AIR QUALITY IN EAST TEXAS

Findings for the 1995-1997 Biennium

from the

University of Texas

FINAL REPORT

Project Number 6100000092-UT between the East Texas Council of Governments and the University of Texas at Austin

October 1997 Revision 1.1

Prepared by

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Date: October 30, 1997

To: NETAC Technical Advisory Committee

From: Mark W. Sweeney, Director of Regional Development and Services

Subject: Final Report and Request for Proposals (RFP)

Attached please find a copy of the *Final Report for the East Texas Monitoring Program* that will be submitted to TNRCC on October 31, 1997. Additional information to be included in Data Volume 3 is also enclosed for your consideration. Please note that the *RFP for the FY* 1998-99 *Air Quality Planning Study* was officially released on October 28, 1997 and was also submitted to the Texas Register for publication. A copy of the final RFP is attached to this memo. If you have any further questions please contact me at (903) 984-8641.

MWS/sp

Attachments

COLLEGE OF ENGINEERING

THE UNIVERSITY OF TEXAS AT AUSTIN

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October 27, 1997

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To: Mark Sweeney East Texas Council of Governments

From: David Allen David Cellon Beckman Professor in Chemical Engineering

Re: Final Report for Project Number 6100000092-UT

I have enclosed the Final Report for the monitoring and data analysis portions of our contract. The revised report responds to all of the comments made by the NETAC Technical Advisory Committee, except as noted in the attachment to this memo. Revisions were only requested for the first of the three volumes of the report. No revisions were requested in the data volumes. Therefore, I have included a revised, unbound version of the first volume, and the final hydrocarbon reactivity calculations, which were missing from volume 3 of the Draft Final Report.

Responses to the Comments from the NETAC Technical Advisory Committee

The revised report incorporates all the suggestions for changes requested by the Technical Advisory Committee, with the following exceptions:

Mr. Jarboe 's Comments:

Comment On page 6, some reference to the fact that 1995 was the hottest year on record for the US should be made in order to give some reference to the unusual circumstances associated with that year.

Response Other reviewers have suggested our analysis be focussed on the data that we have collected. Comparing East Texas ozone levels in 1995 to national data is outside of the scope of the data that we collected and analyzed.

Comment (i)What was the average VOC concentration? (ii)What was the VOC concentration on high ozone days? (iii)What was the most prevalent VOC? (iv)What was the most prevalent highly reactive VOC? (v)Which chemicals most likely contributed most to the formation of ozone in this area? (vi) Are they local, transport or both? *Response* The answers to questions (i), (iii) and (iv) are already in the text or tables. We cannot answer question (ii) because the VOC sampling did not capture all of the high ozone days. Questions (v) and (vi) can only be answered with detailed photochemical modeling.

Comment Sort by maximum ozone formation potential and include observed concentrations.

Response As another reviewer points out, the ozone formation potentials are best used to compare the relative reactivity of individual hydrocarbons within a sample. It is far less valuable in comparing between samples that may be exposed to very different levels of nitrogen oxides. Therefore, the sorting that is requested is an overinterpretation of the data.

Mr. Campbell's Comments:

Comment It is suggested that the report be expanded to include more information on the quantity of volatile organic compounds and nitrogen oxides from major industries as listed in the Point Source Emissions Inventory.

Response The emissions inventory was described in a previous report and was not reproduced in this report.

Comment The report appears to be deficient by not having measurements of ozone concentrations in the air exiting East Texas. It is a known fact that there are many facilities in Harrison, Rusk, and other counties, that are capable of producing the ozone in question. Many of these companies effectively use "stacks" to put pollutants high into the air in order to export them.

Response The budget for this project was only sufficient for one monitoring station. The study plan, approved by the NETAC technical advisory committee, dedicated that site to measuring upwind conditions. Downwind measurements were not part of the study.

Comment There appears to be too much emphasis on what is coming into our region, and not enough on what our local industries are contributing. There is also greater emphasis on volatile organic compounds rather than nitrogen oxides. It appears that our problem will only be solved by concentrating on reducing nitrogen oxides if the report is correct about the VOCs coming from biogenics.

Response There are three separate issues in this comment. One deals with the focus on upwind rather than downwind data. Accurate upwind data are essential inputs for photochemical models, such as the Urban Airshed Model (UAM). The initial round of data

collection described in this report focussed on upwind data so that East Texas could begin UAM analyses. Subsequent data collection could be focussed on collecting downwind measurements and assessing the performance of the modeling.

A second issue raised by the reviewer is the greater emphasis on VOCs rather than nitrogen oxides. The reason for this emphasis was the low levels of nitrogen oxides measured at the Palestine site.

A final issue is that the reviewer suggests that reducing nitrogen oxide emissions will be an effective ozone reduction stmtegy. I encourage all participants in the discussions of air quality in East Texas to recognize that detailed photochemical modeling, with tools such as the UAM, will be required to design ozone reduction strategies.

Mr. Dharmarahjan 's Comments:

Mr. Dharmamjan's specific comments were written into pages of the text. All of his suggestions were incorporated into the final report, with the exceptions noted below.

Comment In the summary and on page 34, the reviewer questions whether photochemical modeling will track individual chemical species.

Response Isoprene is broken out as a separate chemical category in the standard UAM chemistry. Thus, as suggested in the report, isoprene model predictions can be compared to measurements.

Comment In the summary and elsewhere in the report (pages 39, 40), it is suggested that we delete a discussion of the aircraft sampling.

Response Analysis of available aircraft data was specifically requested in our contract. These sections must be retained for us to fulfill our contractual obligations.

Comment On pages 11 and 15, it is suggested that we describe our QA/QC procedures. *Response* The QA/QC procedures are discussed at length in the QA/QC report in the Appendix. All of the calibration data are provided in the data volumes.

Comment On pages 28 and 29, it is suggested that we include time of day in the Tables reporting ozone measurements.

Response We have added most of the supplementary information requested for these Tables. We have not added time of day of the maximum ozone concentration because many of the ozone peaks are very broad and defining a time of day with maximum concentration might or might not be informative, depending on the day. All of the ozone profiles are available in the data volume, so individuals can interpret this aspect of the data as they see fit.

Air Quality Study for East Texas

Source: 1994 and 1995 TNRCC Point Source Emissions Inventories



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SUMMARY

During the summer of 1997, the University of Texas collected air quality data at a number of sites in East Texas. Although ozone levels have been measured for decades in East Texas, there are relatively few measurements available for those constituents which combine to form ozone - NO_x and VOCs. The concentrations of these ozone precursors were measured, along with other air quality data, at one fixed sampling site during the summer of 1997. In addition to the fixed site, air samples were collected on selected days throughout the region.

The sampling programs was designed to answer the following questions.

- Are substantial quantities of ozone and ozone precursors from other regions entering East Texas?
- Is the emissions inventory accurate and complete?

The major findings of the study were:

- On days when high ozone concentrations were observed in East Texas, the air entering the region, based on the prevailing winds, had ozone concentrations that averaged 60 ppb. The air entering the region also contained reactive hydrocarbons and very low levels of nitrogen oxides.
- The concentrations of biogenic hydrocarbons in the air samples, t&n at a variety of locations, were consistent with the estimates made in the emission inventory. In addition, the extensive hydrocarbon sampling done throughout the region will be valuable in establishing the source profiles needed in Urban Airshed Modeling. And, preliminary data from aircraft sampling indicate that these data will be extremely valuable in understanding ozone formation in East Texas when the data are released by Baylor University and the Texas Natural Resource Conservation Commission (TNRCC).

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I. INTRODUCTION

Air quality in East Texas 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 which approaches unhealthful levels over the widest area with the greatest frequency is ozone. Ozone (O_3) 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 crops1. 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 120 parts per billion (ppb). If ozone concentrations, averaged over an hour, exceeded 120 ppb an average of more than once per year over a three year period, then regulations designed to reduce ozone levels would be imposed. As shown in Table I-1, ozone levels exceeded 120 ppb in East Texas 19 times in the 17 year period from 1980 to 1996, with 4 exceedances in the year 1995. In 1997, one additional exceedance was recorded.

Table I-1	Highest ozone	concentrations	observed i	n Fast	Texas from	1980-1997
1 auto 1-1	Ingliest Ozolie	concentrations	UUSCI VCU I	II Last	ICAAS HOIII	1900-1997

Date	Maximum 1 hour
	average ozone concentration
6/21/80	.13 ppm
7/17/80	.14 ppm
6/23/81	.13 ppm
3/1/82	.13 ppm
7/22/82	.15 ppm
8/1/83	.15 ppm
8/15/83	.13 ppm
8/25/83	.16 ppm
9/3/83	.15 ppm
10/8/84	.16 ppm
8/26/85	.13 ppm
8/31/83	.13 ppm
9/5/90	.13 ppm
8/11/92	.129 ppm
8/21/93	.142 ppm
6/20/95	.145 ppm
6/23/95	.145 ppm
7/7/95	.130 ppm
7/18/95	.144 ppm
7/16/97	.139 ppm

¹A separate and distinctly different ozone problem that will not be addressed in this report is the deterioration of the protective ozone layer in the stratosphere (upper atmosphere). The causes and the impacts of the low levels of ozone in the upper atmosphere are very different than the causes and impacts of high levels of ozone in the lower atmosphere. Further, the concentrations of ozone in the upper atmosphere are much higher than would be safe at ground level, so any exchange of ozone between upper and lower atmospheres occurs from the upper atmosphere to the lower atmosphere and is not beneficial.

The high ozone concentrations observed in 1995 renewed concern that East Texas would exceed the NAAQS for ozone. This concern was heightened when, in July, 1997, the U.S. EPA announced a new NAAQS for ozone. The new standard for ozone is complex. It is based on the average ozone concentration over an 8 hour period. The maximum of this 8 hour average is determined for each day (the daily maximum), and these daily maxima are rank ordered for each year. After three years of data have been collected, the 4th highest daily maximum is selected for each of the three years. These three values (4th highest daily maxima for three years) are averaged and the average is compared to the standard of 0.08 parts per million (80 parts per billion). If the average is 84.9 ppb or lower the area is in compliance with the standard. If the average value is 85 ppb or higher, then the area exceeds the standard. The standard is sometimes referred to as a rolling three year average of the fourth highest daily maximum. As shown in Table I-2, ozone levels measured in East Texas have been gradually decreasing over the past 20 years, but are still higher than the new standard.

