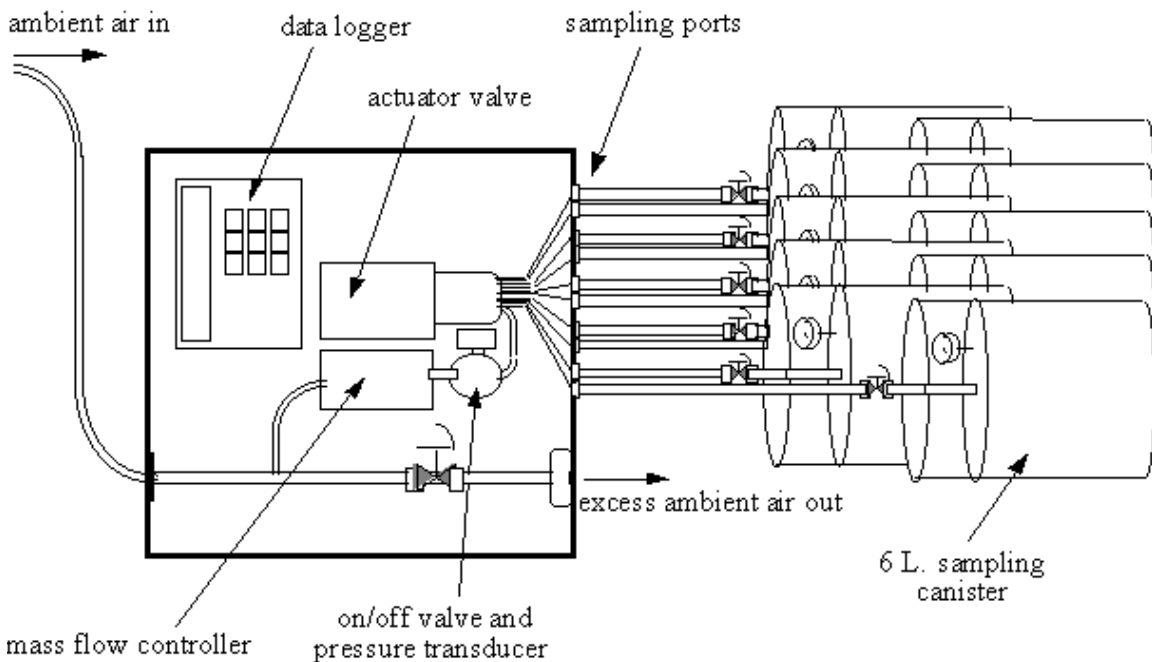
### III.2.3 Speciated Non-Methane Hydrocarbons

A Volatile Organic Compound (VOC) assembly was designed for the collection and analysis of the ambient air samples. The samples were collected using 6 liter Summa® passivated stainless steel canisters, purchased from Meriter. The Summa® technique involves the formation of a pure chrome-nickel oxide on the inside surface of the canister; Summa® passivated vessels have demonstrated effective and stable ambient air storage. The general procedures outlined in the “Determination of Volatile Organic Compounds in Ambient Air using Summa® Passivated Canister Sampling and Gas Chromatographic Analysis” were followed (USEPA, 1989). The assembly consisted of several sections: the autosampler, the doubler, the cryofocuser and GC/FID, and the canister cleaner.

#### Sampling

The hydrocarbon samples from Somerset were collected on an hourly basis by using an autosampler, which was designed by the TNRCC and built by the University of Texas. Hourly hydrocarbon samples were also taken using a critical orifice designed by Entech. Grab samples were collected by opening an evacuated canister. A schematic of an autosampler is presented in Figure III-6.

Figure III-6. Schematic of Autosampler with Canisters



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The autosampler had ten sampling ports; each port was used to collect a canister sample during a one-hour sampling time block. The autosampler could therefore collect up to ten hourly hydrocarbon samples in a single day, without an operator on-site. Prior to sampling, the canisters were evacuated to approximately 30 inches mercury gauge and connected to the autosampler device. The flow into the canisters occurred by virtue of the pressure difference between ambient conditions and the vacuum initially in the canisters. Ambient air was drawn through silica-lined tubing and the mass flow controlled auto-sampler. In the autosampler, the air was directed to one of the 10 canisters using a 10-way valve, and collected in the canister. For each sample, a mass flow controller was used to attain steady mass flow rates into the canister over an hour. The resultant sample represented a one-hour average of ambient air composition. The gauge pressure in the canisters, after sampling was complete, was approximately 5 to 0 inches mercury.

### *Doubler*

After sampling, the canisters were transported to the University of Texas Air Quality Laboratory and prepared for chemical analysis. To allow for optimum functioning of the downstream cryofocuser, the canister pressure had to be increased to above atmospheric pressure. This was done using a doubler, which was designed and built by the TNRCC to consistently and precisely double the pressure in the canisters. Nitrogen, purchased from Air Gas, was used as the diluent. Precision, accuracy and a clean diluent were all necessary features of the pressure increase, because the contents of the canisters were diluted during the doubling, and ambient VOC concentrations were a crucial measurement. A mass flow controller in the doubler was used to control the volume of nitrogen drawn into each canister. A pressure transducer in the doubler noted the precise pressure in the canister prior to and during the dilution. A datalogger controlled the total volume of nitrogen drawn into the canister, based on the pressure transducer readings. The gauge pressure in the canisters after doubling was close to 14.7 psig.

### *Cryofocusing and Data Collection*

After pressure doubling, the canisters were connected to the chemical analysis system. This instrument contained a cryofocuser, gas chromatograph and data acquisition system. An Entech 7000 preconcentrator drew a 400-milliliter sample of the canister volume, and mixed the sample with a 400-milliliter volume of an internal standard at 20 ppbv per standard. The internal standard was added to the sample to assist in the identification of

the unknown components present in the sample. The instrument then sequentially cooled the mixture to  $-185\text{ }^{\circ}\text{C}$ , drew off the overhead gases, and reheated the mixture. By repeating this sequence three times, the preconcentrator decreased the volume of the original 800-milliliter mixture to a volume on the order of a microliter, and increased the concentration of the VOCs in the sample by as many orders of magnitude; this is necessary for the detection system to be able to identify and quantify the components present in the sample.

The chemical analysis system was a Hewlett Packard 5890A gas chromatograph (GC) equipped with a flame ionization detector (FID) or a Hewlett Packard 6890 GC with a Hewlett Packard 5972 mass selective detector (MSD). The GC was fitted with a Hewlett Packard HP-1 column with a 100% dimethylpolysiloxane (gum) coating which enabled the column to effectively retain non-polar hydrocarbon species. The microliter volume of mixture from the cyrofocuser was then automatically desorbed onto the GC column and the GC oven followed a temperature ramping program, detailed in the Table III-3, which allowed for optimum separation of peaks while minimizing the total run time.

Table III-3. Temperature Program for GC/FID Analysis System

Initial temperature ( $^{\circ}\text{C}$ )	final temperature ( $^{\circ}\text{C}$ )	temperature ramp ( $^{\circ}\text{C}/\text{min}$ )	holding time at final temperature (min)
-10	-10	0	5
-10	0	5	0
0	120	10	2
120	160	4	6

This temperature schedule was determined by repetitively running a 51-component hydrocarbon mixture on the chemical analysis system, while changing initial and final temperatures, ramping rates and holding times. This 51-compound calibration mixture will be described in the calibration discussion.

As the GC oven followed its temperature ramping schedule, a chromatogram of the sample was generated using the EZ-Chrom V4.0 software. A chromatogram for a single sample, taken in Somerset, typically had 20-30 peaks, which were over a threshold intensity. A typical chromatogram is shown in Figure III-7. These chromatograms were converted into estimates of VOC concentrations using the calibration methods outlined

below.

The GC system used for hydrocarbon analysis was calibrated using a single internal standard gas mixture obtained from Wilson Oxygen, and five standard gas mixtures (different dilutions of the standard gas mixture) obtained from the Texas Natural Resource Conservation Commission (TNRCC). The internal standard contained 20 ppbv each of 1,2-dichlorotetrafluoroethane (freon 114), 4-bromofluorobenzene, and a,a,a-trifluorotoluene in a balance of nitrogen; the three components appear at early, mid, and late points on the chromatograms, allowing for optimum identification of standard and unknown species for the duration of the chromatography run.

Each TNRCC standard contained 51 hydrocarbon species, which ranged in molecular weight from ethane to nonane. In the original mixture, each component was present at a known concentration. A complete listing of the hydrocarbons for which the GC was calibrated can be found in Table III-4, listed according to their elution order and peak number assignment. The breaks in the numbering scheme are due to species which were found in the ambient samples but were not in the 51-component standard.

Peaks in ambient air samples were identified using retention time ratios. The retention times of the internal standards were identified in each chromatogram based on the intensity of the signals for the standards. The retention times of other peaks were ratioed to the retention times of the internal standards and these ratios were compared to the retention time ratios for the compounds listed in Table III-4. Peak areas were then used to establish concentrations using calibration standards developed using the 51-compound mixture.

To develop the calibrations, five standard dilutions of the 51-component mixture were prepared in the TNRCC laboratory using a zero-air system. The zero-air system generated contaminant free air by drawing ambient air through a particulate filter, a charcoal filter to remove moisture, and an activated carbon canister to remove ozone, nitrogen oxides and hydrocarbons. The five standard dilutions of the 51-component standard are listed in Table III-5.

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Table III-4. Hydrocarbon species in the calibration mixture for the GC/FID analysis system

Peak ID	Compound	Peak ID	Compound
4	Propylene	79	Isopropylbenzene
5	Propane	81	Benzaldehyde/alpha-pinene
7	Isobutane	83	n-propylbenzene
11	1-butene	85	1,3,5-trimethylbenzene
12	n-butane	88	beta-pinene
13	trans-2-butene	89	1,2,4-trimethylbenzene
16	cis-2-butene		
21	Isopentane		
23	1-pentene		
24	n-pentane		
25	Isoprene		
26	trans-2-pentene		
27	cis-2-pentene		
28	2-methyl-2-butene		
30	2,2-dimethylbutane		
31	Cyclopentene		
33	4-methyl-1-pentene		
34	cyclopentane/1,1-dichloroethane		
37	2-methylpentane/MTBE		
41	3-methylpentane		
43	2-methyl-1-pentene		
44	n-hexane		
45	Trans-2-hexene/chloroform		
46	cis-2-hexene		
47	Methylcyclopentane/1,2-dichloroethane		
49	2,4-dimethylpentane		
52	benzene		
54	cyclohexane		
55	2-methylhexane		
56	2,3-dimethylpentane		
57	3-methylhexane		
58	2,2,4-trimethylpentane		
60	n-heptane		
63	methylcyclohexane		
65	2,3,4-trimethylpentane		
66	Toluene		
67	2-methylheptane		
68	3-methylheptane		
69c	butyl acetate		
70	n-octane		
71	Ethylbenzene		
72	p-xylene & m-xylene		
75	Styrene		
76	o-xylene		
77	n-nonane		

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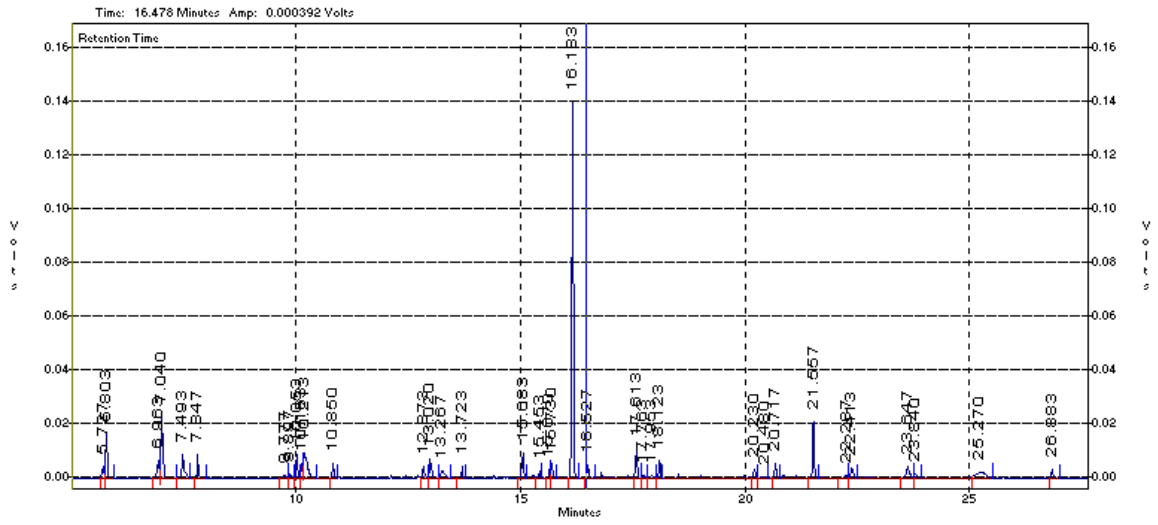


Figure III-7. Typical chromatogram of ambient air sample

Table III-5. Concentration of Individual Hydrocarbons in Calibration Standards

Standard	Average concentration of each component
1 <sup>a</sup>	5 ppbv
2	10 ppbv
3	20 ppbv
4	30 ppbv
5	40 ppbv

<sup>a</sup> Standard 1 was used to calculate method detection limits.

Instrument response was correlated with concentration for each hydrocarbon species in the standard. Linear or polynomial fits to the calibration were determined for each hydrocarbon species and a correlation coefficient greater than .99 for the calibration was considered acceptable.