Table	I-2	Fourth	highest	daily	maximum	ozone	concentrations	in	East	Texas	(8	hour
averag	e)											
(urelir	nina	rv calcu	lation fro	om TN	JRCC, 1997	7)						

Year Journal mights attanty maximum Rothing inference year average 0zone concentration (8 hr. average) (ppb) 1980 99 94 1981 95 95 1982 89 94 1983 93 92 1984 90 91 1985 86 90 1986 7 91 1987 87 91 1988 90 89 1990 89 88 1990 89 89 1991 82 86 1992 80 84 1993 93 85	X	Fourth highest daily maximum	Rolling three year average
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1980	99	94
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1981	95	95
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1982	89	94
19849091198586901986-198787198890891989888819908989199182861992808419939385	1983	93	92
198586901986198787198890198988199089199182199280199393	1984	90	91
1986 1987 87 1988 90 89 1989 88 88 1990 89 89 1991 82 86 1992 80 84 1993 93 85	1985	86	90
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1990 89 89 1991 82 86 1992 80 84 1993 93 85	1989	88	88
1991 82 86 1992 80 84 1993 93 85	1990	89	89
1992 80 84 1993 93 85	1991	82	86
1993 93 85	1992	80	84
	1993	93	85
1994 81 85	1994	81	85
1995 102 92	1995	102	92
1996 83 89	1996	83	89

Because East Texas area has approached both the previous and the new National Ambient Air Quality Standard for ozone, North East Texas Air Care has instituted voluntary programs to reduce emissions that may lead to ozone formation. These initiatives are important not only for preserving human health, but also for preserving the economic vitality of the region. If ozone concentrations exceed standards set by the federal government, mandatory controls would be placed on a wide range of existing and new sources of emissions. Thus, to protect human health and the economy of East Texas, it is essential that voluntary initiatives designed to reduce ozone concentrations be as effective as possible. Determining the effectiveness of ozone reduction strategies is made difficult by the complex chemistry of ozone formation.

Ozone is formed in the lower atmosphere by the reactions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x). The chemistry of ozone formation is controlled by the amounts of NO_x and VOCs present in the atmosphere, the relative reactivity of the VOCs and the nitrogen oxides, and the weather conditions.

In 1997, the University of Texas made measurements of ozone, VOCs and NO_x at an upwind site and VOC concentration measurements over a broad region in East Texas. This report summarizes the progress of this study during the 1997 ozone season (June-October). A parallel report describes progress on emission inventory development.

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II. SCOPE AND OBJECTIVES

During the summer of 1997, the University of Texas collected a air quality data in East Texas. Although ozone levels have been measured for decades in East Texas, there are relatively few measurements available for those constituents which combine to form ozone - NO_x and VOCs. The concentrations of these ozone precursors were measured, along with other air quality data, at one fixed sampling site during the summer of 1997. In addition to the fixed site, air samples were collected on selected days throughout the region. The fixed sampling location is shown in Figure II- 1.

The sampling programs have been designed to answer the following questions.

Are substantial quantities of ozone and ozone precursors from other regions entering East *Texas?* The fixed sampling location used in 1997 was selected, such that on most days, based on prevailing winds, the location would measure the concentration of pollutants in the air entering East Texas. By measuring the concentrations of ozone and ozone precursors in the air entering East Texas, it will be possible to estimate the fraction of the ozone due to emissions of air pollutants in East Texas.

Is the emissions inventory accurate and complete? The measurements of VOCs made at each site will be compared to chemical fingerprints of known emission sources. This comparison will help to determine whether the current inventory of emissions for East Texas is consistent with ambient measurements.

Figure II-1 Sampling locations in East Texas



III. SAMPLING LOCATIONS AND METHODS

III.1 Sampling Locations

The sampling locations selected for this study were chosen to complement existing air quality monitoring done by the TNRCC. The TNRCC installed Longview's Continuous Air Monitoring (CAM) station at Gregg County Airport in 1973. A second CAM monitor was established at Pounds Field in Tyler in 1994. The TNRCC reports the daily maximum concentrations from these ozone monitors to the EPA. The EPA uses the data from these official sites to determine whether East Texas is in attainment of the NAAQS for ozone.

The function of these CAM sites is to determine the maximum ozone concentration for East Texas. The locations for these state monitors were chosen to be generally downwind of emission sources, where the maximum ozone concentrations were anticipated to occur. These two monitors are not designed to provide data on ozone concentrations in the air entering East Texas. In addition, the CAM sites do not provide information on the concentrations of ozone precursors - NO_x and VOCs.

To complement the data collected at the Gregg County and Tyler CAM sites, one fixed sampling site was established and grab samples were collected at approximately ten sites throughout the region. The sampling locations are shown in Figures III-1 and III-2. The fixed site was located at the Palestine airport. The site was selected so that it would measure the concentrations of ozone and ozone precursors entering East Texas when winds were out of the south, the prevailing wind direction for the summer. The plan for the ozone season was to use the Palestine site until the prevailing winds shifted from the south to the north. When the winds began to come out of the north, the site was scheduled to be moved to the municipal airport at Jefferson. During the summer of 1997, however, winds measured at Palestine continued to be largely out of the south through the end of September, and as noted later in this report, the maximum ozone levels recorded at the Palestine site occured in September. Because the prevailing winds continued from the south, the fixed sampling site was kept at Palestine for the entire season.

At the Palestine site, a sampling shed was equipped with monitors for ozone and NO_x , as well as an autosampler for collecting air samples in Meriter canisters. A tower was mounted to the side of the shed. A Young meteorological instrument mounted on the top of the 3 meter tower provided continuous measurements of wind speed and wind direction. The raw voltage outputs from the meteorological instruments were fed into a Campbell 21X

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data logger, which converted the wind speed and direction signals to miles per hour and degrees, respectively. The continuous data from the ozone, chemiluminescent NO_x , and wind instrumentation were also stored in the Campbell Datalogger and downloaded by telephone through a modern. The datalogger was programmed to record 5 minute and hourly averages of ozone, NO, NO₂, NO_x, 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 shed was controlled to 78° F.

The Palestine site, and the two CAM sites operated by the TNRCC formed a network of upwind and downwind monitoring locations, capable of characterizing ozone concentrations in East Texas. The sites operated for the entire 1997 ozone season. Validated data collection began at the Palestine site on June 4, 1997 and ended on October 6, 1997. Table III-1 presents a summary of the technologies that are being used to make the measurements. Sample periods for each measurement are also indicated in Table III-1.

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

Table III- 1: DATA MEASUREMENT METHODS

The monitoring site was designed using the guidelines for a State and Local Air Monitoring Site (SLAMS). As with all SLAMS sites, quantitative objectives for data quality were established. These are listed in Table III-2.

This project, however, will not result in data to be used to determine attainment of National Ambient Air Quality Standards. More details concerning data quality objectives can be found in the Appendix containing the Quality Assurance Project Plan.

Measurement	Method detection Limit	Accuracy	Precision	Completeness
O ₃	1.0 ppbv	90 to 110 %	<u>+</u> 10%	80%
NO and NO _x	1.0 ppbv	80 to 120%	<u>+</u> 20%	80%
Hydrocarbons	2.5 ppbc (1)	75 to 125%	<u>+</u> 25%	80%
Wind Speed	1.0 m/s	$\pm 1 \text{ m/s}(2)$	$\pm 2 \text{ m/s}(3)$	80%
Wind Direction	not applicable	<u>+</u> 10 °	<u>+</u> 20 °	80%

Table 111-2. DATA QUALITY OBJECTIVES

(1) this quality objective is based on the worst case hydrocarbon

(2) based on differences with intercomparison instruments - accuracy data for these measurements are not part of the contract.

(3) based on root mean squared differences with intercomparison instruments - accuracy data for these measurements are not part of the contract.





Figure III-2 Locations at which grab samples were collected (Points 10, 11, 12, 13,23, 47,55,57, downtown Longview and 10 mi west of Tyler)



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III.2 Sampling Methods

111.2.1 Ozone (0^3) and Nitrogen Oxides (NO_x)

 O_3 , 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 5.0 pm teflon filter placed near the instrument inlet.

Nitric oxide concentrations were measured by O_3 , 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 effected 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-3 and 111-4. 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, calibration was performed by titrating the NO with controlled amounts of ozone. Ozone used in the calibrations was from a Dasibi Model 1000 ozone transfer standard. 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.

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Final Report for the East Texas Monitoring Program





Datalogger (Ozone ppb field reading)



Datalogger (Ozone ppb field reading)

Revision 1.1





Revision 1.1

111.2.2 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 at Palestine were collected on an hourly basis by using an autosampler which was designed by the TNRCC and built by the University of Texas. The grab samples were collected by opening an evacuated canister. A schematic of an autosampler is presented in Figure 111-5.





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 gage and connected to the autosampler device. The flow into the canisters ocurred by virtue of the pressure difference between ambient conditions and the vacuum initially in the canisters. Ambient air was drawn through silica sealed tubing and the mass flow controlled autosampler. 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 gage 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 cryofocusser, 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. Ultra-pure nitrogen, purchased from Wilson Oxygen, 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 ultra-pure 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 ultra-pure nitrogen drawn into the canister, based on the pressure transducer readings. The gage pressure in the canisters after doubling was close to 14.7 psig.

Cryofocussing 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. A Tekmar Aerocan/Desorber/Cryofocuser (A/D/C) drew a 100 milliliter sample of the canister volume, and mixed the sample with a 100 millilitervolume of an internal 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

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-185 °C, drew off the overhead gases, and reheated the mixture. By repeating this sequence three times, the A/D/C decreased the volume of the original 200 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 589OA gas chromatogmph (GC) equipped with a flame ionization detector (FID) or a 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 111-3, which allowed for optimum separation of peaks while minimizing the total run time.

initial temperature (°C)	final temperature (°C)	temperahue ramp (°C/min)	holding time at final temperature (min)
20	20	0	5
20	120	10	0
120	160	4	2
120	100	4	2

This temperature schedule was determined by repetitively running a 57 component hydrocarbon mixture on the chemical analysis system, while changing initial and final temperatures, ramping rates and holding times. This 57 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 EZChrom V4.0 software. A chromatogram for a single sample, taken in Palestine, typically had 20-30 peaks which were over a threshold intensity. A typical chromatogram is shown in Figure 111-6. These chromatograms were converted into estimates of VOC concentrations using the calibration methods outlined below. Over the course of analyzing the samples taken during the 1997 East Texas Study, approximately 100 different peaks (representing different compounds) were identified.

The GC system used for hydrocarbon analysis was calibrated using a single internal

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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 5 ppbv each of 1,2-dichlorotetmfluoroethane (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 57 hydrocarbon species which ranged in molecular weight from ethane to undecane. In the original mixture, each component was present at a known concentration, which varied from component to component, but was approximately 1 ppmv. A complete listing of the hydrocarbons for which the GC was calibrated can be found in Table 111-4, listed according to their elution order and peak number assignment. The breaks in the numbering scheme represent species which were found in the ambient samples but were not in the 57 component standard. Five standard dilutions of the 57 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 57 component standard are listed in Table III-5

Calibrations were also performed for a few additional compounds. These compounds were primarily oxygenated hydrocarbons such as aldehydes, ketones and alcohols. The standards for these species were also obtained from TNRCC and the calibration procedures were the same as for the 57 compound hydrocarbon mixture.

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Peak Number	Compound Name	Peak	Compound Name
INUIIIDEI	Compound Name	Inullidei	Compound Name
2	ethylene / acetylene	49	2,3-dimethylpentane
3	ethane	52	benzene
4	propylene	54	cyclohexane
5	propane	55	2-methylhexane
7	isobutane	56	2,3-dimethylpentane
11	1-butene	57	3-methylhexane
12	n-butane	58	2,2,4-trimethylpentane
13	t-2-butene	60	n-heptane
16	c-Zbutene	63	methylcyclohexane
18	3-methyl-1-butene	65	2,3,4_trimethylpentane
21	isopentane	66	toluene
23	1-pentene	67	2-methylheptane
24	n-pentane	68	3-methylheptane
25	isoprene	70	n-octane
26	t-2-pentene	71	ethylbenzene
27	c-Zpentene	72	pxylene
28	2-methyl-2-butene	75	styrene
30	2,2-dimethylbutane	76	o-xylene
33	4-methyl- 1-pentene	77	n-nonane
34	cyclopentane	79	isopropylbenzene
35	2,3-dimethylbutane	83	n-propylbenzene
37	2-methylpentane	84	a-pinene
41	3-methylpentane	85	1,3,5~trimethylbenzene
43	2-methyl- 1-pentene	89	1.2.4-trimethylbenzene
44	n-hexañe	91	decane
45	trans-2-hexene	94	b-pinene
46	cis-2-hexene	98	undecane
47	methylcyclopentane		

Table 111-4. Hydrocarbon species in the calibration mixture for the GC/FID analysis system

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Figure III-6 Typical chromatogram of ambient air sample

Palestine

7-16-97, 9em-10em



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standard	average concentration of each component		
1	5 ppbv		
2	10 ppbv		
3	20 ppbv		
4	20 ppbv		
5	25 ppbv		

 Table 111-5.
 Concentration of Individual Hydrocarbons in Calibration Standards

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 .97 for the calibration was considered acceptable.

To convert the peaks in the chromatogmm into estimates of hydrocarbon concentrations, the area associated with each peak in the chromatogam was determined. The area for each peak was converted into concentration using the appropriate calibration curve determined using the standards described in Table 111-5. For compounds that were not in the calibration mixture, a calibration derived by averaging all the standard species was used.

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 prefered 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 chromatogmm to confirm that equipment failures had not occured 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 proceedure had to be high, considering that the ambient hydrocarbon concentrations were on the order of a part per billion by volume. A

TNRCC cleaning protocol was followed closely. A schematic of the cleaning apparatus is displayed in Figure 111-7.



Figure 111-7. Schematic of Canister Cleaning Apparatus

The apparatus could accomodate up to six canisters; cleaning took approximately 3 hours to complete. Prior to cleaning, the canisters were emptied of their ambient sample contents to a fume. hood, and 100 μ 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 ultra-pure nitrogen gas to 30 psi, and purged using a Varian SD200 compressor to 29.4 inches Hg. The first and fourth cycles called for combined filling and heating of the canisters till they were hot to the touch and at 30 psi (to volatilize all water in the canisters), in addition to extended purges of approximately 45 minutes in duration. The second and third cycles called for filling of the canisters to 30 psi with ultra-pure nitrogen followed by immediate purging of the canisters to 29.4 inches Hg (approximately 5 minutes). At the end of the last cycle, each canister is removed from the cleaning apparatus, injected with 100 μ L of water, and set aside ready for sampling.

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. A sample form is provided in the Appendix. The completed forms are maintained in a study archive.

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III.3 Sampling Schedule

The air quality measurements were made from June 4 through October 6, 1997. Continuous monitoring for ozone, NO,, wind speed, and wind direction was performed at Palestine twenty-four hours a day, every day for the bulk of the ozone season. Although data monitoring and collection was continuous, some data were lost due to data system problems, and routine calibrations. These limited data gaps are noted in the Appendix.

For the VOCs, intensive sampling was conducted on selected days. Table III-6 shows the intensive sampling days for the Palestine site. Grab samples were also collected at a variety of sites in the region. These are described in Table 111-7.

Date (day of week)	Sampling periods	
7/11/97 (Friday)	6-7am, 7-&m, 8-9am, 9-10am, 10-1 lam, 1 1-12n, 12-1pm	
7/16/97 (Wednesday)	6-7am, 7-8am, 8-9am, 9-10am, 10-1 lam, 1 1-12n, 12-1pm, 1-2pm	
7123197 (Wednesday)	6am-2pm, 2-10pm, 10pm-6am	
7/24/97 (Thursday)	6am-2pm, 2- 10pm	
7/25/97 (Friday)	6am-2pm, 2- 10pm	
8/13/97 (Wednesday)	1 lam, 12n, 1:30pm, 2pm (grab samples at Palestine)	
8114197 (Thursday)	6-7am, 7-8am, 8-9am, 9-10am, 10-11am, 12-1pm, 1-2pm	
8/27/97 (Wednesday)	6-7am, 7-8am, 8-9am, 9-10am, 10- 1 lam, 1 1- 12n, 12- lpm, 1-2pm	

Table III-6 Sampling days for VOC analyses at the Palestine site

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Date	Sampling time	Location		
8/26/97	10:45am	10 miles west of Tyler on Hwy 3 1		
8/26/97	10:05am	Hwy 31 and Hwy 198		
8/26/97	11:45am	Longview Cobb Activity Center		
8/26/97	3:40pm	0.5 mi north of Texas Eastman		
8/26/97	3:40pm	0.5 mi north of Texas Eastman		
9/26/97	1pm	LaGloria Oil & Gas		
9/26/97	1pm	LaGloria Oil & Gas		
9/26/97	1: 13am	Palestine site		
9/26/97	7:35am	Palestine site		
9/26/97	4:32pm	Stroh Brewery		
9/26/97	4:33pm	Stroh Brewery		
9/26/97	3:45pm	Trident NGC		
9/26/97	7:OOpm	Hwy 350 and Hwy 79		
9/26/97	6: 15pm	Hwy 4602 and Hwy 2274 (near 279 and Summer-field)		
9/26/97	5:15pm	42 and Brightwell (outside Kilgore)		
9/26/97	5:50pm	15 mi from 42 and Brightwell (Oil pumps)		
9/26/97	4:15pm	American National Can		
9/26/97	4:15pm	American National Can		
9/26/97	6:45pm	FM 747 and CR 3218 near 79		
9/26/97	5:30pm	Exxon Gas Plant		
9/26/97	5:35pm	Exxon Gas Plant		
9/26/97	1: 15pm	Bonar Packaging		
9/26/97	11:30am	CR 3402 and Hwy 31		
9/26/97	3:46pm	Warren Petrochemical		
9/26/97	2:37pm	Petrol ite Corporation		
9/26/97	2:45pm	Petrolite Corporation		

 Table III7
 Sampling days and locations for grab samples

8/26/97 was a Tuesday; 9/26/97 was a Friday

IV. RESULTS AND DISCUSSION

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

IV.1 Ozone Concentrations in East Texas and Regional Transport of Ozone

One objective of this study was to compare the concentrations of ozone measured at the Palestine site to ozone concentrations measured at the Gregg County and Tyler CAM sites. Of particular concern are the dates of high ozone concentration recorded at the CAM sites. The 10 days with the highest ozone concentrations measured at Gregg County airport are listed in Table IV- 1. Also listed are the wind direction, the ozone concentrations measured on the same day and the prior day at the Palestine site.

Date	Ozone (ppb) Ozone (ppb)		Ozone (ppb)	Ozone (ppb) at	Average Wind
	Gregg Co.	at Tyler	atPalestine	Palestine on	direction
	TNRCC site	TNRCC site		previous day	
Wed. 7/16/97	139	59	65	70	light and var.
Sun. 7/27/97	124	64	54	47	Sto SE
Tues. 7/29/97	122	94	77	54	S to SE
Fri. 7/18/97	117	91	60	64	SE
Thurs. 7/24/97	111	64	65	54	S
Mon. 7/28/97	110	74	54	54	S to SE
Wed. 6/25/97	110	65	44	39	Sto SE
Mon. 7/14/97	106	56	49	48	S to SE
Tues. 9/2/97	106	76	63	84	E
Sat. 7/19/97	102	77	60	60	SE

Table IV-1 Days with high ozone concentrations, measured at Gregg County airport

The results in Table IV-1 indicate that ozone transported into the region and emissions within East Texas can both have large influences on maximum ozone levels in Fast Texas. For days with high ozone levels at the Gregg County Airport, the upwind sites generally measured ozone concentrations averaging more than 60 ppb. For some high ozone events, such as the July 29 episode, ozone levels at Palestine approached 80 ppb, with additional ozone formation potential available in the ozone precursors transported along with the

ozone. In contrast, for the June 25 episode, the ozone levels recorded at Palestine are low relative to the Gregg County concentrations.