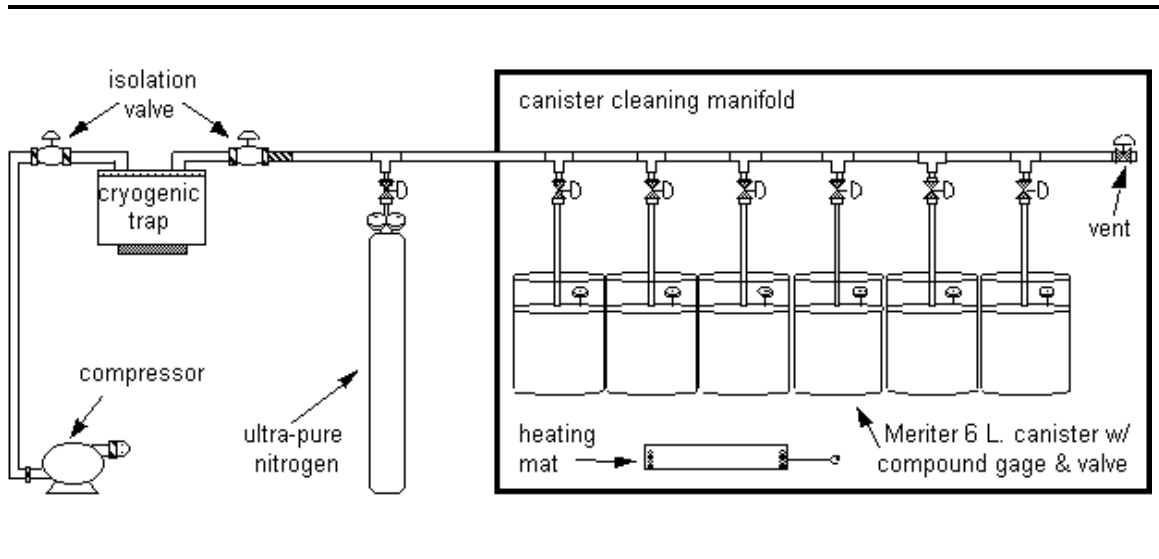
While the calibration equations are written in parts per billion by volume, concentrations in this report will frequently be expressed as parts per billion carbon. These units reflect the moles of carbon per mole of air, rather than the molecules of hydrocarbon per mole of air. The ppbC units are preferred because the moles of carbon available for reaction is a better indicator of hydrocarbon reactivity than the number of molecules of hydrocarbon.

A data integrity check was performed on each chromatogram to confirm that equipment failures had not occurred during the concentration and GC run. The area counts and retention times of the internal standards were compared to those generated from a canister with only internal standard in it. By doing this, system failures could be identified and the associated data file tagged.

#### *Canister Cleaner*

Once the air in the canisters was analyzed for its hydrocarbon content, the canisters were cleaned. The efficiency of the cleaning procedure had to be high, considering that the ambient hydrocarbon concentrations were on the order of a part per billion by volume (ppbv). A TNRCC cleaning protocol was followed closely. A schematic of the cleaning apparatus is displayed in Figure III-8.

Figure III-8. Schematic of Canister Cleaning Apparatus



The apparatus could accommodate up to sixteen canisters; cleaning took approximately 3 hours to complete. Prior to cleaning, the canisters were emptied of their ambient sample contents and 100  $\mu$ L of distilled water was injected into each canister. Water is believed to improve the efficiency of the cleaning. The cleaning procedure consisted of four fill and purge cycles. The canisters were filled with nitrogen gas to 20 psi and heated for 5 minutes. After heating, the canisters were vented to atmospheric pressure and pumped down to 29.4 inches of Hg using a Varian SD200 vacuum pump for 20 minutes. The second cycle called for filling of the canisters to 30 psi followed by immediate venting of the canisters to 5 psi. In the third cycle, the canisters were filled to 30 psi, vented to 5 psi and then vacuumed to 29.4 inches of Hg for 20 minutes. The fourth cycle was a repeat of the third cycle. At the end of the last cycle, a canister was picked at random for a clean check on the GC/FID. A chain of custody form was attached to all of the sampling canisters. The chain of custody form accompanied the canisters from the air monitoring site through all preparatory procedures to analysis and cleaning. The chain of custody form included the site name, sample identification number, date and time of collection, and initials of the person responsible for the collection, delivery, analysis and cleaning. The completed forms are maintained in a study archive.

### ***III.3 Sampling Schedule***

The meteorological data, ozone and NO<sub>x</sub> concentrations were measured throughout the year for the TNRCC site. In this report, data analysis will focus on measurements made from April 1, 1999 to October 24, 1999, during the ozone season. Although data monitoring and collection was continuous, some data were lost due to routine calibrations and a few, limited data system problems. These limited data gaps are noted in the Appendix.

The air quality measurements for the Somerset site began as soon as the site was made available to the University of Texas (April 9). The site was shut down on October 26, 1999. Continuous monitoring for ozone, NO<sub>x</sub>, wind speed, and wind direction was performed at the Somerset site twenty-four hours a day, throughout the measurement period. Although data monitoring and collection was continuous, some data were lost due to routine calibrations and a few, limited data system problems. These limited data gaps are noted in the Appendix.

For the VOCs, intensive sampling was conducted on selected days. The goal of this sampling was to determine typical concentrations of VOCs at the Somerset site and the spatial variation in hydrocarbon concentrations throughout the region. Table III-6 lists the intensive sampling days.

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Table III-6 Sampling days for VOC analyses around the San Antonio area.

<i>Date (site)</i>	<i>Ozone Action Day</i>	<i>Sampling periods</i>
6/18/99 ( <i>Somerset</i> )	*	6-7am, 7-8am, 8-9am, 9-10am, 10-11am, 11-12n, 12-1pm, 1-2pm
6/30/99 ( <i>Somerset</i> )		6-7am, 7-8am, 8-9am, 9-10am, 10-11am, 11-12n, 12-1pm, 1-2pm
7/2/99 ( <i>Somerset</i> )		6-7am, 7-8am, 8-9am, 9-10am, 10-11am, 11-12n, 12-1pm, 1-2pm
7/14/99 ( <i>Somerset</i> )		6-7am, 9-10am, 10-11am, 12-1pm
7/16/99 ( <i>Somerset</i> )		6-7am, 7-8am, 8-9am, 9-10am, 10-11am, 11-12n, 12-1pm, 1-2pm
8/11/99 ( <i>Somerset</i> )		12-1pm
9/1/99 ( <i>Calaveras</i> )	*	2:30pm, 2:38pm, 2:45pm, 3:00pm, 3:08pm, 3:14pm, 3:22pm, 3:30pm, 3:39pm (grab samples)
9/3/99 ( <i>Calaveras</i> )		1:27pm, 1:35pm, 1:48pm, 1:57pm, 2:13pm, 2:43pm, 3:15pm, 3:28pm (grab samples)
9/4/99 ( <i>Institute of Texan Cultures</i> )		11:20am, 11:30am, 11:40am (grab samples)
9/7/99 ( <i>Calaveras</i> )		4:00pm, 4:02pm, 4:04pm (grab samples)
9/10/99 ( <i>Calaveras</i> )	*	2:07pm, 2:20pm, 2:45pm, 2:56pm, 3:05pm, 3:17pm, 3:20pm, 3:23pm (grab samples)
9/11/99 ( <i>Institute of Texan Cultures</i> )		10:35am, 10:45am, 10:55am, 11:05am (grab samples)
10/9/99 ( <i>Camp Bullis and Selma Water Tank</i> )		10:20am, 10:30am, 11:10am, 11:25am (grab samples)

## IV. RESULTS AND DISCUSSION

The results of the study are organized into sections on ozone concentrations and ozone precursor concentrations.

### *IV.1 Ozone Concentrations in San Antonio*

Daily maximum ozone concentrations observed at the Calaveras Lake CAMS 59 and Somerset sites are reported in Figures IV-1 and IV-2. The daily maxima generally ranged from 30 ppbv to 100 ppbv (1-hour average).

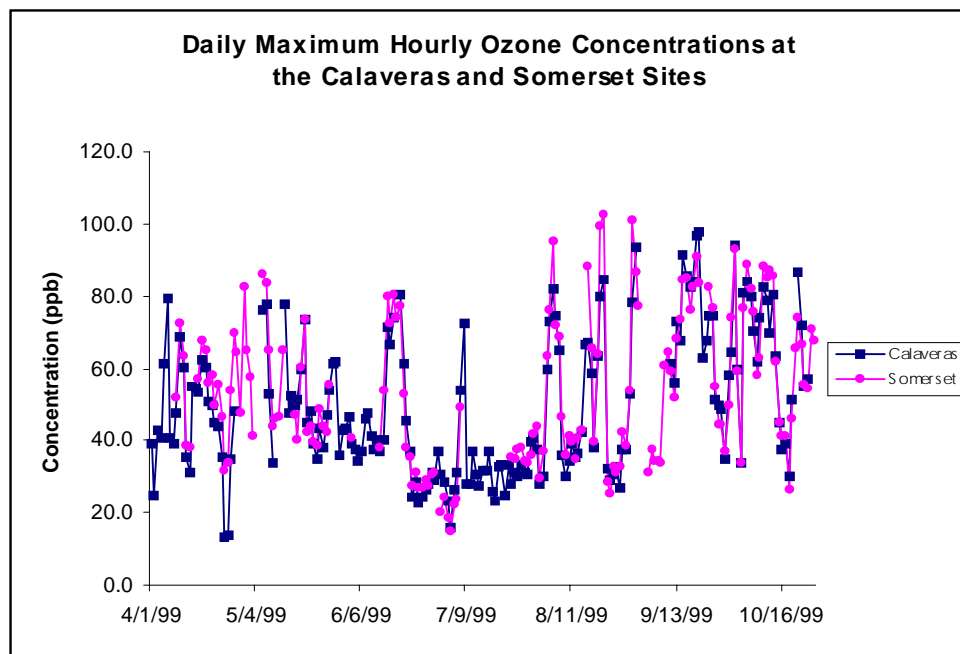


Figure IV-1. Daily maximum hourly ozone concentrations at the Calaveras and Somerset sites in San Antonio, 1999

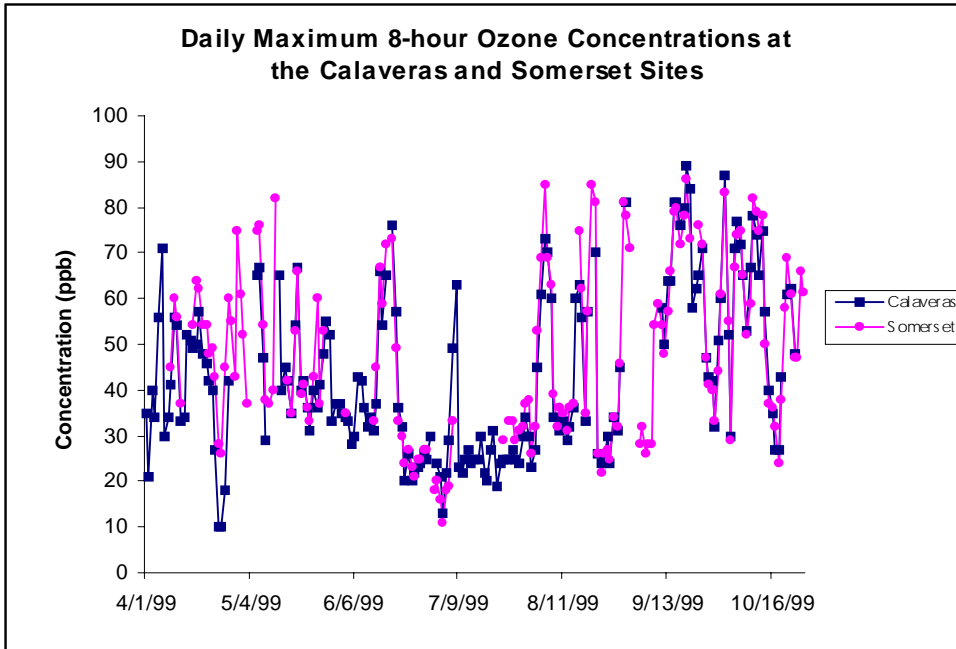


Figure IV-2. Daily maximum ozone concentrations (8-hour average) at the Calaveras and Somerset sites in San Antonio, 1999

The data in Figures IV-1 and IV-2 show that on most days, when ozone concentrations are moderate, the maximum ozone concentrations recorded at Calaveras and Somerset were quite similar. On a small number of days, however, particularly days with high ozone concentrations, there were significant differences between the maximum ozone concentrations recorded at Calaveras and Somerset.

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The data in Figures IV-3A and IV-3B show the dependence of ozone concentration at the Somerset and Calaveras sites, respectively, on wind direction. On each day during the ozone season, the wind direction at the time of maximum ozone concentration was assigned to one of 16 wind directions. The maximum ozone concentrations for all of the days during the sampling period were then averaged for each wind direction. This value is illustrated as the length of the bar for each wind direction. The data indicate that ozone concentrations were highest when winds were out of the north, southwest, and east for Somerset and out of the northwest for Calaveras.

Figures IV-4A and IV-4B show the frequency of wind directions observed during the summer of 1999. The data for Figures IV-4A and IV-4B are averaged over all days during the summer of 1999 (April – October 1999). Of particular interest, however, are the days when ozone concentrations were high. The wind directions and average ozone concentrations observed on the ten days with the highest observed ozone concentrations at the Somerset and Calaveras sites are shown in Figures IV-5A and IV-6A and Figures IV-5B and IV-6B, respectively. Figures IV-6A and IV-6B show a very different distribution of wind directions than Figures IV-4A and IV-4B. Although winds from the west, north, northeast, and east were rare during the ozone season, days with winds out of these directions account for over half of the high ozone days.