Another way to examine the data is to consider the days when the Palestine site indicated high regional levels of ozone. Table IV-2 provides data for the 10 days with the highest ozone concentrations, at the Palestine site.

Date	<i>Ozone (ppb) at</i> Palestine site	Ozone (ppb) at Gregg Co. TNRCC site	Ozone (ppb) at Tyler TNRCC site	<i>Ozone (ppb) at</i> TNRCC site on following day	Average wind direction
9/1/97	84	90	83	106	Е
9/9/97	81	97	94	66	SE/N/SE
8/31/97	79	71	81	91	StoSE
8/1/97	78	59	91	64	E
9/28/97	77	97	92		StoSE
7/29/97	77	122	94	73	S toSE
8/21/97	76	87	87	41	S toSE
7/31/97	75	92	94	59	NE
9/5/97	75	67	76	86	E
8/5/97	71	87	101	78	StoSE

Table IV-2 Days with high regional ozone concentrations, measured at Palestine

Most of the days with high regional concentrations of ozone occured in August and September. These days were only occasionally associated with high ozone levels recorded at the Gregg County airport.

To summarize, a major objective of this study was to quantify the transport of ozone into East Texas, and to assess the relative contribution from local emissions to maximum ozone concentrations in East Texas. While photochemical modeling of individual episodes will be necessary for detailed interpretation, several findings are clear.

The levels of ozone at a site upwind of East Texas (based on prevailing winds) are frequently greater than the commonly assumed value of 40 ppb. A summary of the data for 1997 are shown in Figure IV-1. Table IV- 1 shows that on days when high ozone concentrations were measured at Gregg County airport, regional ozone levels recorded

- at Palestine were, on average, approximately 60 ppb. Maximum ozone concentrations at Tyler on these same days averaged slightly over 70 ppb.
- •On days when high concentrations of ozone were recorded at Palestine, the high values frequently persisted well into the night, indicating that the high ozone levels were a regional phenomenon on these days. These high regional ozone levels were not frequently associated with the highest ozone concentrations at the Gregg County airport, however.

Figure IV-1 Maximum daily ozone concentrations (1 hour average) recorded at the Palestine site



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IV.2 Ozone precursor concentrations

The previous section compared concentrations of ozone measured at a rural, upwind site to concentrations of ozone measured at the Gregg County airport. The goal of these comparisons was to assess the extent of regional transport of ozone into East Texas. Ozone is not the only species that can be transported on a regional scale, however. Ozone precursors, NO_x and VOCs, can also be transported. This section will report on regional background levels of NO_x and VOCs and will report on concentrations of VOCs throughout the region.

IV.2.1 Nitrogen oxides (NOx)

Concentrations of NO, NO_2 , and NO_x were measured at the Palestine site. As shown in the Appendix, NO_x concentrations at the Palestine site were typically very low, less than 10ppb. These values are similar to other nitrogen oxide measurements made at rural sites in eastern Texas by the University of Texas. Occasional concentrations in excess of 10 ppb were recorded but no patterns were evident in the measurements and these short concentration spikes may have been due to runway activity at the airport.

IV.2.2 VOC Sampling and Analysis

In contrast to the low regional background levels observed for NO_x the regional background levels for VOCs were significant. This was expected because the emission inventory for East Texas indicates high regional emissions of VOCs from vegetation (primarily trees) and the long atmospheric lifetimes of some hydrocarbons allow transport over long distances.

During the summer of 1997, approximately 80 air samples were collected and analyzed for VOC concentrations. These samples were of two types. One set of samples was collected at the Palestine site to characterize regional background levels, particularly for biogenic emissions (from vegetation). A second set of samples was collected near some of the major hydrocarbon sources in East Texas. The purpose of these samples was to allow for a performance evaluation of the emission inventory.

Most Commonly Detected Hydrocarbon Species at the Palestine site A total of over 100 different hydrocarbon species have been detected in the air samples. There are a smaller

number of hydrocarbons that were common to many samples, regardless of wind direction and speed, and the time of day. A list of these commonly detected species are listed in Table IV-3. A compilation of the data collected is provided in the Appendix.

			Overall			
			Frequency		Avo	a
RT (min)	Peak ID	Compound	Out of 40 Avg	Area Co	nc(ppb	v)
2.808	3	ethane	29	4995		23.7
3.083	?	?	39	5286	-	
3.358	?	?	37	683	-	
3.525	9	isobutane/ISTD 1	40	1011		0.8
3.575	9b	acetaldehyde	38	13137		24.6
3.75	11	1 -butene	39	6955		4.5
3.9	?	?	39	3504	-	
4.175	?	?	24	1412	-	
4.967	19	ethanol	21	1496		3.7
5.083	?	?	25	518	-	
5.233	20b	2-propanal	39	2779		4.3
5.35	21	isopentane	40	2814		1.6
5.508	?	?	39	16065	-	
5.758	23	1 -pentene	39	2245		1.2
6.083	24	n-pentane	39	1788		1.6
6.225	25	isoprene	39	2400		1.4
6.992	?	?	39	804	-	
7.9	33	4-methyl-1 -pentene	38	1212		0.6
8.242	35	2,3-dimethylbutane	25	1029		0.8
8.383	37	2-methylpentane	26	981		0.5
8.475	38	?	37	2237	-	
8.6	40	butylaldehyde	40	1666		1.6
8.858	41	3-methylpentane	35	2851		1.2
9.467	44	n-hexane	37	1045		0.5
10.458	49	2,4-dimethylpentane	24	1125		0.4
11.15	52	benzene	39	1194		0.9
11.367	?	?	33	1176	-	
11.825	56	2,3-dimethylpentane	32	1442		0.9
12.017	57	3-methylhexane	36	1026		0.4
12.4	58	2,2,Ctrimethylpentane	39	3422		1.2
12.625	59	ISTD 2 - aaa-TFT	40	28971	-	
13.042	61	?	40	895	-	
13.708	?	?	23	944	-	
14.192	65	2,3,4-trimethylpentane	32	1583		0.6
14.333	66	toluene	40	2902		1.8
14.608	67	2-methylheptane	22	1020		0.4
17.108	72	p-xylene	20	857		0.3
18.408	78	ISTD 3 - 4-BFB	40	15044	-	
19.208	81	benzaldehyde	40	1284		0.6
20.658	89	1,2,4-trimethylbenzene	39	1011		0.4

Table IV-3 Most commonly detected hydrocarbon species at the Palestine site.

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The commonly detected species include biogenics (e.g., isoprene), inert hydrocarbons that can be transported over long distances (e.g., ethane), products of photochemical reactions (e.g., propanal, benzaldehyde) and reactive aromatics that are likely the result of ubiquitous automotive emissions (e.g., toluene, trimethybenzene). The average concentration of identified species was approximately 80ppb, 250 ppbC.

Table IV-3 lists hydrocarbon species commonly found at high concentration. Although most of the common species were in the VOC calibration mixture and could therefore be identified immediately, approximately 25% of the compounds have not been identified. It is likely that at least some of these unknowns are functionalized hydrocarbons. Among the identified species, the peak number is consistent with the peak listing in Section III. Because the data acquisition system was calibrated to be able to identify and quantify these species, their concentrations are also known, within ± 0.15 ppbv.

Biogenic hydrocarbons Of the hundred or so hydrocarbon species detected in the samples collected at Palestine and throughout East Texas, some of the most significant are appinene, and isoprene. These three compounds are emitted in significant quantities by vegetation and are believed to constitute approximately 80% of the hydrocarbon emissions in the five county East Texas area. Based on emission inventory calculations done for North Central Texas by the University of Texas (Allen, et al., 1997), it is anticipated that most of the biogenic emissions will be isoprene from deciduous trees. Therefore, isoprene should be detected and was detected in virtually every sample collected. The concentrations observed in the samples ranged'from a few ppbC to more than 10 ppbC.

Ideally, the isoprene concentrations would be compared directly to the emission inventory estimates. The first step in such a comparison would be to obtain a detailed spatial distribution of isoprene emissions. This is necessary because isoprene is emitted in widely varying amounts by different tree species, and tree species distributions can vary widely. Mappings of species distributions and isoprene emissions for the Palestine area have been performed by the University of Texas for the Texas Natural Resource Conservation Commission (Allen, et al., 1997) and are given in Figures IV-2 and IV-3. Converting these emission estimates into isoprene concentration estimates would require detailed dispersion modeling that accounted for the reactivity of isoprene. Such modeling is outside

the scope of this project, however, an indirect comparison can be made based on data for Houston. The biogenics emission inventory for Harris County has been estimated to be approximately 370 tons/day (as compared to approximately 550 tons/day for the 5 county East Texas region). Measured isoprene concentrations in Harris County generally peaked at slightly below 10ppbC and agreed with values predicted based on the emissions inventory and the Urban Airshed Model within a factor of 2. These data from Houston indicate that the isoprene measurements of approximately 10 ppbC made throughout East Texas are generally consistent with the preliminary emission inventory. Urban Airshed Modeling will be required to perform more detailed comparisons.

Hydrocarbon reactivity The detailed composition of VOCs can be used to evaluate the performance of the emission inventory, as noted in the discussion of biogenic emissions. It can also be of value in assessing the overall ozone formation potential of the hydrocarbons. The ozone formation potential of hydrocarbons can be evaluated in a number of ways. The method used in this report relies on the Maximum Incremental Reactivity(MIR), as defined by Carter (1994). The MIR is an estimate of the amount of ozone that could be formed by a hydrocarbon, if it were contacted with the precise concentration of nitrogen oxides that would yield the maximum amount of ozone under typical urban' conditions. In this sense, it is an upper bound on the ozone formation' potential of a hydrocarbon, since most of the hydrocarbons will not encounter precisely the correct amount of nitrogen oxides to yield the maximum amount of ozone. Because of this limitation, the ozone formation potential should be used to interpret the relative reactivities within a single sample. They should not be used to compare samples or to estimate actual ozone formation.

Despite these limitations, the importance of considering reactivity, rather than just concentration, is evident from the data in Table IV-4. The mass of ozone formed per unit mass of hydrocarbon can vary from as low as 0.25 to more than 10. So, some hydrocarbons are 40 times more potent than others in forming ozone. Among the most reactive species are the aromatics (generally associated with liquid fuels) and the biogenics.





Counties **ULC** Legend Crops Outside Domain Bosque County Crops Clay County Crops Collin County Crops Cooke County Crops Coryell County Crops Dallas County Crops Denton County Crops Ellis County Crops Erath County Crops Famin County Crops Grayson County Crops Hamilton County Crops Hill County Crops Hunt County Crops Jack County Crops Johnson County Crops Kaufman County Crops Lampasas County Crops Limestone County Crops McLennan County Crops Milam County Crops Montague County Crops Navarro County Crops Parker County Crops Robertson County Crops Rockwall County Crops Tarrant County Crops Wise County Crops Ashe Juniper Parks/Woods Bluestem Grass Cottonwood-Hackberry-Saltcedar Bald Cypress-Water Tupelo Swamp Elm-Hackberry Grass Forest Live Oak-Ashe Juniper parks Live Oak-Ashe Juniper Woods Live Oak-Ashe Juniper Parks Live Oak-Mesquite-Ashe Juniper Parks Marsh Barrier Mesquite-Lotebush Brush Mesquite Brush Oak-Mesquite-Juniper Parks/Woods Other Pecan Elm Pine-Hardwood Forest Post Oak Parks/Woods Post Oak Woods, Forest, and Grassland Post Oak Wood/Forest Silver-Bluestem-Texas Wintergrass Urban or Water Willow Oak-Water Oak-Blackgum Forest Water Oak-Elm-Hackberry Forest Residential Office Retail Institutional Hotel-Motel Industrial Transportation and Communication Roadway Utilities Airport Parks and Recreation Landfill Construction Flood Control



Figure IV-3. Distribution of isoprene emissions near Palestine

Isoprene Emission Rates Using BEIS3.0 Emission Factors



Isoprene Emission Rates ton/day/grid cell



Grid Cell Dimensions: 4 km x 4km Emission Factors taken for: 1700 umol/m2/s 34 oC

Peak Number	Compound Name	Maximum Ozone Formation Potential (g ozone/g VOC)
0	othylong / gootylong	74
2	ethylene / acetylene	0.25
3		9.4
4	ргоруше	0.48
5	propane	1.21
/	1 butene	8.9
11	n butana	1.02
12	t 2 butene	10.0
15	c Zbutene	10.0
10	3 methyl 1 hutene	6.2
18	jsopentane	1.38
21	1 pontono	6.2
25	n pentane	1.04
24	isoprope	9.1
25	t_2pentene	8.8
20	c-2pentene	8.8
28	2-methyl_2-butene	6.4
20	2 - dimethylbutane	0.82
30	4-methyl- 1-pentene	
34	cyclopentane	2.4
35	2.3 dimethylbutane	1.07
33	2,5_uniterryroutane 2-methylpentane	1.5
37 41	3-methylpentane	1.5
41	2-methyl- 1-pentene	_
4 5 ЛЛ	n-hexane	0.98
45	trans-2-hexene	6.7
46	cis-2-hexene	6.7
40	methylcyclopentane	2.8
47	2 3-dimethylpentane	1.31
52	benzene	0.42
54	cyclohexane	1.28
55	2-methylhexane	1.08
56	2.3-dimethylpentane	1.31
57	3-methylhexane	1.40
58	2.2.4-trimethylpentane	0.93
60	n-heptane	0.81
63	methylcyclohexane	1.8
65	2.3.4-trimethylpentane	1.6
66	toluene	2.7
67	2-methylheptane	0.96
68	3-methylheptane	0.99
70	n-octane	0.60
71	ethylbenzene	2.7
72	p-xylene	6.6
75	styrene	2.2

Table IV-4.Maximum Incremental Ozone Formation Potential for Identified Hydrocarbons

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76	oxylene	6.5	
77	n-nonane	0.54	
79	isopropylbenzene	2.2	
83	n-propylbenzene	2.1	
84	a-pinene	3.3	
85	13.5-trimethylbenzene	10.1	
89	1.2.4-trimethylbenzene	8.8	
91	decane	0.46	
94	b-pinene	4.4	
98	undecane	0.42	

The MIR values shown in Table IV-4 were used to predict the ozone formation potential of each of the hydrocarbon samples. The complete results are presented in the Appendix and can be used to assess the relative reactivities of individual hydrocarbons within a sample.

V. AIRCRAFT SAMPLING

The Texas Natural Resource Conservation Commission has funded Baylor University to conduct aircraft sampling of ozone and ozone precursors in the East Texas area. Baylor University and the TNRCC have not yet validated the data and therefore the full data are not yet available. The TNRCC was willing to release, however, brief descriptions of the aircraft flights and the maximum ozone concentrations measured on some of those flights. Through the end of August (the most current data available), 8 flights had been performed in the East Texas region. A summary of the limited available data is given in Table V- 1.

Date	Location of flight (as described by Baylor)	Maximum ozone concentration measured (ppb)
5/16/97	Tyler/Longview/Marshall	not reported
7/17/97	Tyler/Longview/Marshall	130
7/20/97	Arlington/ Tyler/Iongview/Marshall	113
7/25/97	Tyler/Longview/Marshall	118
8/2/97	Northeast Texas	130
8/24/97	TylerLongviewlMarshall	not reported
8/25/97	Power Plants	not reported
8/28/97	Tyler/Longview/Marshall	not reported

Table V-1 Aircraft sampling data as reported by Baylor and the TNRCC

More complete data for some of these flights would be of great value in understanding ozone formation in East Texas. For example, the flight on 7/17/97 was performed the day after the Gregg County monitor recorded an ozone concentration of 139 ppb - the highest value of the season. The data from the 7/17/97 flight could be used to assess the geographical extent of the high ozone values. The data on 7/13/97 were taken during an episode of continental haze. While ozone levels were high at Gregg County during this period (117 and 102 ppb on 7/18 and 7/19), the ozone concentrations at Palestine were low. It would be useful to know how far south the boundary of the high ozone concentrations reached.

VI. FINDINGS

During 1997, an extensive body of data was collected on air pollutant concentrations in East Texas. Analysis of these data has led to the following conclusions.

On days when high ozone concentrations were observed in East Texas, the air at a site upwind of the region (based on prevailing winds) had ozone concentrations that averaged 60 ppb. The air at this site also contained reactive hydrocarbons and very low levels of nitrogen oxides.

The concentrations of biogenic hydrocarbons irl air samples collected throughout the region were consistent with the estimates made in the emission inventory.

In addition, extensive hydrocarbon sampling was done throughout the region. These data will be valuable in establishing the source profiles needed in Urban Airshed Modeling. And, preliminary data from aircraft sampling indicate that these data will be extremely valuable in understanding ozone formation in East Texas when they are released by Baylor and the TNRCC.

VII. IMPLICATIONS FOR FUTURE STUDIES

Recommendations for future studies are as follows:

- 1. Urban Airshed Modeling for East Texas is recommended to quantitatively examine the effect that local emission reductions will have on maximum ozone concentrations,
- 2. The installation of additional permanent monitors in rural locations is recommended to allow accurate determinations of upwind inputs and downwind impacts, and
- 3. Concentrations of VOCs, nitrogen oxides and other air quality data should be made at the Gregg County airport, particularly during periods with high ozone concentrations.

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.

Carter, W. P. L., "Development of Ozone Reactivity Scales for Volatile Organic Compounds", *Journal of the Air and Waste Management Association*, 44, 881-899 (1994).

National Research Council (1991) <u>Rethinking The Ozone Problem in Urban</u> and Regional Air Pollution, National Academy Press, Washington, D.C.

TNRCC (1997) personal communication.

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).

Appendices

Appendix 1: Air Quality Data Appendix 2: Quality Assurance Project Plan

Appendix 1: Air Quality Data

Approximately 500 pages of data are available as separate attachments

Appendix 2: Quality Assurance Project Plan

QUALITY ASSURANCE PROJECT PLAN

for the

EAST TEXAS NEAR NON-ATTAINMENT AREA STUDY (AMBIENT MONITORING COMPONENT)

Project Number 610000092-UT between the East Texas Council of Governments and the University of Texas at Austin

> March 1997 Revision 1.3

Prepared by

Professor David Allen Department of Chemical Engineering The University of Texas at Austin Austin, Texas 78712 (tel. 512-471-0049) (fax 512-471-7060) email allen@che.utexas.edu

TEXAS NATURAL RESOURCE CONSERVATION COMMISSION

ProtectingTexas by Reducing and Preventing Pollution

July 10, 1997

David T. Allen, Ph.D., P.E. Professor of Chemical Engineering University of Texas at Austin Chemical Engineering Bldg. 3.462 Austin, Texas 787 12-O 162

Dear Dr. Allen:

On April 3, 1997, the Texas Natural Resource Conservation Commission (TNRCC) received the Quality Assurance Project Plan (QAPP) for the East Texas Near Non-Attainment Area Study (Ambient Monitoring Component), version 1.3, dated March 1997. This plan is expected to address quality measures for the ambient air measurement support work expected to be conducted during May 1997 to August 1997.

I reviewed the plan on April 10, 1997 and find that the plan complies with the functional requirements of the U.S. Environmental Protection Agency (EPA) QA/R5 guidance document as specified in the contract requirements. It is noted that the measurement program, as planned, will not be in compliance with some aspects of 40CFR58 specifications and guidance. Since the measurement dataset you are gathering is intended for general information about the potential factors influencing ozone formation and transport in a specific geographical area and are not to be considered for regulatory compliance or inclusion in the National Aerometric Information Retrieval System (AIRS) database, the exceptions to the 40CFR58 specifications that you have noted in the QAPP should not compromise the utility of the dataset for the intended purpose.