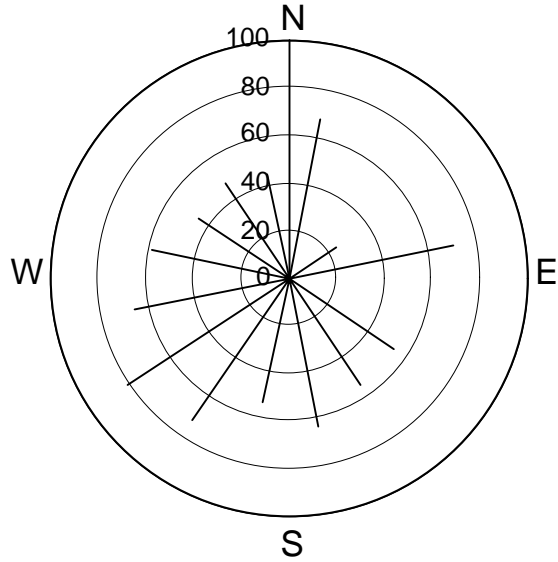
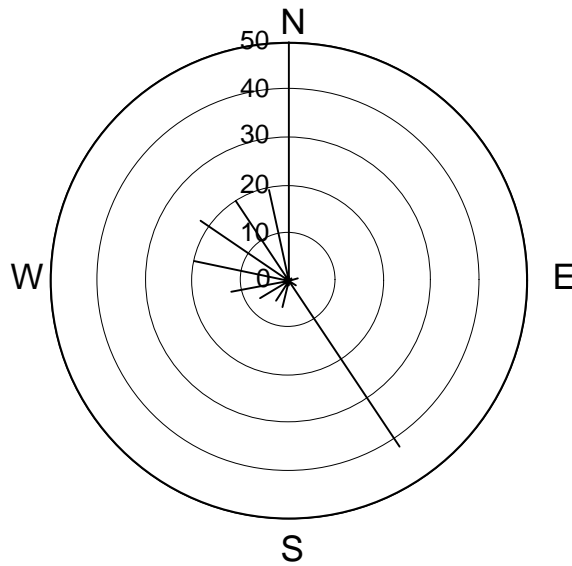


Figure IV-3A. Average daily maximum 1-hour ozone concentrations at Somerset as a function of wind direction; data are from April 9, 1999 through October 26, 1999. (The wind direction at the time of maximum ozone concentration was determined for all of the days during the sampling period. These daily maxima were then averaged for each wind direction. This value is illustrated as the length of the bar for each wind direction)

Figure IV-4A. Wind direction frequency distribution at the time of maximum ozone concentrations at Somerset. The data are reported as the number of days during which the winds originated from each of 16 directions. Data are for April 9, 1999 through October 26, 1999.





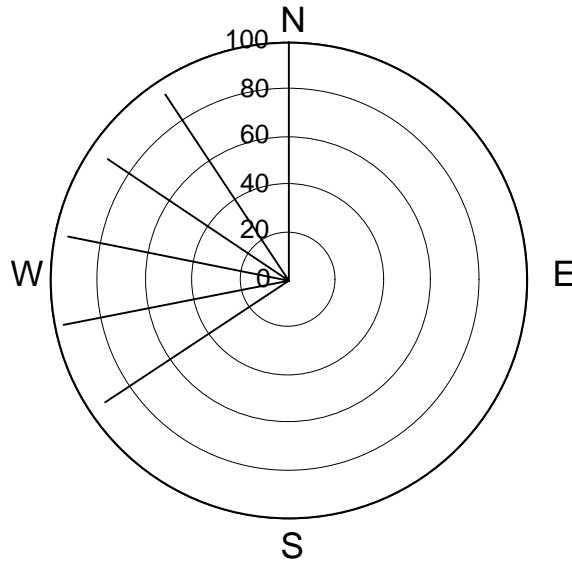


Figure IV-5A. Average daily maximum 1-hour ozone concentrations at Somerset as a function of wind direction; data are for the 10 days with the highest ozone concentrations 8/5/99 (4 pm), 8/16/99 (4 pm), 8/20/99 (4 pm), 8/21/99 (5 pm), 8/30/99 (5 pm), 9/19/99 (3 pm), 10/1/99 (3 pm), 10/5/99 (4 pm), 10/10/99 (6 pm), and 10/12/99 (4 pm); the wind direction at the time of maximum ozone concentration was determined for each of the days; these daily maxima were then averaged for each wind direction. This value is illustrated as the length of the bar for each wind direction)

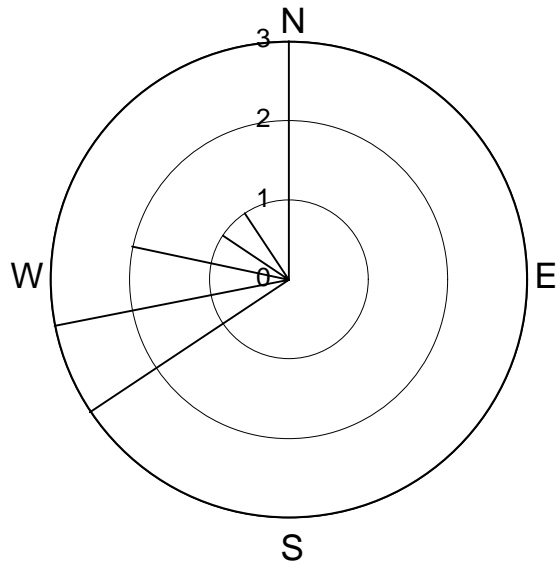


Figure IV-6A. Wind direction frequency distribution at the time of maximum ozone concentrations at Somerset. The data are reported as the number of days during which the winds originated from each of 16 directions. Data are for the 10 days with the highest ozone concentrations (8/5/99 (4 pm), 8/16/99 (4 pm), 8/20/99 (4 pm), 8/21/99 (5 pm), 8/30/99 (5 pm), 9/19/99 (3 pm), 10/1/99 (3 pm), 10/5/99 (4 pm), 10/10/99 (6 pm), and 10/12/99 (4 pm))

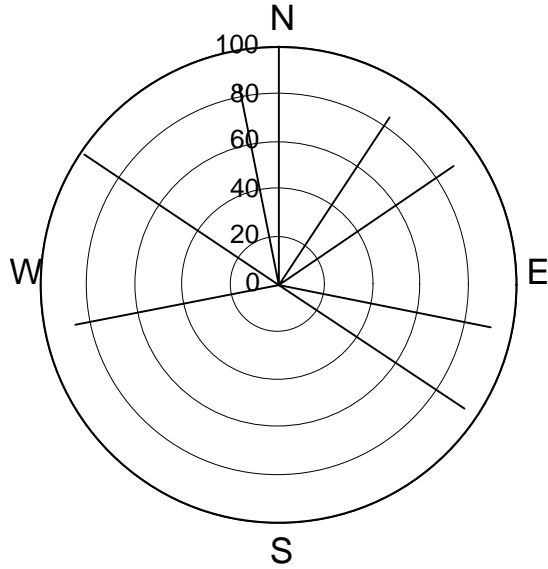


Figure IV-5B. Average daily maximum 1-hour ozone concentrations at Calaveras as a function of wind direction; data are for the 10 days with the highest ozone concentrations 8/21/99 (1 pm), 8/31/99 (1 pm), 9/15/99 (4 pm), 9/16/99 (3 pm), 9/18/99 (12 n), 9/19/99 (11 am), 9/20/99 (4 pm), 10/1/99 (2 pm), 10/5/99 (2 pm), and 10/21/99 (3 pm); the wind direction at the time of maximum ozone concentration was determined for each of the days; these daily maxima were then averaged for each wind direction. This value is illustrated as the length of the bar for each wind direction)

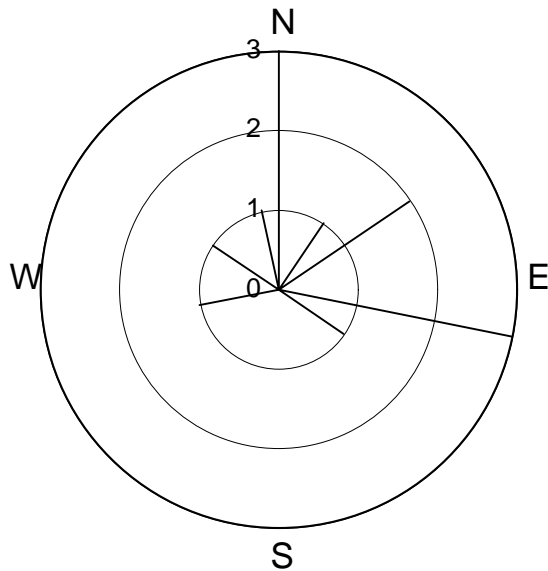


Figure IV-6B. Wind direction frequency distribution at the time of maximum ozone concentrations at Calaveras. The data are reported as the number of days during which the winds originated from each of 16 directions. Data are for the 10 days with the highest ozone concentrations (8/21/99 (1 pm), 8/31/99 (1 pm), 9/15/99 (4 pm), 9/16/99 (3 pm), 9/18/99 (12 n), 9/19/99 (11 am), 9/20/99 (4 pm), 10/1/99 (2 pm), 10/5/99 (2 pm), and 10/21/99 (3 pm))

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The ten days with the highest ozone concentrations measured at Calaveras in San Antonio are listed in Table IV-1. Five out of the ten peak ozone events at Calaveras occurred in the month of September.

Table IV-1. Days with high ozone concentrations, measured at Calaveras Lake

<i>Date</i>	<i>Peak Ozone (ppbv) at CAMS 59 Calaveras</i>	<i>Peak Ozone (ppbv) at CAMS 23 San Antonio Northwest</i>	<i>Peak Ozone (ppbv) at CAMS 58 Camp Bullis</i>	<i>Peak Ozone (ppbv) at Somerset Site</i>	<i>Wind direction at CAMS 59</i>
9/20/99	98	106	101	84	296
9/19/99	97	95	97	91	91
10/1/99	94	91	100	93	132
8/31/99	93	108	97	87	108
9/15/99	92	93	89	85	57
10/21/99	87	66	70	74	252
9/16/99	85	94	84	85	66
8/21/99	85	109	88	102	346
9/18/99	84	102	109	82	90
10/5/99	84	96	87	89	31

The ten days with the highest ozone concentrations measured at the Somerset site are listed in Table IV-2. Five out of the ten peak ozone events at Somerset occurred during the month of August.

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Table IV-2. Days with high ozone concentrations, measured at the Somerset site.

<i>Date</i>	<i>Peak Ozone (ppbv) at Somerset Site</i>	<i>Peak Ozone (ppbv) at CAMS 59 Calaveras</i>	<i>Peak Ozone (ppbv) at CAMS 23 San Antonio Northwest</i>	<i>Peak Ozone (ppbv) at CAMS 58 Camp Bullis</i>	<i>Wind Direction at Somerset</i>
8/21/99	102	85	109	88	252
8/30/99	101	78	101	83	245
8/20/99	100	80	92	74	281
8/5/99	95	82	120	96	252
10/1/99	93	94	91	100	333
9/19/99	91	97	95	97	311
10/5/99	89	84	96	87	270
8/16/99	88	67	109	100	249
10/10/99	88	82	79	77	237
10/12/99	87	70	76	72	230

Peak ozone concentrations in the San Antonio region are generally recorded at CAMS 23 and CAMS 58, which are generally downwind of the urban center. The daily maximum 1-hour ozone concentration exceeded 100 ppbv for a total of 8 days at CAMS 23 and 5 days at CAMS 58. The daily maximum 1-hour ozone concentration was between 90 and 99 ppbv for a total of 11 days at CAMS 23 and 7 days at CAMS 58. Of particular interest is the relationship between high ozone concentrations at CAMS 23 and CAMS 58 and ozone concentrations at Somerset. High ozone concentrations at Somerset correspond to high ozone concentrations at CAMS 23. In Figures IV-7 through IV-16, the hourly ozone concentrations at CAMS 23 and Somerset are shown for the days with the top ten one-hour ozone concentrations at CAMS 23.

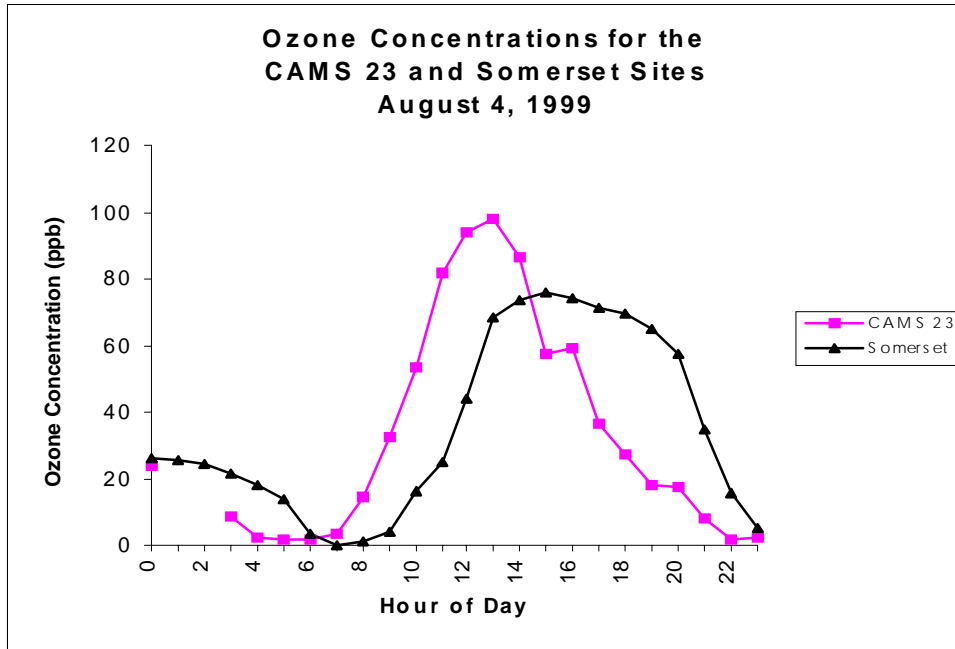


Figure IV-7. Ozone concentrations for the CAMS 23 and Somerset sites on August 4, 1999.