TNRCC will accept and approve the QAPP as it is currently constructed and will use the data gathered during the 1997 monitoring season to evaluate the representativeness of the plan for continued use in the 1998 monitoring season. Should you have any questions or concerns, please contact me.

My apology for the delay in conveying formal written approval of the QAPP.

Sincerely he Ken Kozacky Quality Assurance Coordinator

Quality Assurance Project Plan Approval Form

Approved by:

Roger Ramon
Field and Laboratory Activities Leader
The University of Texas at Austin

Chris Quigley Project Quality Assurance Officer The University of Texas at Austin

David Allen Program Director The University of Texas at Austin

Ken Rozacky Quality Coordinator - Monitoring Operations Division Texas Natural Resource Conservation Commission

Division Director - Monitoring Operations Division

Texas Natural Resource Conservation Commission

Doyle Pendleton

2

Date

Date

Date

Date

Dale

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Section A3 Distribution List

DISTRIBUTION LIST

EAST TEXAS COUNCIL OF GOVERNMENTS

Mark Sweeney, East Texas Council of Governments, 3800 Stone Road, Kilgore, Texas 75662

NORTH EAST TEXAS AIR CARE

Gene Dworsky, Northeast Texas Air Care, P.O. Box 7444, Longview, Texas 75607

TEXAS NATURAL RESOURCE CONSERVATION COMMISSION

Doyle Pendleton, Texas Natural Resource Conservation Commission, P.O. Box 13087, Austin, Texas 7871 I-3087

Jim Price, Texas Natural Resource Conservation Commission, P.O. Box 13087, Austin, Texas 787 11-3087

Ken Rozacky, Texas Natural Resource Conservation Commission, P.O. Box 13087, Austin, Texas 7871 1-3087

THE UNIVERSITY OF TEXAS AT AUSTIN

David Alien, The University of Texas. Center for Energy Studies, Pickle Research Campus, Building 133. 10100 Bumet Road, Austin. Texas 78758

Roger Ramon, The University of Texas, Center for Energy Studies, Pickle Research Campus. Building 133. 10100 Bumet Road. Austin. Texas 78758

Chris Quigley, The University of Texas, Center for Energy Studies, Pickle Research Campus, Building 133. 10100 Burner Road, Austin. Texas 78758

Section A4 Project Organization

PROJECT ORGANIZATION

An organization diagram for the project is given in Figure A4- 1. Individual responsibilities are outlined below.

A4.1 Project Sponsor

The sponsor of the project is the East Texas Council of Governments, which has received funding from the Texas Natural Resource Conservation Commission (TNRCC) to inventory emissions and to perform air quality monitoring. This Quality Assurance Project Plan (QAPP) deals with the monitoring component of the study. A separate QAPP has dealt with the emission inventory.

A4.2 Project Coordinator

The coordinator of the project is Professor David Allen of the University of Texas at Austin. He will coordinate the development of the QAPP, the development and distribution of reports, and all sampling activities.

A4.3 Project Review

Mark Sweeney of the East Texas Council of Governments (ETCOG) will review project planning materials and reports.

A4.4 Field and Laboratory Activities Leader

Roger Ramon of the University of Texas at Austin will be responsible for field and laboratory activities, including maintaining equipment, maintaining records, coordinating data transfer, coordinating equipment operation, developing operating procedures, and assuring that QAPP requirements are met.

A4.5 Field and Laboratory Support

Dae Kim, Tamara Stiner. Christine Wiedinmyer and Beth Wittig, all of the University of Texas at Austin, will provide technical support and documentation of all sampling and analytical activities. They will assist Roger Ramon in preparing data quality assessment reports.

A4.6 Data Management Support

Roger Ramon will coordinate data management.

A4.7 Data Analysis Support

David Allen will provide data analysis support. determining whether data quality objectives have been met and preparing reports on data analysis for the project.

A4.8 Quality Assurance Officer

Chris Quigley of the University of Texas will be responsible for conducting laboratory and field audits.



Figure A4-1 Project organization chart

The interaction between the University of Texas (UT), the East Texas Council of Governments, and the Texas Natural Resource Conservation Commission is illustrated in Figure A4-1. The East Texas Council of Governments (ETCOG) is the primary sponsor of the project and Mark Sweeney is the project monitor. Mr. Sweeney and ETCOG are advised by North East Texas Air Care (NETAC), a non-profit group which promotes air quality in East Texas. The project will be performed by the University of Texas and its subcontractor Pollution Solutions. David Allen is the Project Director supervising both the emission inventory and monitoring portions of the project. The emission inventory is being performed by Pollution Solutions and a separate Quality Assurance Project Plan (QAPP) has been submitted for that portion of the project. This QAPP describes the monitoring portion of the project, which will be done by the University of Texas. Roger Ramon is the Field and Laboratory Activities Leader. He will supervise the work of the field and laboratory staff. Chris Quigley will perform quality assurance audits and will interact with Dr. Allen and Mr. Ramon. The TNRCC will provide technical input for all aspects of the project.

Section A5 Problem Definition/Background

PROBLEM DEFINITION/BACKGROUND

The goal of this project is to perform ambient air sampling and analysis that will assist the East Texas Council of Governments in developing strategies for reducing ozone levels in their Metropolitan Planning Area. The sampling will be performed during the summer of 1997.

The specific objectives of the ground level ambient sampling program are:

- to provide data suitable for verifying the emission inventory of hydrocarbons and nitrogen oxides in the East Texas region;
- to determine the ambient ratio of reactive hydrocarbons to nitrogen oxides in East Texas;
- to estimate the importance of biogenic emissions in the East Texas airshed: and
- to estimate the extent to which ozone precursors are transported into the region.

Achieving these objectives will require the collection of accurate. precise and validated data on the concentrations of hydrocarbons and nitrogen oxides during the period of May through August of 1997.

Section A6 Project/Task Description

PROJECT/TASK DESCRIPTION

This project is designed to determine the concentrations of ozone, nitrogen oxides and gas phase hydrocarbons in ambient air sampled in East Texas. Table A6.1 presents a summary of the technologies that will be used to make the measurements. The equipment will be deployed at the sampling site beginning in April, 1997. Mr. Quigley will perform a quality assurance audit of the deployed equipment before the collection of validated data begins. TNRCC personnel, including Ken Rozacky, will be invited to the audit. Validated data collection is expected to begin on May 15,1997 and end on August 3 1, 1997. The end date is fixed by the end of the contract period. If an extension of the contract is granted, sampling will continue until October 3 1, 1997.

Sample periods for each measurement are indicated in Table A6.1. The sampling site has been tentatively located at the municipal airport in Palestine. ETCOC has obtained permission to use the site and another possible site at a municipal airport near Jefferson. These sites are shown on the maps in Figures A6-1 and A6-2.

On a monthly basis, the measurement and quality control information will be available, on request, for the project participants to review. The data will be in the form of tabular listings of date, time, parameter and "as collected" value. The quality measurements will include date, time, parameter and error statistic for each quality assurance check performed. These reports will be maintained by the project's Field and Laboratory Activities Leader, Roger Ramon. The Quality Assurance Officer, Chris Quigley, will perform the monthly quality audits.

Table A6-1

Compound	Method	Sampling Time	Frequency
Hydrocarbons	Canister sampling and	1 hour	6th day sample
	GC/FlD or GC/MS		
	analysis		
Ozone	UV Photometry	5 min	Continuous
Nitrogen oxide	Chemiluminescent	5 min	Continuous
Nitrogen dioxide	Chemiluminescent	5min	Continuous
Total oxides of nitrogen	Chemiluminescent	5 min	Continuous
Wind direction	vane	5min	Continuous
Wind speed	cup anemometer	5 min	Continuous

DATA MEASUREMENT METHODS

Figure A6-1. Sampling location in Palestine



Figure A6-2 Sampling location in Jefferson



Section A7 Data Quality Objectives for Measurement Data

DATA QUALITY OBJECTIVES FOR MEASUREMENT DATA

The objectives of the project are to:

- I. validate the emission inventory for hydrocarbons and nitrogen oxides
- II. determine the ambient ratio of reactive hydrocarbons to nitrogen oxides
- III. estimate the importance of biogenic emissions
- IV. estimate the extent to which ozone and ozone precursors are transported into the area

Achieving these objectives will require an accuracy of $\pm 25\%$ in hydrocarbon

concentrations, $\pm 35\%$ in hydrocarbon to nitrogen oxides ratio and $\pm 10\%$ in ozone concentrations.

Table A7-1 specifies the Data Quality Objectives (accuracy, precision, and completeness) as well as the targeted detection limits for the study. These objectives are drawn from the TNRCC Quality Assurance Project Plan for NAMS, SLAMS and PAMS Monitoring in Texas (RG-97, September, 1994). The TNRCC objectives are designed to meet the requirements of Title 40, Code of Federal Regulations, Part 58 (40 CFR 58)

The parameters defined for each ambient measurement in Table A7-1 are:

- limit of detection;
- measurement system accuracy objective;
- measurement system precision objective; and
- data completeness objective: 80% of all possible measurements during the sampling period should be valid. For continuous monitoring, "all possible measurements" means 24 hours per day. For non-continuous monitoring, "all possible measurements" means all scheduled measurements (e.g. hydrocarbon sampling every 6th day).

Documentation of success or failure to meet the required Data Quality Objectives (DQOs) will be provided at the completion of the study in the Quality Assurance Report.

Table A7-1

DATA QUALITY OBJECTIVES

Measurement	Method detection Limit	Accuracy	Precision	Completeness
O ₃	1.0 ppbv	90 to 110 %	<u>+ 10%</u>	80%
NO and NO _x	1.0 ppbv	80 to 120%	<u>+ 20</u> %	80%
Hydrocarbons	2.5 ppbc (1)	75 to 125%	<u>+ 25</u> %	80%
Wind Speed	1.0 m/s	$\pm 1 \text{ m/s}(2)$	$\pm 2 \text{ m/s}(3)$	80%
Wind Direction	not applicable	<u>+</u> 10 °	<u>+</u> 20 °	80%

(1) this quality objective is based on the worst case hydrocarbon

(2) based on differences with intercomparison instruments - accuracy data for these measurements are not part of the contract.

(3) based on root mean squared differences with intercomparison instruments accuracy data for these measurements are not part of the contract.

Section A8 Project Narrative

This section is not required for this plan.

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Section A9 Special Training Requirements/Certification

No special training or certifications are required for this project.

Revision 1.3

3/31/97

Section A10 Documentation and Records

DOCUMENTATION AND RECORDS

Records will include sufficient information to reconstruct each final reported measurement. This includes, but is not limited to, information on instrument preparation, calibration, sample collection, sample handling, quality control checks, "as collected" measurement values, and an audit trail for any modifications made to "as collected" values.

'Difficulties encountered in sampling or analysis will be documented in narratives and all electronic versions of data sets will reflect the limitations associated with measured values.

Mechanisms for recordkeeping will include:

- Sampling information and Chain-of-custody forms
- Instrument calibration data forms
- Electronic run logs
- Electronic and manual daily activity logs
- Electronic and manual data processing and validation logs

All project documents will be retained at the University of Texas for at least two years. Reports will be retained for at least 5 years.

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Section B1 Sampling Process Design

SAMPLING PROCESS DESIGN

The sampling will be done in a specially equipped trailer or shed. A sampling inlet will be placed approximately 2 meters above the roof of the trailer. The samples will be drawn through teflon tubing into the trailer or shed, which will house the ozone and NOx analyzers, as well as the hydrocarbon canisters. The trailer or shed will be air conditioned. Meteorological measurements will be made approximately 2 meters above the roof of the trailer. The meterological data collected at the trailer or shed will be complemented by other meteorological data collected at the sampling site, which is an airport.

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Revision 1.3

313 1/97

Section B2 Sampling Methods Requirements

SAMPLING METHODS REQUIREMENTS

The surface based air monitoring sites will be designed using the guidelines for a State and Local Air Monitoring Site (SLAMS). This project, however, will not result in data to be used to determine attainment of National Ambient Air Quality Standards. Therefore, modest deviation from SLAMS protocols are acceptable. Among these deviations will be the following.

1.) Monitoring for both chemical and meteorological parameters will be conducted at a minimum height of 2 meters above the trailer or shelter roof unless documentation exists to prove that sampling at a lower height will provide data that is free of localized interferences.

2.) All calibration gases must be introduced to the sampling train as close to the inlet as possible to account for changes in measured ambient concentration due to the effects of the sampling system.

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3/3 1/97

Section B3 Sample Handling and Custody

SAMPLE HANDLING AND CUSTODY

All discrete and intermittent samples collected during the East Texas Near Non-Attainment Area Study that require preparation or analysis at a remote laboratory will be accompanied by a chain of custody form. These samples will be exclusively hydrocarbon canisters. The chain of custody form will accompany the canisters from the air monitoring site through all preparatory procedures to analysis. The chain of custody form will include the site name, sample identification number, date and time of collection, and initials of the person responsible for the collection, delivery and analysis. Custody of a sample will not be transferred unless the recipient initials the custody form. A sample form is attached. The completed forms will be maintained in a permanent study archive.

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3/3 1/97
Section B4 Analytical Methods Requirements

ANALYTICAL METHODS REQUIREMENTS

The Study will collect ambient atmospheric composition and meteorological data from ground based stations. Data will be collected on both a continuous and "grab" sample basis. The following chemical data are scheduled to be collected on a continuous basis:

- Ozone;
- Nitrogen oxide; and
- Nitrogen dioxide.

In addition to the monitoring of continuous chemical parameters, speciated non-methane hydrocarbons may be measured by the collection of discrete or "grab" samples.

B4.1 Continuous Gas Monitoring Procedures

The Study will conduct continuous monitoring of the following chemicals.

Ozone (O_3)

 O_3 measurements will be conducted by reference or equivalent Ultraviolet photometry absorption monitoring equipment operating in the range of 0 to 200 ppbv. Instruments operated at these sites will have a minimum detectable sensitivity of 1 ppbv. All connections to the ozone photometric analyzer, that contact the ambient sample, will be constructed of teflon, glass, or other inert materials. The air sampling line will be equipped

with a 5.0 μ m teflon filter placed near the instrument inlet. The ozone analyzer will be calibrated as detailed in Section B7. Calibration standards will be supplied using either an ultraviolet photometer standard, or a ozone transfer standard calibrated against a UV photometer. The system utilized for dilution of the ozone standard must be capable of providing flow rates within $\pm 2\%$ range of accuracy. Span, precision and zero check standards will be analyzed a minimum of once every 12 days. All ozone data collected will be stored in an on-site acquisition system. Method 417, "Continuous Monitoring of Ozone in the Atmosphere by Ultraviolet Photometric Instruments", from the third edition of Methods of Air Sampling and Analysis provides an in-depth discussion of the required analytical method.

Nitric Oxide (NO) and Nitrogen Dioxide (NO₂)

Nitric oxide measurements will be conducted by reference or equivalent O_3 chemiluminescence method monitoring equipment. The instrument will be operated within the dynamic range of 0 to 200 ppby. Operation in this range should allow the instrument to achieve an instrument detection limit of 1.0 ppby. All connections to the instrument, that contact the ambient air sample or the quality control standards, will be constructed of

teflon, glass, or other inert materials. The air sampling line will be equipped with a $5.0 \,\mu m$ teflon filter placed near the instrument inlet. The nitric oxides analyzer will be calibrated as detailed in Section B7. Span, precision and zero check standards will be analyzed at the

appropriate frequency as delineated in Section B7. A certified source of nitric oxide and dilution system capable of providing flow rates accurate to within ± 2 % will be used to introduce nitric oxide standards and to conduct either calibration or precision/span checks. All data on nitric oxides will be stored in an on-site data acquisition system. Method 417, "Continuous Monitoring of Nitric Oxide and Nitrogen Dioxide in the Atmosphere by Chemiluminescence", from the third edition of <u>Methods of Air Sampling and Analvsis</u> provides an in-depth discussion of the required analytical method.

B 4.2 Discrete Chemical Monitoring Procedures

Speciated Non-Methane Hydrocarbons

Speciated non-methane hydrocarbon analyses will be performed using gas chromatography. A list of the target analytes that will be measured using the speciated nonmethane hydrocarbon protocol is presented in Table B4-1. The sampling involves the passive or active collection of whole air samples in canisters. The analysis of these samples is conducted at a later time using a gas chromatograph equipped with a cryogenic preconcentrator. Canister sampling procedures are described in detail in the <u>Compendium</u> of Methods for the Determination of Toxic Organic Compounds in Ambient Air. TO- 14 and in the "Determination of Volatile Organic Compounds (VOCs) in Ambient Air using Summa Passivated Canister Sampling and Gas Chromatographic Analysis" (EPA/600/4-89-017). A four point (including zero) calibration of the gas chromatograph will be conducted using a 57 compound standard (the compounds are listed in Table B4-1) prior to sample analysis and/or when the daily analysis of the mass standard indicated the system is not within quality control limits. A 57 component retention time standard is analyzed either every third day of continuous operation, at GC start-up, or whenever a shift in retention time of one or more of the internal standards added to a sample can not be attributed to matrix interferences. Internal standards are added to all standards, blanks and samples.

It is anticipated that a number of peaks will be observed in the chromatograms that are not among the 57 compounds in the standard. These peaks will be integrated and used to assess total hydrocarbon concentrations, but identifying these peaks is outside the scope of this project.

Table B4-1

LIST OF PROTOCOL HYDROCARBON SPECIES TO BE IDENTIFIED AND REPORTED DURING FIELD PROGRAMS

#	SPECIES NAME	CAS-#
1	ETHENE (ETHYLENE)	74-85-1
2	ETHYNE (ACETYLENE)	74-86-2
3	ETHANE	74-84-0
4	PROPENE (PROPYLENE)	115-07-1
5	PROPANE	74-98-6
6	2-METHYLPROPANE (ISO-BUTANE)	75-28-5
7	1-BUTENE	106-98-9
8	N-BUTANE	106-97-8
9	TRANS-2-BUTENE	624-64-6
10	CIS-2-BUTENE	590-18-1
11	ISO-PROPYLETHYLENE	563-45-1
12	2-METHYLBUTANE (ISO-PENTANE)	78-78-4
13	1-PENTENE	109-67-1
14	N-PENTANE	109-66-0
15	TRANS-2-PENTENE	627-20-3
16	2-METHYL-1,3,-BUTADIENE (ISOPRENE)	78-79-5
17	CIS-2-PENTENE	646-04-8
18	2-METHYL-2-BUTENE	513-35-9
19	2,2-DIMETHYLBUTANE	75-83-2
20	4-METHYL-1-PENTENE	691-37-2
21	CYCLOPENTENE	287-92-3
22	2,3-DIMETHYLBUTANE	79-29-8
23	2-METHYLPENTANE (ISO-HEXANE)	107-83-5
24	3-METHYLPENTANE	96-14-0
25	2-METHYL-1-PENTENE	763-29-1
26	N-HEXANE	110-54-3
27	TRANS-2-HEXENE	4050-45-7
28	CIS-2-HEXENE	7688-21-3
29	2,4-DIMETHYLPENTANE	108-08-7
30	METHYLCYCLOPENTANE	96-37-7
31	2-METHYLHEXANE	591-76-4
32	CYCLOHEXANE	I 10-82-7
33	BENZENE	71-43-2
34	3-METHYLHEXANE	589-34-4
35	2,3-DIMETHY LPENTANE	565-59-3
36	ISOOCTANE	540-84-1
37	N-HEPTANE	142-82-5
38	METHYLCYCLOHEXANE	108-87-2

Table B4-1(con't)

LIST OF PROTOCOL HYDROCARBON SPECIES TO BE IDENTIFIED AND REPORTED DURING FIELD PROGRAMS

#	SPECIES NAME	CAS-#
39	2,3,4-TRIMETHYLPENTANE	565-75-3
40	2-METHYLHEPTANE	592-27-8
41	3-METHYLHEPTANE	589-81-1
_ 42	TOLUENE	108-88-3
43	N-OCTANE	111-65-9
44	ETHYL-BENZENE	100-41-4
45	M-XYLENE	108-38-3
46	P-XYLENE	106-42-3
47	NONANE	111-84-2
48	STYRENE	100-42-5
49	O-XYLENE	95-47-6
50	α-PINENE	2437-95-8
51	ISOPROPYLBENZENE (CUMENE)	98-82-8
52	N-PROPYLBENZENE	103-65-1
53	N-DECANE	124-18-5
54	1,3,5-TRIMETHYLBENZENE	108-67-8
_55	1,2,4-TRIMETHYLBENZENE	95-63-6
_56	β-PINENE	18172-67-3
57	UNDECANE	1120-21-4

B4.3 Corrective Actions

The most common corrective action anticipated for these analyses is the relinearization of calibration curves following span checks, 3 point and 5 point calibrations. Any other corrective actions will be undertaken only with the approval of the project Quality Assurance Officer.