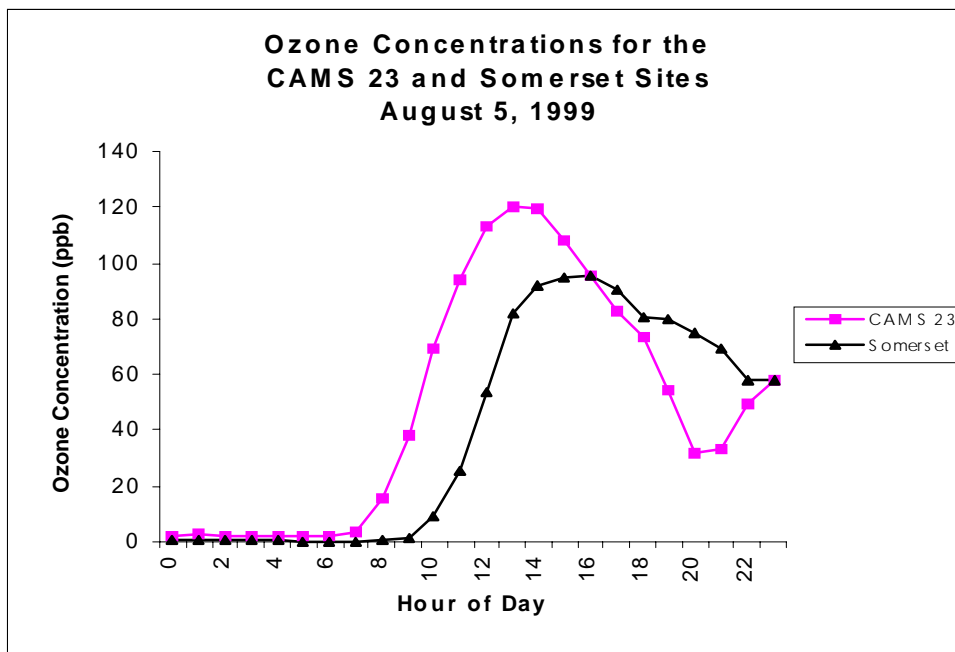


Figure IV-8. Ozone concentrations for the CAMS 23 and Somerset sites on August 5, 1999.

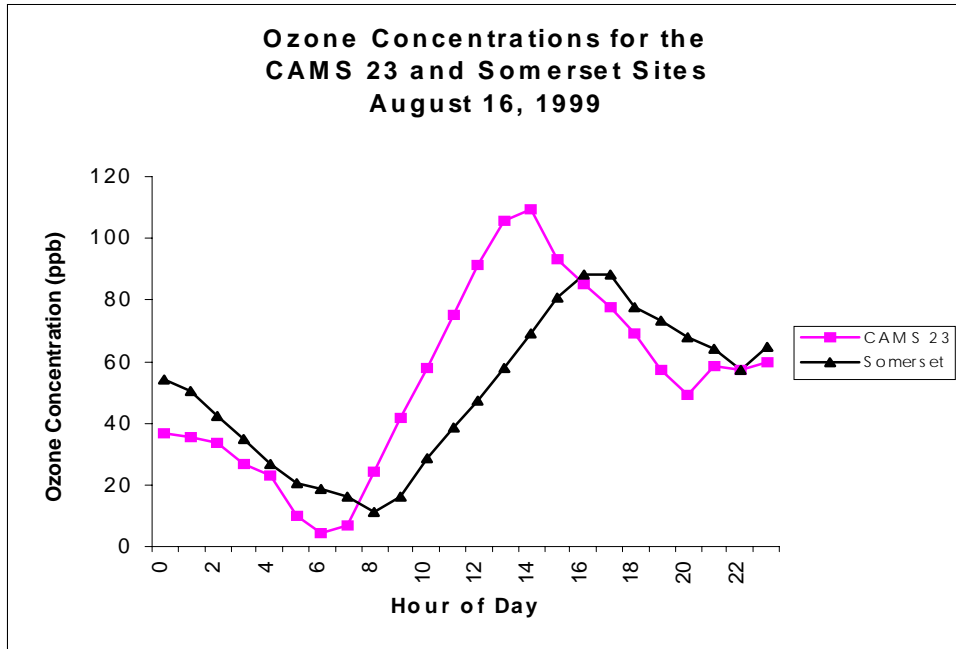


Figure IV-9. Ozone concentrations for the CAMS 23 and Somerset sites on August 16, 1999.

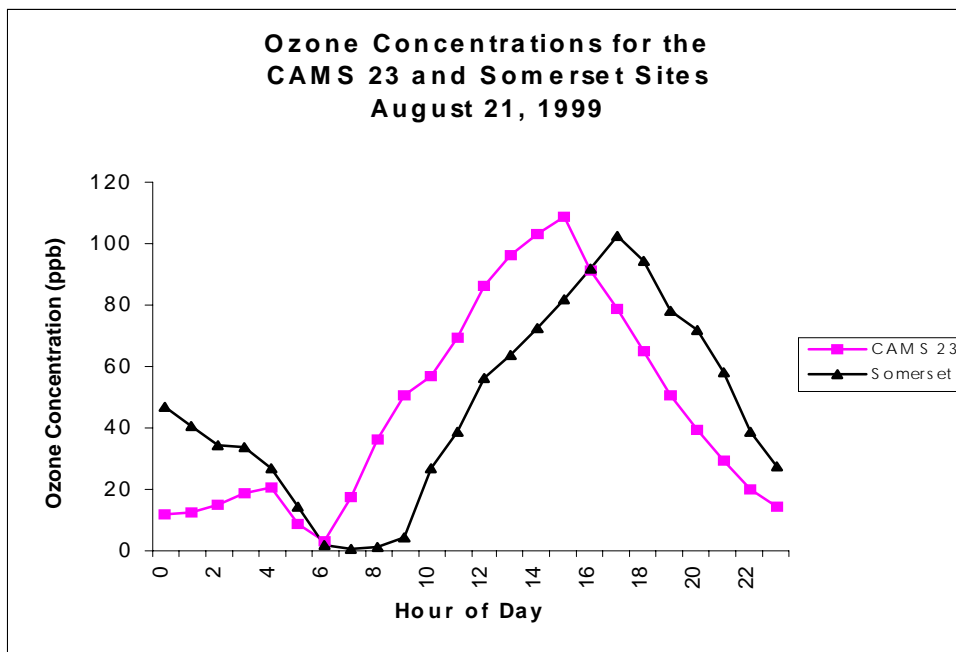


Figure IV-10. Ozone concentrations for the CAMS 23 and Somerset sites on August 21, 1999.

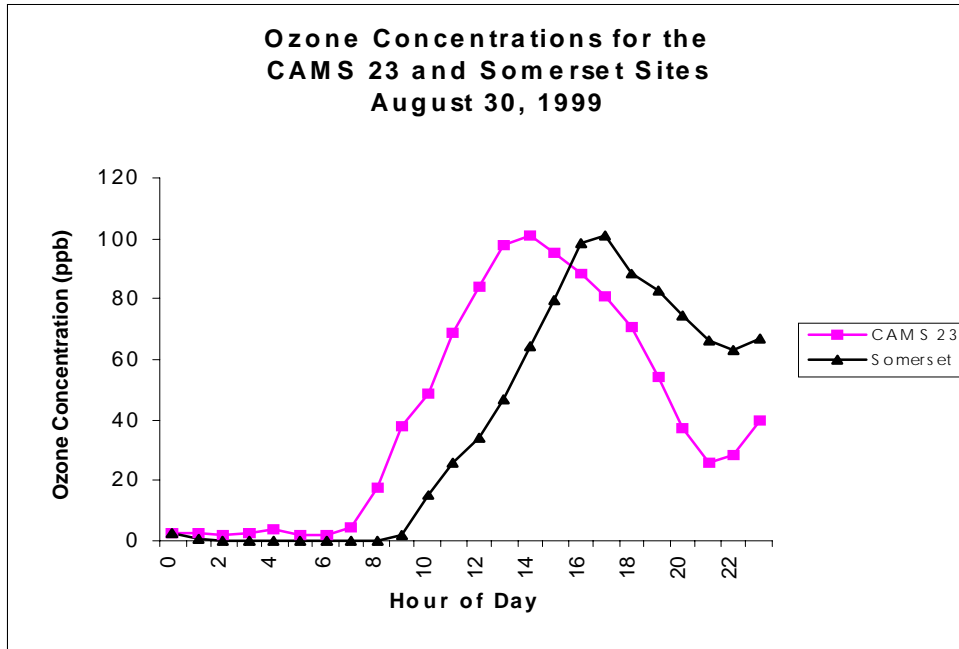


Figure IV-11. Ozone concentrations for the CAMS 23 and Somerset sites on August 30, 1999.

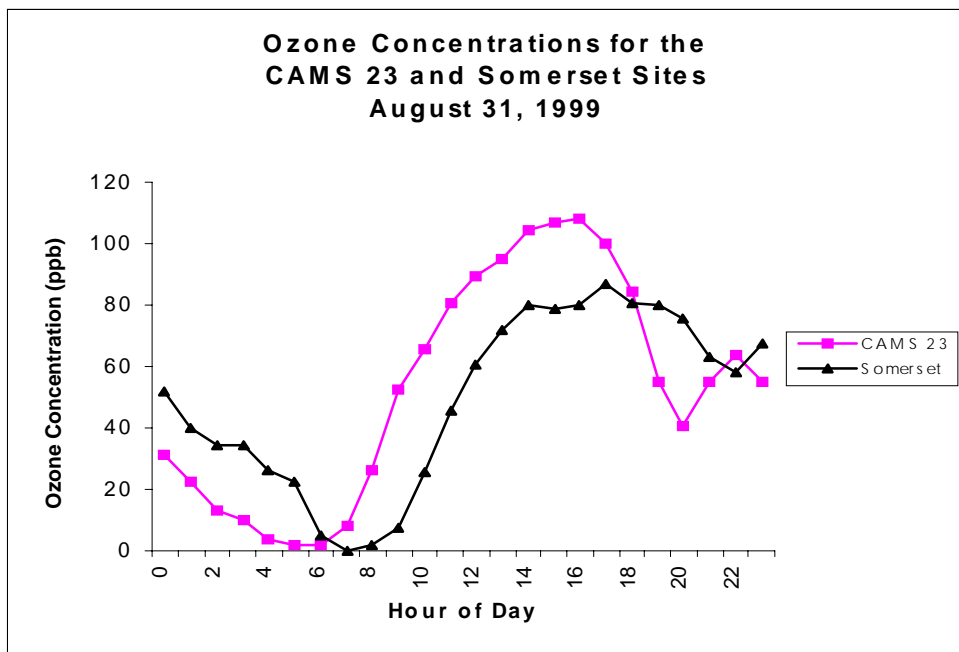


Figure IV-12. Ozone concentrations for the CAMS 23 and Somerset sites on August 31, 1999.

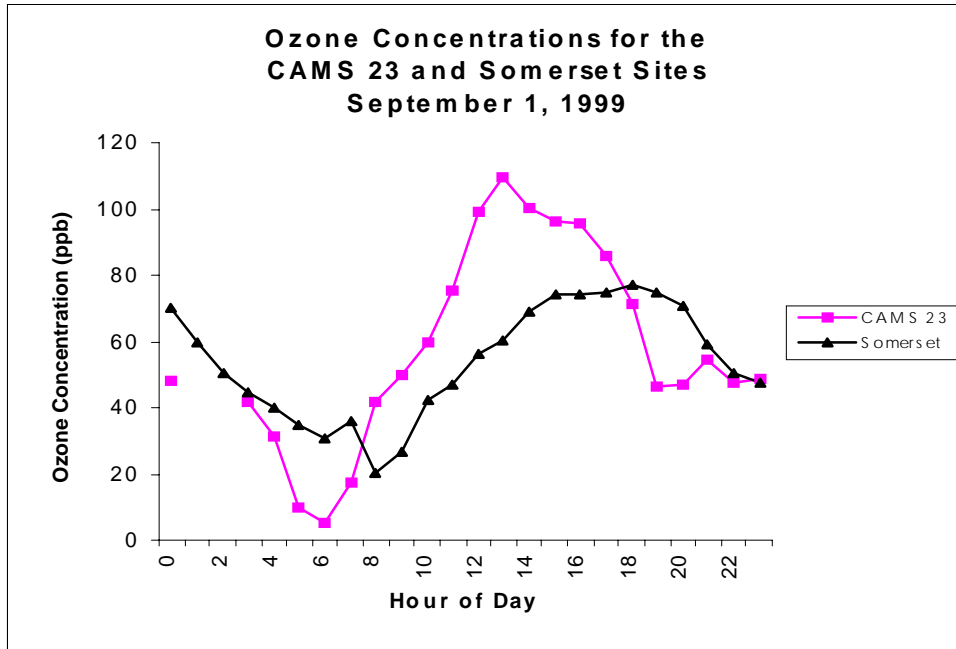


Figure IV-13. Ozone concentrations for the CAMS 23 and Somerset sites on September 1, 1999.

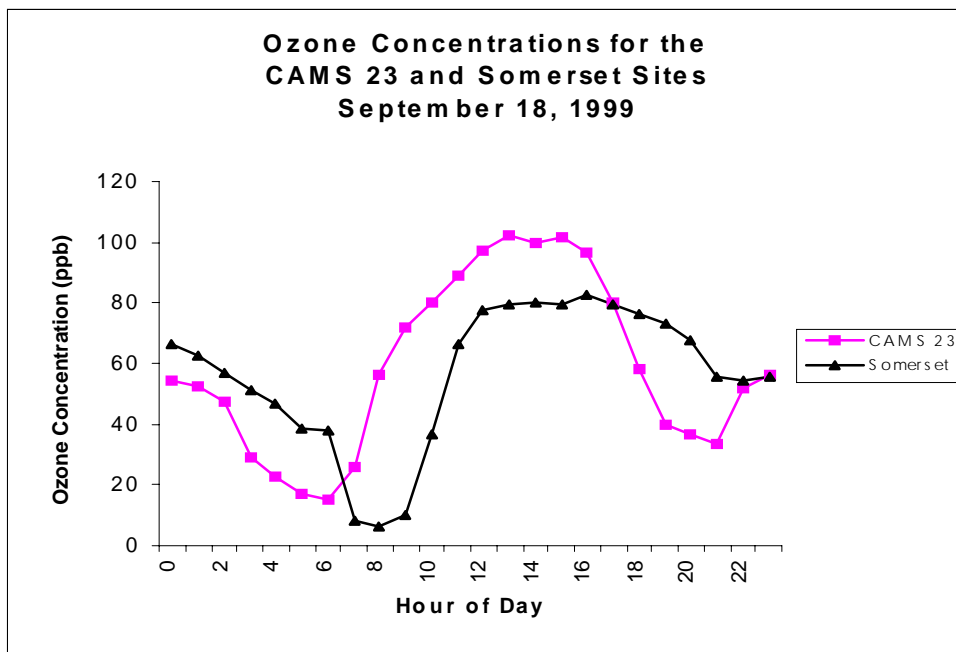


Figure IV-14. Ozone concentrations for the CAMS 23 and Somerset sites on September 18, 1999.

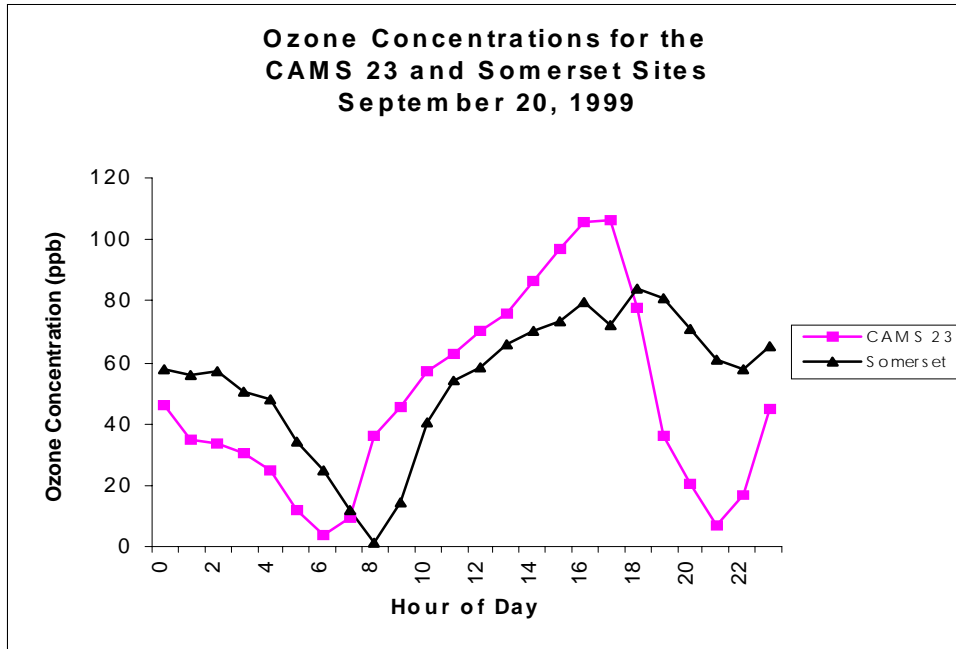


Figure IV-15. Ozone concentrations for the CAMS 23 and Somerset sites on September 20, 1999.

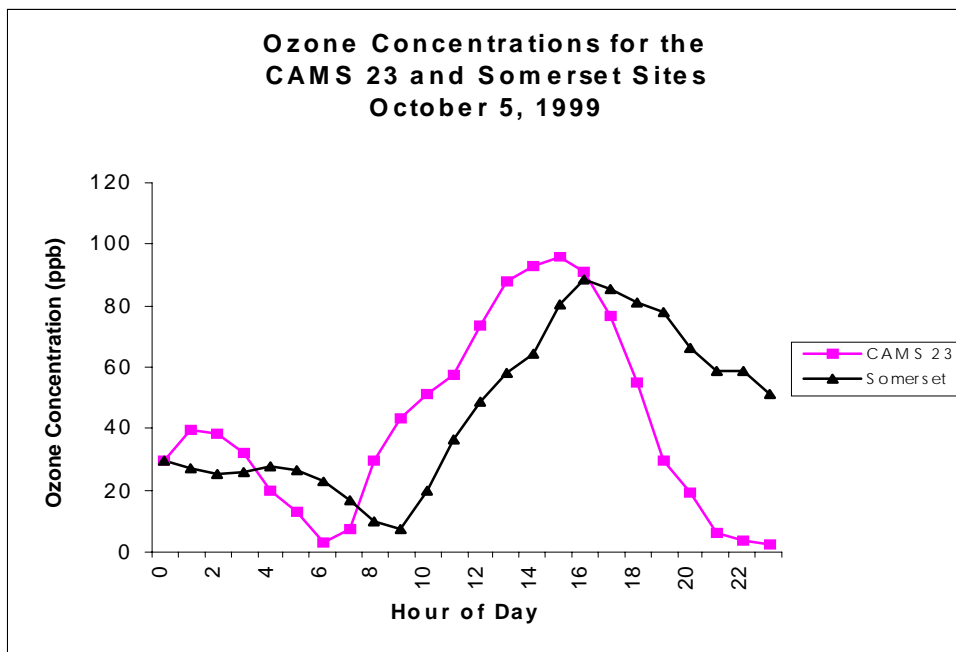


Figure IV-16. Ozone concentrations for the CAMS 23 and Somerset sites on October 5, 1999.

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The daily maximum ozone concentrations for the entire sampling period are presented in Table IV-3.

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Table IV-3. Maximum 1-hour concentrations for San Antonio region.

Date	Time of Maximum at Calaveras	Calaveras Wind Speed (mph)	Calaveras Wind Direction (degrees)	Calaveras Ozone Concentration (ppbv)	CAMS 23 Ozone Concentrations (ppbv)	CAMS 58 Ozone Concentrations (ppbv)	Somerset Ozone Concentration (ppbv)
4/1/99	1700	8	119	39	40	42	
4/2/99	1400	7.3	125	25	29	31	
4/3/99	2400	9.4	62	43	45	49	
4/4/99	300	8.6	44	40	46	48	
4/5/99	1300	8.5	325	61	67	65	
4/6/99	1700	6.2	112	79	81	68	
4/7/99	1400	13	130	41	44	38	
4/8/99	1400	12.8	180	39	34	37	
4/9/99	1500	11.6	159	47	50	48	52
4/10/99	1700	11.5	42	68	64	52	72
4/11/99	2100	4.9	66	60	75	64	64
4/12/99	1100	5.4	91	36	51	52	39
4/13/99	1400	13.2	135	31	33	36	38
4/14/99	1400	16.3	257	55	60	59	
4/15/99	1600	12.9	14	54	54	57	
4/16/99	1400	6.7	17	54	55	55	57
4/17/99	1700	1.9	151	62	76	71	68
4/18/99	1300	7.6	200	60	67	67	65
4/19/99	1700	10.4	163	51	54	55	56
4/20/99	1700	15.6	132	50	56	56	58
4/21/99	400	14.6	163	45	48	48	50
4/22/99	1400	8.6	144	44	57	58	55
4/23/99	1700	8.8	115	36	47	46	47
4/24/99	1400	5	116	13	31	34	32
4/25/99	1700	10.6	56	14	33	32	34
4/26/99	1200	2.5	91	35	50	46	54
4/27/99	1400	5.9	145	48	71	61	70
4/28/99					62	55	64
4/29/99					52	46	48
4/30/99					95	90	83
5/1/99					62	61	65
5/2/99					55	55	58
5/3/99					37	34	41
5/4/99					40	34	
5/5/99					70	57	
5/6/99	1600	1	52	76	79	56	86
5/7/99	1700	5	137	78	84	68	83
5/8/99	900	7	148	53	67	62	65
5/9/99	1500	10	132	34	38	37	44
5/10/99					45	45	46
5/11/99					43	38	47
5/12/99					18	50	65
5/13/99	1900	3.9	127	78		64	
5/14/99	1300	12.5	134	47		39	
5/15/99	1400	12.9	134	53		46	
5/16/99	1200	16	152	50		47	47
5/17/99	2400	5.1	170	51		40	40
5/18/99	1400	6	28	60	56	52	60
5/19/99	1500	8.2	129	73	67	62	74
5/20/99	1600	11.7	131	45	42	46	42
5/21/99	1500	8.9	131	48	41	43	44
5/22/99	1700	8.6	137	39	39	41	40
5/23/99	1600	4.4	172	35	54	57	39
5/24/99	1200	3.2	159	43	67	71	49
5/25/99	1500	9	147	38	46	43	44

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Date	Time of Maximum at Calaveras	Calaveras Wind Speed (mph)	Calaveras Wind Direction (degrees)	Calaveras Ozone Concentration (ppbv)	CAMS 23 Ozone Concentrations (ppbv)	CAMS 58 Ozone Concentrations (ppbv)	Somerset Ozone Concentration (ppbv)
5/26/99	2100	15.2	61	47	47	47	43
5/27/99	900	8.7	54	54	84	69	56
5/28/99	1500	14.9	24	61	58	54	
5/29/99	1400	5.4	106	62	84	69	
5/30/99	1800	9.4	135	36	35	38	
5/31/99	1700	9.8	133	43		42	
6/1/99	1800	12.4	137	44	1	44	
6/2/99	1500	13.3	136	47	44	40	
6/3/99	1600	12.7	137	39	39	38	41
6/4/99	1600	14.2	135	37	37	38	
6/5/99	1500	17.4	132	34	34	32	
6/6/99	1400	13.1	139	37	37	35	
6/7/99	1400	7.7	140	46	49	45	
6/8/99	1700	11.6	114	47	55	53	
6/9/99	1600	12.8	125	41	44	43	
6/10/99	1700	10	122	38	39	41	
6/11/99	1700	9.5	114	40	41	41	
6/12/99	1700	8.3	97	37	62	53	38
6/13/99	1600	9.5	45	40	44	37	54
6/14/99	1600	9.7	33	71	61	50	80
6/15/99	1600	4.3	10	67	58	48	73
6/16/99	1500	7.5	48	74	71	56	81
6/17/99					64	57	74
6/18/99	1600	8.5	73	80	88	77	77
6/19/99	800	7.3	126	61	62	60	53
6/20/99	600	10.8	123	46	37	41	38
6/21/99	900	8.9	143	37	31	39	35
6/22/99	1200	13.3	145	24	28	30	28
6/23/99	1300	12	185	28	35	37	31
6/24/99	1100	5.8	135	23	39	34	27
6/25/99	1700	11.8	68	24	48	56	27
6/26/99	1300	12.4	153	27	31	33	29
6/27/99	1600	10.9	131	28	32	31	28
6/28/99	1700	11.2	131	31	37	41	31
6/29/99	1700	8.8	138	29	35	38	31
6/30/99	1700	14.7	133	37	38	38	
7/1/99	1800	13.9	132	30	32	32	20
7/2/99	1200	11.9	144	29	33	29	24
7/3/99	1600	13	124	23	25	26	18
7/4/99	1300	9.5	137	16	24	24	15
7/5/99	1400	6.8	132	27	35	32	22
7/6/99	1500	2.7	29	31	70	72	24
7/7/99	1500	5.4	53	54	71	49	49
7/8/99	1200	4.7	75	72	91	70	
7/9/99	1700	12.7	118	28	44	44	
7/10/99	1600	12.5	131	28	36	40	
7/11/99	1500	12	44	37	43	36	
7/12/99	1700	4.3	73	31	47	52	
7/13/99	2000	7.6	141	28	30	30	
7/14/99	1800	12	114	32	32	30	
7/15/99	1600	11.6	129	32	32	31	
7/16/99	1500	8.5	102	37	41	37	
7/17/99	1800	8.2	142	26	30	27	
7/18/99	1200	8	201	23	29	31	
7/19/99	1400	6.3	119	33	37	35	
7/20/99	1200	4.1	157	33	59	54	
7/21/99	1400	16.3	136	25	26	30	
7/22/99	1800	9	119	33	31	30	
7/23/99	1700	6.8	111	28	49	56	36
7/24/99	1400	7.1	123	31	58	60	35
7/25/99	1700	9.8	118	30	45	45	37
7/26/99	1700	12.2	123	33	38	40	38
7/27/99	1700	12.7	132	31	31	32	34
7/28/99	1900	11.1	129	31	45	47	34
7/29/99	1800	11.9	134	39	44	51	36

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Date	Time of Maximum at Calaveras	Calaveras Wind Speed (mph)	Calaveras Wind Direction (degrees)	Calaveras Ozone Concentration (ppbv)	CAMS 23 Ozone Concentrations (ppbv)	CAMS 58 Ozone Concentrations (ppbv)	Somerset Ozone Concentration (ppbv)
7/30/99	1800	12.5	121	41	46	47	42
7/31/99	1600	11.9	123	37	47	50	44
8/1/99	1500	9.3	134	28	39	39	30
8/2/99	1800	4.2	95	30	66	54	37
8/3/99	1200	3.4	109	60	78	63	63
8/4/99	1500	6.8	113	73	98	67	76
8/5/99	1200	2	18	82	120	96	95
8/6/99	1100	5	108	74	95	87	72
8/7/99	1000	4	161	65	84	81	69
8/8/99	1300	6.9	143	36	54	58	46
8/9/99	1700	6.6	148	30	45	53	36
8/10/99	1600	9.6	140	35	44	47	41
8/11/99	1900	11.9	142	39	39	42	39
8/12/99	1900	12.5	134	35	36	37	35
8/13/99	1700	8.1	152	37	48	58	41
8/14/99	1400	3.5	129	42	77	71	43
8/15/99	1400	6.5	112	66	74	69	
8/16/99	1700	7.1	97	67	109	100	88
8/17/99	900	2.3	45	59	76	71	65
8/18/99	1800	4.6	100	38	49	54	40
8/19/99	1200	2.8	108	63	79	62	64
8/20/99	1200	2.7	7	80	92	74	100
8/21/99	1300	3.8	346	85	109	88	102
8/22/99	1700	9.4	57	32	36	35	29
8/23/99	1300	11	69	29	28	32	26
8/24/99	1600	4.9	106	31	31	34	33
8/25/99	1600	5.4	113	33	38	41	31
8/26/99	1700	7	183	27	42	56	33
8/27/99	1500	4.1	108	38	64	74	42
8/28/99	1700	7.6	153	37	62	64	38
8/29/99	1400	5.2	21	53	66	56	54
8/30/99	1400	6.6	17	78	101	83	101
8/31/99	1300	2.6	108	93	108	97	87
9/1/99					109	107	77
9/4/99					32	34	31
9/5/99					48	46	37
9/6/99					45	51	34
9/7/99					32	38	34
9/8/99					35	48	34
9/9/99					71	71	61
9/10/99					59	62	65
9/11/99	1400	10.1	160	61	60	65	59
9/12/99	1600	6.2	121	56	54	59	52
9/13/99	1500	14	50	73	66	61	68
9/14/99	1500	7.7	49	68	75	68	73
9/15/99	1600	7.8	57	92	93	89	85
9/16/99	1500	8.4	66	85	94	84	85
9/17/99	1100	8.6	137	83	82	82	76
9/18/99	1200	3.9	90	84	102	109	82
9/19/99	1100	0.8	91	97	95	97	91
9/20/99	1600	1.3	296	98	106	101	84
9/21/99	1400	12.1	6	63	67	72	
9/22/99	1700	4.2	54	68	57	56	
9/23/99	1500	4.5	154	75	92	92	82
9/24/99	1300	7	174	74	75	85	77
9/25/99	1600	12.5	141	51	46	53	55
9/26/99	1500	11.6	162	50	42	48	44
9/27/99	1700	11	145	49	44	49	44
9/28/99	1700	6.9	73	35	48	51	37
9/29/99	1500	15.5	25	58	44		50

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Date	Time of Maximum at Calaveras	Calaveras Wind Speed (mph)	Calaveras Wind Direction (degrees)	Calaveras Ozone Concentration (ppbv)	CAMS 23 Ozone Concentrations (ppbv)	CAMS 58 Ozone Concentrations (ppbv)	Somerset Ozone Concentration (ppbv)
9/30/99	1700	1.4	357	65	75	76	74
10/1/99	1400	7.8	132	94	91	39	93
10/2/99	1000	7.7	171	60	65	54	59
10/3/99	1700	9.2	91	34	45	63	34
10/4/99	1300	17.1	33	81	61	67	77
10/5/99	1400	4.8	31	84	96	96	89
10/6/99	1200	6.3	32	80	89	87	82
10/7/99	1400	7.7	126	70	71	81	76
10/8/99	1000	4.5	82	62	60	58	58
10/9/99	1500	5.1	352	74	59	53	63
10/10/99	1500	7.4	30	82	79	47	88
10/11/99	1700	8.3	34	79	80	42	85
10/12/99	1500	4.8	50	70	76	37	87
10/13/99	1300	3.4	43	80	88	58	86
10/14/99	1200	6.1	153	63	68	71	62
10/15/99	1900	9.8	151	45	38	69	45
10/16/99	900	9.2	168	38	41	100	41
10/17/99	300	7.8	333	39	32	71	41
10/18/99	1000	13.5	20	30	26	54	26
10/19/99	1700	9.4	16	51	42	62	46
10/20/99					57	74	66
10/21/99	1500	3.1	252	87	66	88	74
10/22/99	1500	1.5	273	72	62	35	67
10/23/99	1600	13	39	55	51	32	56
10/24/99	1600	5.6	41	57	50	34	54

## ***IV.2 Ozone Precursor Concentrations***

A major objective of this monitoring study was to determine ambient concentrations of hydrocarbons and nitrogen oxides. These data can be used in evaluating the performance of emission inventories and photochemical grid modeling of San Antonio. Both  $\text{NO}_x$  and hydrocarbons were measured throughout the 1999 ozone season.  $\text{NO}_x$  was measured continuously with minor down times for calibrations, span checks, instrument maintenance, and instrument failures. 76 air samples were collected and analyzed for hydrocarbons. The samples were collected on days with both moderate and high ozone concentrations.

### ***IV.2.1 Nitrogen Oxides ( $\text{NO}_x$ )***

Concentrations of  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_x$  were measured at CAMS 59 in San Antonio (Calaveras Lake) by the TNRCC and by the University of Texas at the Somerset site. At both sites concentrations of  $\text{NO}_2$  and  $\text{NO}_x$  were typically below 10 ppbv. On occasion  $\text{NO}_2$  and  $\text{NO}_x$  reached levels between 40 and 100 ppbv.  $\text{NO}$  concentrations were typically about 1 ppbv occasionally reaching 10 ppbv. These concentrations are low, relative to polluted urban levels of  $\text{NO}_x$  of 50 to 250 ppbv. A comprehensive listing of hourly  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_x$  data is provided in the data volume. Daily maximum  $\text{NO}_x$  concentrations are shown in Table IV-4.

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Table IV-4. Maximum daily NO<sub>x</sub> concentrations.

<i>Date</i>	<i>Time of Maximum at Calaveras (24 hour clock)</i>	<i>Calaveras Wind Speed (mph)</i>	<i>Calaveras Wind Direction (degrees)</i>	<i>Calaveras NO<sub>x</sub> (ppbv)</i>	<i>Somerset NO<sub>x</sub> (ppbv)</i>
4/6/99	500	5.5	4	28.6	
4/7/99	600	5	126	8.8	
4/8/99	500	3	175	21.8	
4/9/99	600	4.3	120	9.1	8.1
4/10/99	900	3.2	36	11.9	22.0
4/11/99	100	2.1	82	9.2	33.7
4/12/99	700	6.1	66	9.4	14.2
4/13/99	500	5.4	139	6	1.9
4/14/99	300	15.9	336	21.6	
4/15/99	700	13.3	342	29.7	
4/16/99	2100	3.2	84	16	2.0
4/17/99	600	2.6	252	73.5	2.5
4/18/99	1900	2.9	139	20	2.0
4/19/99	600	1.6	162	74	1.8
4/20/99	600	5.9	148	14	2.1
4/21/99	600	11.5	159	3.6	2.1
4/22/99	1700	11	116	7.3	2.3
4/23/99	1600	8.7	124	7.8	2.0
4/24/99	2000	5.7	118	5.1	11.6
4/25/99	600	6.7	14	12.8	5.5
4/26/99					20.5
4/27/99					9.9
4/28/99					8.2
4/29/99					8.2
4/30/99	1500	7.8	91	1.9	5.7
5/1/99	100	6.6	56	0	2.8
5/2/99	100	9.1	128	0	2.1
5/3/99	600	7.1	151	0.2	3.0
5/4/99	1900	4	148	25	
5/5/99	1800	3.5	229	22.5	
5/6/99	700	9.8	18	8.2	22.3
5/7/99	2000	4.9	131	25.8	48.0
5/8/99	1800	5.8	127	5.9	10.4
5/9/99	1600	12.8	135	1.6	2.0
5/10/99					7.2
5/11/99	700	0.8	221	16.7	19.8
5/12/99	600	4.7	176	6.3	7.8
5/13/99	600	9.3	55	4.3	
5/14/99	600	4.8	149	1.3	
5/15/99	100	9.8	119	0	
5/16/99	100	7.2	118	0	2.7
5/17/99	600	6.5	131	2.5	2.4
5/18/99	400	4.2	63	4.2	21.8
5/19/99	600	5.7	45	6.5	26.3
5/20/99					4.0
5/21/99					3.6
5/22/99					5.5
5/23/99					9.0
5/24/99					22.1
5/25/99	600	2.2	196	11.8	7.6
5/26/99	600	4.2	158	6.6	10.0
5/27/99	300	8.7	355	13.2	10.9
5/28/99	400	3.1	121	4.3	
5/29/99	1200	4.5	0	19.8	
5/30/99	1900	9.8	141	3.4	
5/31/99	400	3	171	3.9	
6/1/99	500	5.5	169	5.6	
6/2/99	500	8.5	158	4.1	

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<i>Date</i>	<i>Time of Maximum at Calaveras (24 hour clock)</i>	<i>Calaveras Wind Speed (mph)</i>	<i>Calaveras Wind Direction (degrees)</i>	<i>Calaveras NO<sub>x</sub> (ppbv)</i>	<i>Somerset NO<sub>x</sub> (ppbv)</i>
6/3/99	600	5.8	157	6.8	3.2
6/4/99	500	6.5	139	4.6	
6/5/99	2200	7.9	126	2.4	
6/6/99	400	4.6	124	3	
6/11/99	300	4.7	133	3.4	
6/12/99	2200	4.9	135	3.5	3.2
6/13/99	1900	17.9	31	13	10.8
6/14/99	2400	5.7	300	16.3	22.3
6/15/99	400	5.2	350	21.8	16.8
6/16/99	2400	1.3	174	22.9	18.2
6/17/99					23.1
6/18/99	600	7	61	6.5	13.6
6/19/99	2200	4.6	64	5.3	5.2
6/20/99	2300	5.9	51	4.5	13.8
6/21/99	1000	4.1	133	6.2	5.1
6/22/99	600	6.4	128	7.2	13.6
6/23/99	600	9.4	179	3.7	6.0
6/24/99	500	5.2	143	6.6	5.9
6/25/99					10.3
6/26/99	600	7.8	149	3.8	2.5
6/27/99	2300	11.1	144	2.9	2.4
6/28/99	600	9.7	166	3.5	2.2
6/29/99	600	3.8	123	8.3	5.2
6/30/99	1400	13.9	151	5.1	
7/1/99					2.1
7/2/99	600	7.5	146	3.3	2.9
7/3/99	600	3.4	85	2.2	2.1
7/4/99	1900	3.2	162	3.5	4.0
7/5/99	2000	4.4	130	7	19.7
7/6/99	400	1.9	88	5.8	14.7
7/7/99					10.2
7/17/99					10.0
7/18/99					4.6
7/19/99					5.0
7/20/99					7.7
7/21/99					12.0
7/22/99					4.3
7/23/99	2000	4.9	128	10.6	4.1
7/24/99	500	0.8	220	11.2	12.1
7/25/99	600	1.5	107	8.8	13.9
7/26/99	600	2.7	84	2.5	7.2
7/27/99	600	3.2	74	5.9	5.7
7/28/99	600	3.8	172	7.1	5.1
7/29/99	500	3.1	136	14.5	1.0
7/30/99	600	2.6	102	5.8	9.0
7/31/99	2100	9.2	140	1.1	8.5
8/1/99	2400	3.4	155	1.6	3.1
8/2/99	600	2.2	73	6	2.9
8/3/99	600	2	142	58.8	5.6
8/4/99	500	2.3	156	61.6	36.3
8/5/99					70.7
8/6/99					28.9
8/7/99					5.1
8/8/99					4.2
8/9/99					5.4
8/10/99	600	1.5	160	25.8	16.2
8/11/99	600	4.1	150	8.9	
8/12/99	600	8.9	162	2.2	
8/13/99	600	2.6	126	12.2	

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<i>Date</i>	<i>Time of Maximum at Calaveras (24 hour clock)</i>	<i>Calaveras Wind Speed (mph)</i>	<i>Calaveras Wind Direction (degrees)</i>	<i>Calaveras NO<sub>x</sub> (ppbv)</i>	<i>Somerset NO<sub>x</sub> (ppbv)</i>
8/14/99	2000	4.4	119	5.2	
8/15/99	500	2.9	281	11.6	
8/18/99					27.5
8/19/99					38.9
8/20/99					17.8
8/21/99					42.2
8/22/99					18.9
8/23/99					9.6
8/24/99					11.2
8/25/99					19.2
8/26/99					17.8
8/27/99					12.3
8/28/99					8.0
8/29/99					27.0
8/30/99					51.6
8/31/99					28.3
9/1/99					8.7
9/4/99	600	4.2	125	2.4	5.6
9/5/99	2300	2.7	144	13.4	6.9
9/6/99	2200	0.9	176	22.1	17.2
9/7/99	400	1	149	30.9	40.9
9/8/99	600	1.7	112	79.8	27.0
9/9/99	600	0.9	161	90.2	46.0
9/10/99	600	3.3	142	29.9	29.1
9/11/99	500	2.3	150	9.9	4.9
9/12/99	1900	6.7	158	3.7	5.3
9/13/99	700	6.3	15	17.2	18.5
9/14/99	200	10.6	25	8.1	20.1
9/15/99	700	7.3	60	11.3	20.4
9/16/99	700	5.4	16	14.5	51.6
9/17/99	1900	3.9	146	18.5	49.4
9/18/99	1900	4.5	134	10.8	24.6
9/19/99	1900	5.9	152	13.7	9.3
9/20/99	600	3.2	224	71.8	24.2
9/21/99	100	1.9	117	6.7	
9/22/99	1900	3.4	96	11.3	
9/23/99	500	3	51	38.4	55.0
9/24/99	500	2.1	92	51.4	46.4
9/25/99	600	4.9	137	4.4	5.3
9/26/99	700	5.4	121	2.1	5.4
9/27/99	700	3.9	140	9.8	7.7
9/28/99	700	4	60	3.2	8.0
9/29/99	2300	5.3	50	17.3	41.6
9/30/99	1900	3.9	117	23.1	32.5
10/1/99	300	2.4	89	11	
10/2/99	400	3.6	142	9.8	
10/3/99	2100	4.8	132	13.9	
10/4/99	700	7.3	26	13.5	
10/5/99	700	10.3	32	15.7	
10/6/99	600	5.8	38	16	
10/7/99	700	5	41	10.5	
10/8/99	500	4.8	357	39.4	
10/9/99	800	8.5	350	22.1	
10/10/99	100	4.9	346	13.7	
10/11/99	700	7.4	31	17.3	
10/12/99	700	5.7	29	25.5	
10/13/99	500	2.3	33	18.8	
10/22/99	700	2	271	90.5	
10/23/99	100	2.7	300	42.5	
10/24/99	1900	3.6	137	27.4	

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Daily maximum  $\text{NO}_x$  concentrations varied significantly, depending on wind direction. Concentrations were usually highest at Somerset when winds were from the south, southwest, east, and northeast and lowest when winds were from the northwest (Figure IV-17A) as compared to Calaveras Lake where the higher concentrations are most notable out of the west (Figure IV-17B). The analyses for  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_x$  for the whole summer for both sites are illustrated in Figures IV-19A and B through IV-24A and B.

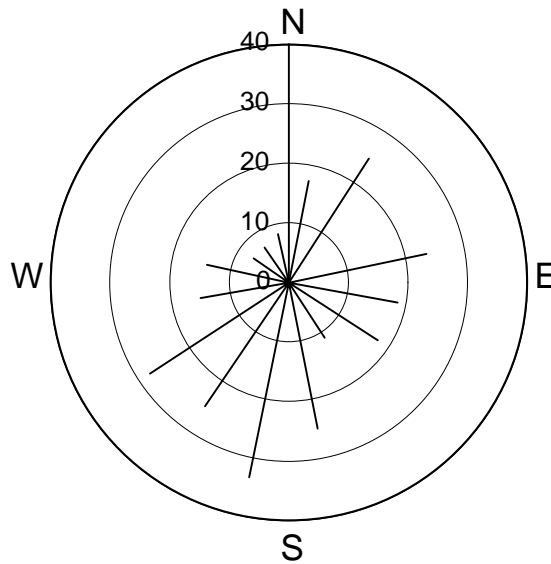


Figure IV-17A. Average daily maximum  $\text{NO}_x$  concentrations at Somerset as a function of wind direction; data are from April 9, 1999 through September 30, 1999. (The wind direction at the time of maximum  $\text{NO}_x$  concentration was determined for all of the days during the sampling period. These daily maxima for the season were then averaged for each wind direction. This value is illustrated as the length of the bar for each wind direction)

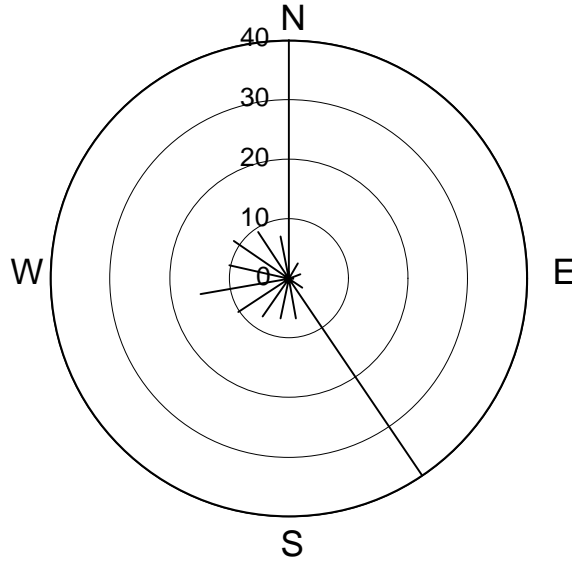


Figure IV-18A. Wind direction frequency distribution at the time of maximum  $\text{NO}_x$  concentrations at Somerset. The data are reported as the number of days during which the winds originated from each of 16 directions. Data are for April 9, 1999 through September 30, 1999.

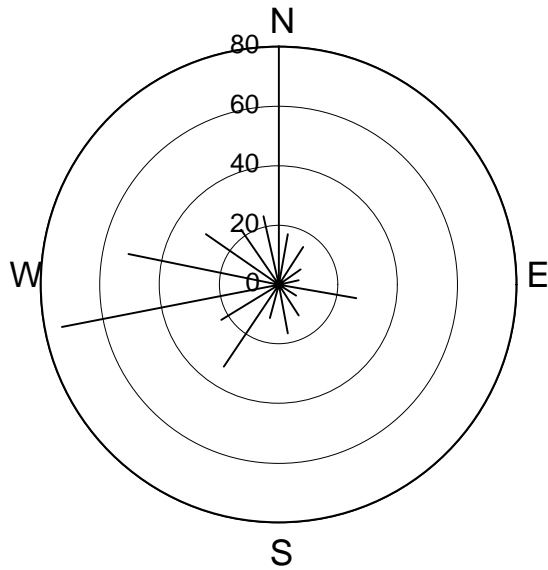


Figure IV-17B. Average daily maximum  $\text{NO}_x$  concentrations at Calaveras as a function of wind direction; data are from April 6, 1999 through October 24, 1999. (The wind direction at the time of maximum  $\text{NO}_x$  concentration was determined for all of the days during the sampling period. These daily maxima for the season were then averaged for each wind direction. This value is illustrated as the length of the bar for each wind direction)

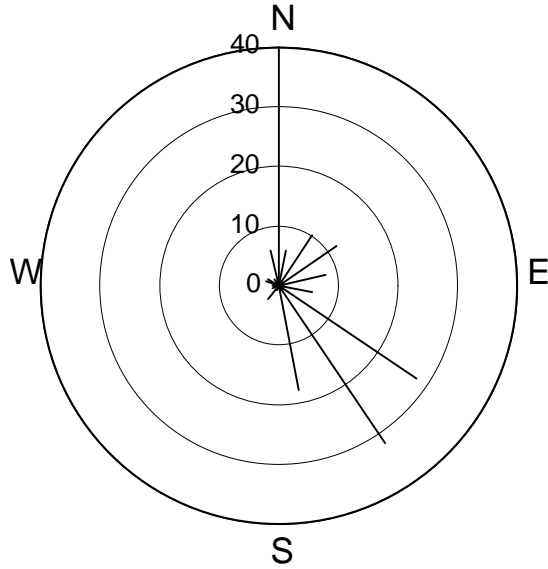


Figure IV-18B. Wind direction frequency distribution at the time of maximum  $\text{NO}_x$  concentrations at Calaveras. The data are reported as the number of days during which the winds originated from each of 16 directions. Data are for April 6, 1999 through October 24, 1999.

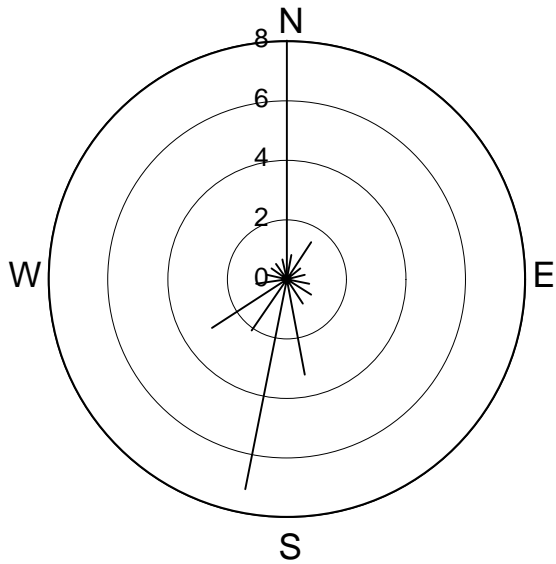


Figure IV-19A. NO concentrations at Somerset as a function of wind direction; data are from April 9, 1999 through September 30, 1999. (The wind direction and NO concentrations at for each hour were determined for the sampling period. These NO concentrations associated with each wind direction were then averaged. This value is illustrated as the length of the bar for each wind direction)

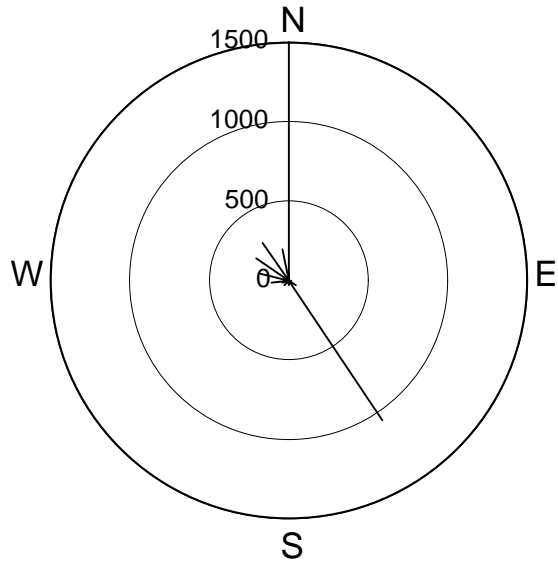


Figure IV-20A. Wind direction frequency distribution for the entire study period at Somerset. The data are reported as the number of hours during which the winds originated from each of 16 directions. Data are for April 9, 1999 through September 30, 1999.

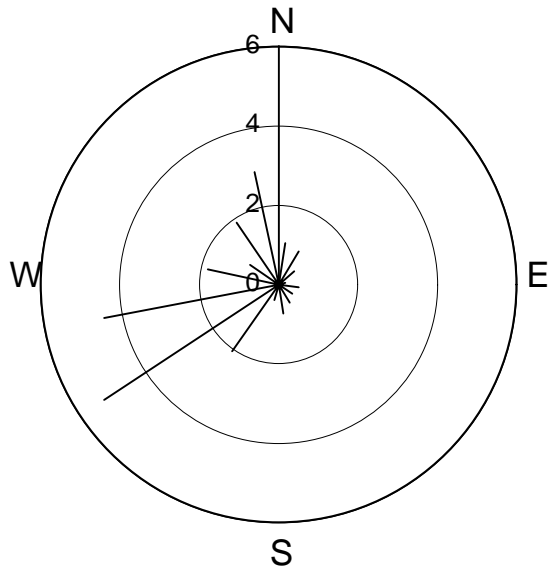


Figure IV-19B. NO concentrations at Calaveras as a function of wind direction; data are from April 6, 1999 through October 24, 1999. (The wind direction and NO concentrations at for each hour were determined for the sampling period. These NO concentrations associated with each wind direction were then averaged. This value is illustrated as the length of the bar for each wind direction)



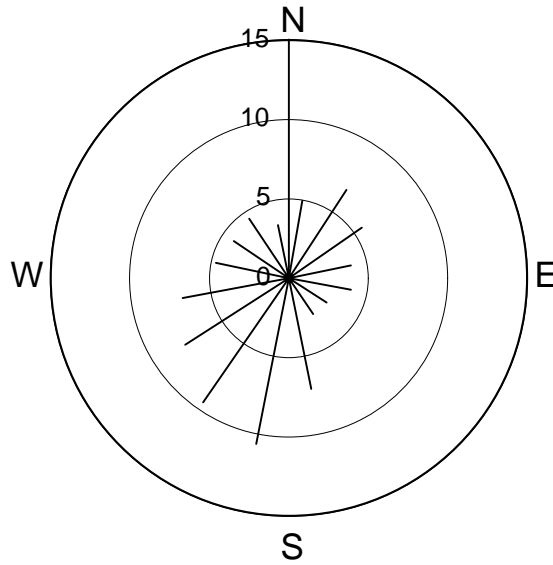


Figure IV-21A. NO<sub>2</sub> concentrations at Somerset as a function of wind direction; data are from April 9, 1999 through September 30, 1999. (The wind direction and NO<sub>2</sub> concentrations at for each hour were determined for the sampling period. These NO<sub>2</sub> concentrations associated with each wind direction were then averaged. This value is illustrated as the length of the bar for each wind direction)

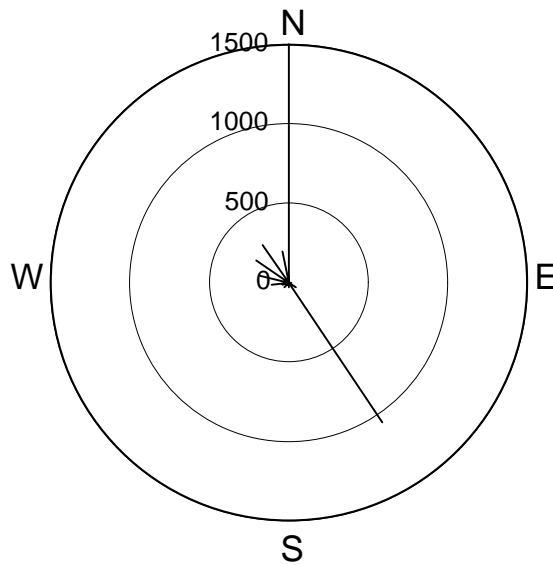


Figure IV-22A. Wind direction frequency distribution for the entire study period (when NO<sub>2</sub> was sampled) at Somerset. The data are reported as the number of hours during which the winds originated from each of 16 directions. Data are for April 9, 1999 through September 30, 1999.

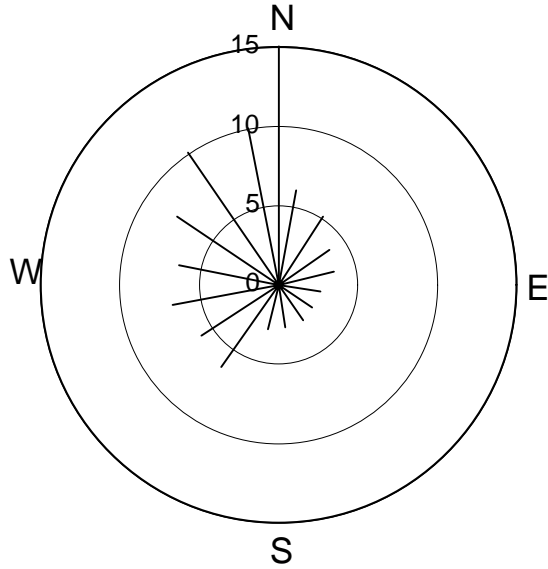


Figure IV-21B. NO<sub>2</sub> concentrations at Calaveras as a function of wind direction; data are from April 6, 1999 through October 24, 1999. (The wind direction and NO<sub>2</sub> concentrations at for each hour were determined for the sampling period. These NO<sub>2</sub> concentrations associated with each wind direction were then averaged. This value is illustrated as the length of the bar for each wind direction)

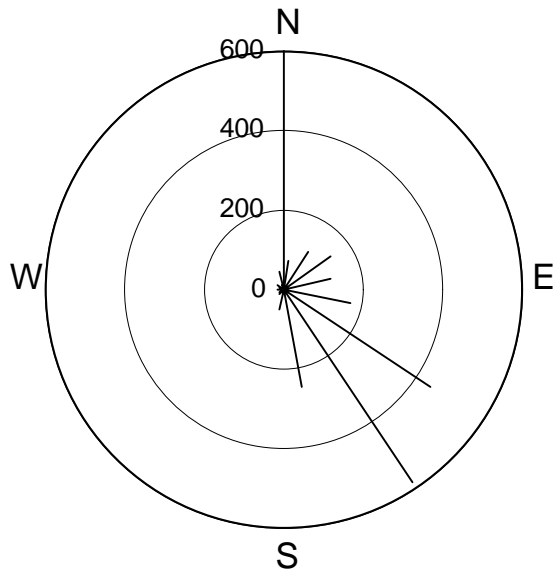


Figure IV-22B. Wind direction frequency distribution for the entire study period (when NO<sub>2</sub> was sampled) at Calaveras. The data are reported as the number of hours during which the winds originated from each of 16 directions. Data are for April 6, 1999 through October 24, 1999.

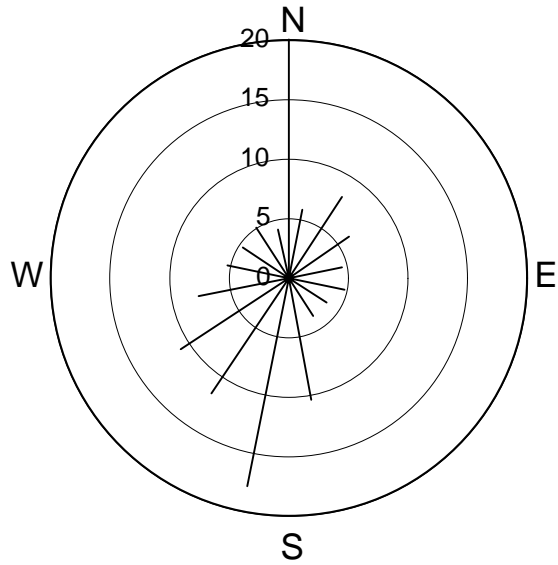


Figure IV-23A. NO<sub>x</sub> concentrations at Somerset as a function of wind direction; data are from April 9, 1999 through September 30, 1999. (The wind direction and NO<sub>x</sub> concentrations at for each hour were determined for the sampling period. These NO<sub>x</sub> concentrations associated with each wind direction were then averaged. This value is illustrated as the length of the bar for each wind direction)

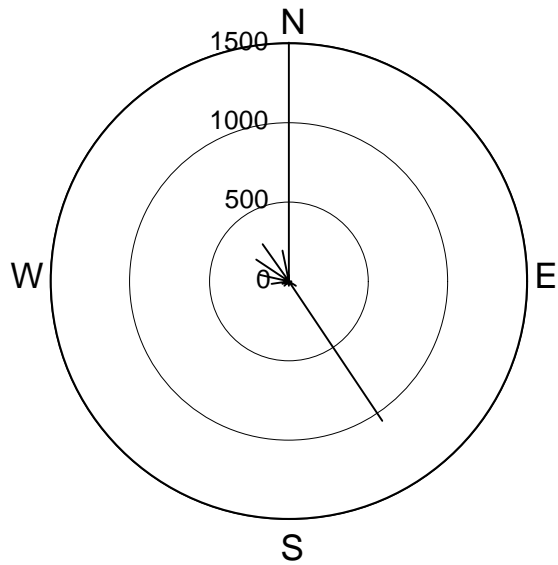


Figure IV-24A. Wind direction frequency distribution for the entire study period (when NO<sub>x</sub> was sampled) at Somerset. The data are reported as the number of hours during which the winds originated from each of 16 directions. Data are for April 9, 1999 through September 30, 1999.

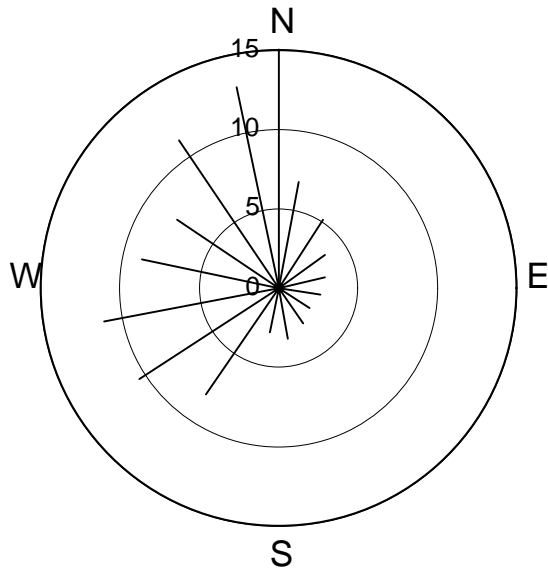


Figure IV-23B. NO<sub>x</sub> concentrations at Calaveras as a function of wind direction; data are from April 6, 1999 through October 24, 1999. (The wind direction and NO<sub>x</sub> concentrations at for each hour were determined for the sampling period. These NO<sub>x</sub> concentrations associated with each wind direction were then averaged. This value is illustrated as the length of the bar for each wind direction)

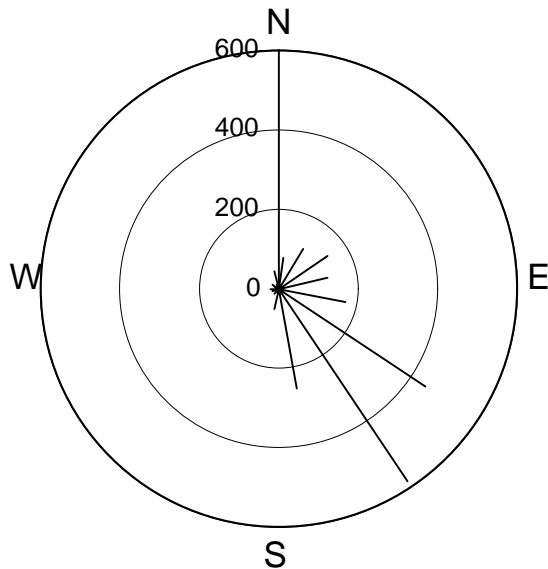


Figure IV-24B. Wind direction frequency distribution for the entire study period (when NO<sub>x</sub> was sampled) at Calaveras. The data are reported as the number of hours during which the winds originated from each of 16 directions. Data are for April 6, 1999 through October 24, 1999.

### ***IV.2.2 VOC Sampling and Analysis***

76 air samples were collected and analyzed. About one-third of the samples were taken on an ozone action day. Approximately half of the air samples were hourly samples, the other half being grab samples. Hydrocarbon concentrations were typically 50 to 400 ppbC with an average concentration of approximately 140 ppbC.

*Most Commonly Detected Hydrocarbon Species in high concentrations at the Somerset site.* For each sample, the five compounds with the highest ppbC concentrations were determined. An inventory of the compounds most commonly found at high concentrations at the Somerset site is listed in Table IV-5. A complete compilation of the data is provided in the data volume.

Table IV-5. Ten compounds most commonly found at high concentrations at the Somerset site

<i>Peak ID</i>	<i>Compound name</i>	<i># times compound was found in top 5</i>	<i>Average ppbC</i>
75	styrene	24	22.6
77	n-nonane	23	11.5
83	n-propylbenzene	16	26.3
89	1,2,4-trimethylbenzene	13	36.8
60	n-heptane	9	5.5
24	n-pentane	5	49.7
12	n-butane	5	9.0
5	propane	5	10.4
41	3-methylpentane	4	4.6
44	n-hexane	3	10.4
57	3-methylhexane	3	4.5
71	ethylbenzene	3	5.5

Based on emission inventory calculations done by the University of Texas (Allen, et al., 1997), it is anticipated that most of the biogenic emissions will be significant in eastern Texas and that isoprene from deciduous trees will be dominant species associated with biogenic emissions. Although isoprene was not detected at high concentrations, it was detected in 42 out of 76 samples collected. The concentrations observed in the samples averaged about 2.2 ppbC. The highest recorded concentration of isoprene for the 1999 ozone season at San Antonio was 5.6 ppbC.

### ***IV.2.3 VOC/NO<sub>x</sub> RATIOS***

VOC to NO<sub>x</sub> ratios are often used in qualitative assessments of the effectiveness of VOC and NO<sub>x</sub> emission reductions. Table IV-6 lists the peak ozone concentrations and the corresponding average VOC to NO<sub>x</sub> ratios for that day. The dates and times for all VOC/NO<sub>x</sub> ratios used in creating Table IV-6 are listed in Table IV-7.

Table IV-6. Average VOC/NO<sub>x</sub> ratios for days when VOCs were collected.

<i>Date</i>	<i>Peak Ozone (ppbv)</i>	<i>Average VOC/NO<sub>x</sub></i>	<i>Minimum NO<sub>x</sub> concentration used in VOC/NO<sub>x</sub> ratio</i>
6/18/99	77	27	12
6/30/99		195	1
7/2/99	24	72	2
7/14/99			
7/16/99		19	8
8/11/99	39	12	2

In general, the VOC to NO<sub>x</sub> ratios for the season were high, usually indicating NO<sub>x</sub> limitation in the area.

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Table IV-7. VOC/NO<sub>x</sub> ratios.

<i>Date</i>	<i>Time</i>	<i>Wind Direction</i>	<i>NO<sub>x</sub> ppbv</i>	<i>VOC ppbc</i>	<i>VOC/NO<sub>x</sub></i>
6/18/99	600	234	8	243	31
	700	213	11	206	19
	800	235	14	309	22
	900	254	10	118	12
	1000	267	8	160	20
	1100	267	8	221	28
	1200	269	6	261	45
	1300	282	4	156	41
6/30/99	600	352	1	253	275
	700	352	1	243	226
	800	350	2	440	288
	900	352	3	242	76
	1000	354	1	217	215
	1100	353	1	360	355
	1200	346	2	209	92
	1300	354	7	223	34
7/2/99	600	329	3	156	61
	700	322	3	186	74
	800	332	3	146	53
	900	341	3	215	74
	1000	342	3	337	122
	1100	337	2	127	51
	1200	335	2	238	96
	1300	335	4	175	41
7/14/99	600	343		280	
	600	345		313	
	1000	353		183	
	1200	346		200	
7/16/99	600	265	10	387	38
	700	220	13	411	32
	800	265	15	257	17
	900	306	14	121	9
	1000	12	9	137	16
	1100	4	8	132	16
	1200	342	8	144	18
	1300	345	11	71	6
8/11/99	1200	357	2	29	12

## **V. Regional Transport of Ozone**

Past studies have shown evidence of regional transport of ozone contributing to high ozone concentrations detected in San Antonio. To determine the possible origins of transported ozone, backward trajectories were calculated using NOAA's HYSPLIT model. The model regresses the motion of the air parcel from 3 PM CST to 32 hours preceding the arrival of the air parcel. Backward trajectories for the ten days with the highest 8-hour averages at both of the Somerset and Calaveras sites are shown in the Appendix. A trajectory for one of these days was not available because of missing data.

The dates of high ozone occurrences and the origins of the respective air parcels are shown in Table V-1. For many of the days with high ozone concentrations, backward trajectories indicate that the air parcels traveled through the Corpus Christi area before entering the San Antonio region. The trajectories also indicate transport from other areas with moderate to high ozone levels such as East Texas, Dallas-Fort Worth, Houston-Beaumont, and various parts of Louisiana.

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Table V-1. Origins of air parcels arriving in San Antonio for the ten days with the highest peak ozone concentrations (8-hour average concentrations) at the Somerset and Calaveras sites.

Date	Somerset Top Ten Day	Calaveras Top Ten Day	8-hour Average Ozone Concentration (ppbv) (Somerset, Calaveras)	Origins of Air Parcel
8/5/99	*		95, 82	Houston-Beaumont, Louisiana, Corpus Christi
8/16/99	*		88, 67	Houston-Beaumont, Corpus Christi, Dallas-Fort Worth
8/20/99	*		100, 80	Corpus Christi, East Texas
8/21/99	*	*	102, 84	Corpus Christi, Central Texas (Austin-San Antonio corridor)
8/30/99	*		101, 78	Central Texas (Austin-San Antonio corridor)
8/31/99		*	87, 93	Houston-Beaumont, East Texas, Victoria
9/16/99		*	85, 85	Houston-Beaumont, Louisiana
9/18/99		*	82, 84	Corpus Christi, Victoria, Gulf Coast, East Texas
9/19/99	*	*	91, 97	Corpus Christi, Victoria, Gulf Coast
9/20/99		*	84, 98	Corpus Christi, Victoria, Gulf Coast, Houston-Beaumont
10/1/99	*	*	93, 94	Corpus Christi, Victoria, Houston-Beaumont, West Texas
10/5/99	*	*	89, 84	Dallas-Fort Worth, East Texas
10/10/99	*		88, 82	Dallas-Fort Worth, East Texas
10/12/99	*		87, 70	East Texas, Louisiana
10/21/99		*	74, 87	Central Texas, Panhandle

## **REFERENCES**

Allen, D.T., Quigley, C., Strange, W. and Wiedinmyer, C., "Leaf Biomass Density for North Central Texas", Report to the Texas Natural Resource Conservation Commission, September 25, 1997.

USEPA (1989) "Determination of Volatile Organic Compounds (VOCs) in Ambient Air using Summa Passivated Canister Sampling and Gas Chromatographic Analysis" (EPA/600/4-89-017).