B 4.4 Meteorological Monitoring Procedures

The study will monitor the following surface level meteorological parameters:

- wind speed; and
- wind direction;

All meteorological equipment will meet or exceed the accuracy and performance specifications described in the "Quality Assurance Handbook for Air Pollution Measurement Systems" (EPA, 1989) and the "On-Site Meteorological Program Guidance for Regulatory Modeling Applications" (EPA, 1987).

Ambient temperature data will be available from the Palestine airport, where sampling is being conducted. The internal temperature in the trailer will also be monitored to insure the proper operation of the equipment. Both of these measurements are not part of the study contract.

Section B5 Quality Control Requirements

QUALITY CONTROL REQUIREMENTS

The quality control procedures required for both the chemical and meteorological measurements conducted during the Study may be considered to consist of two distinct, yet complimentary functions; calibration and monitoring of equipment performance. Table B5-1 is provided to assist in developing a program of quality control activities. The frequencies and concentration levels for both the calibration and analysis of span and precision check standards may deviate from these requirements based on site conditions and/or research needs, and are to be determined by the project director.

B5.1 Continuous Gas Monitors

Quality control activities for the continuous gas monitors will consist of calibration, analysis of span check standards, precision check standards and zero check standards. These standards shall be introduced into the air monitoring equipment following the same pathways as the ambient samples.

Calibration

The procedures and frequencies for calibration of the continuous gas monitors are given in Section B7 of this plan. The calibration will be evaluated using a least squares fit. The calibration should be linear over the working range of the instrument. However, due to the low ambient levels of specific species, the working range of the instrument may encompass a concentration range where the instrument response is non-linear.

The slope of the linear regression will be determined using the equation:

$$SLOPE = \frac{\sum xy - [(\sum x)(\sum y)]/n}{\sum x^2 - (\sum x)^2/n}$$

where the independent variable, x, is the standard concentration and the dependent variable, y, is the instrument response and n is the number of data pairs.

The y intercept will be determined using the equation:

y Intercept =
$$\frac{\sum y}{n} - (slope)(\frac{\sum x}{n})$$

where the independent variable. x. is the standard concentration and the dependent variable, y, is the instrument response and n is the number of data pairs.

To assess the "fit" of the linear regression to the calibration data the correlation coefficient (R^2) is determined using the following equation:

$$R^2 = \frac{(\sum xy)^2}{\sum x^2 \sum y^2}$$

where the independent variable, x, is the standard concentration and the dependent variable, y, is the instrument response and n is the number of data pairs.

The correlation coefficient must be greater than 0.995 for the calibration to be accepted as linear. If the calibration is determined to be non-linear then the calibration equation must be expressed as the polynomial with the best "least squares" fit. The correlation coefficient must be greater than 0.995 for the calibration equation to be acceptable.

Zero, Span and Precision Check Standards

The analysis of zero check standards, span check standards and precision check standards will allow the project personnel to monitor the performance of the analytical system and conduct corrective actions prior to collection of data that does not meet the DQOs. These analyses will be conducted every 12 days. Span, precision, and zero check standards will be analyzed from known standards. The percent difference for each analysis of the span check standard and the precision check standard will be calculated using the equation:

$$\%D = \frac{\overline{x} - x_i}{\overline{x}}$$

where \mathbf{x}_i is the result of the span or precision check standard and x is the actual concentration of the span or precision check standard.

The difference should be within the limits for precision as given in Section A7.

B 5.2 Discrete Chemical Parameters

The major portion of the quality control activities for the discrete chemical monitoring parameters will be conducted at the analytical laboratory. These activities will include at a minimum, calibration, frequent analysis of standards of known and documentable concentration, analysis of blanks, analysis of duplicate samples, and other quality control procedures deemed necessary by the analyst. Documentation of all quality control activities and the associated quality control data will be maintained at the laboratory and will be made available upon request.

B5.3 Meteorological Monitors

If possible, all meteorological monitoring equipment will be calibrated prior to installation by intercomparison with instruments such as sodars. These intercomparisons are not part of the monitoring contract. however.

B5.4 Corrective Actions

Periodic relinearization of calibration curves is likely to be the most common corrective action undertaken for this project. Any other corrective action will only be undertaken with the approval of the project Quality Assurance Officer.

Table B5-1 QUALTTY CONTROL REQUIREMENTS

					14 V	000-00		direction
	NA	NA	NA	NA	PUC T	0 3600	oldeneye II	Wind
								speed
1	NA	NA	NA	A	$\pm 2 \text{ m/s}$	0-50 m/s	I II available	Wind
compounds		std						
target	days	of n-butane		days				carbons
>2.5 ppbc c	Every 12	%0.51,>Cl%		Every 12	R ² >0.995	0-20 ppbc	Start	Hydro-
>-5 ppbv	days			days				NÇ,
vqdd 01>	Every 12	%D< 20.0%	160/40	Every 12	$R^{2}>0.995$	0-200 ppbv	Start & End	NQand
>-10.0	days			days				
<10.0 ppb	Every 12	%D<15.0%	160/40.0	Every 12	R ² >0.995	0-200 ppbv	Start & End	Ç
Valid	Frequency	Valid	Level (ppbv)	Frequency	Valid	Kange	Frequency	
ULSC	ZERC		SPAN/PREC			CALIBRATION		

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Table B5-1QUALITY CONTROL REQUIREMENTS

		CALIBRATION			SPAN/PREC		ZER	JSTD
	Frequency	Range	Valid	Frequency	Level (ppbv)	Valid	Frequency	Valid
O_3	Start & End	0-200 ppbv	R ² >0.995	Every 12 days	160/40.0	%D<15.0%	Every 12 days	<10.0 ppbv >-10.0
$NO and NO_2$	Start & End	0-200 ppbv	R ² >0.995	Every 12 days	160/40	%D<20.0%	Every 12 days	<10 ppbv >-5 ppbv
Hydro- carbons	Start	0-20 ppbc	R ² >0.995	Every 12 days		%D< 15.0% of n-butane std	Every 12 days	>2.5 ppbc of target compounds
Wind speed	II available	0-50 m/s	$\pm 2 \text{ m/s}$	NA	NA	NA	NA	
Wind direction	II available	0-360°	± 20°	NA	NA	NA	NA	

Section B6 Instrument Inspection and Maintenance Requirements

INSTRUMENT INSPECTION AND MAINTENANCE REQUIREMENTS

At a minimum, the routine maintenance activities to be conducted at all surface based air monitoring sites, will include the following when appropriate.

- 1. Visual inspection of the site surroundings and enclosure.
- 2. Record of the instrument enclosure temperature.
- 3. Visual inspection of instruments, data logger wiring connections, sample lines, filters, and flow rates.
- 4. Scheduled preventative maintenance as recommended by the equipment manufacturer, including filter changes.
- 5. Review of instrument output to ensure that the collected data is reasonable.
- 6. Review of stored data for anomalous behavior.
- 7. Update of log book and preventative maintenance check list.

Additional inspection and maintenance activities will follow the TNRCC Preventative Maintenance Instructions Manual. Local TNRCC representatives will be invited to inspect the site before sampling commences. If instruments are found to be inoperable during sampling. they will be returned to the University of Texas for repair or replacement. If the instruments are operable but are not meeting the data quality objectives, the project Quality Assurance Officer will decide whether to remove the equipment or to continue to operate. if operation continues, all data collected with the compromised instrument will be flagged.

To maximize the completeness of the study, spare instruments will be maintained. One spare NO, analyzer will be available for 3 instuments that will be in the field (for this study and two other concurrent studies). One spare ozone analyzer will be available for 3 instruments that will be in the field (for this study and two concurrent studies).

Section B7 Instrument Calibration and Frequency

INSTRUMENT CALIBRATION AND FREQUENCY

B7.1 Continuous Gas Monitors

All continuous gas monitoring equipment will be calibrated at the beginning and end of the study period. In addition, calibration of a continuous gas monitor will be required after any equipment maintenance or repair that may effect instrument response or if quality control standards are found to be outside the specific quality control limits. Prior to calibration all in-service continuous gas monitors will receive 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. Unless otherwise noted calibration refers to the analyses of standards, the adjustment of instrument response, and the calculation of an equation expressing the concentration of a particular analyte in terms of instrument response. All calibration gas standards will be from a source of known and documentable concentration. Nitrogen oxide and nitrogen dioxide will be calibrated using an NO cylinder. NO calibration will be done directly. NO, calibration will be performed by titrating the NO with controlled amounts of ozone. Ozone will be from a Dasibi Model 1000 ozone transfer standard. A minimum of five data points. including zero, spanning the working range of the instrument will be used to conduct both the calibration and the unadjusted calibrations. The calibration will be evaluated using a least squares fit.

B 7.2 Hydrocarbon Analysis

The gas chromatograghy system used for hydrocarbon analysis will be calibrated using standard gases obtained from the Texas Natural Resource Conservation Commission. Dilution gases will be added to these standards to obtain at least three standards for each hydrocarbon to be analyzed. Dilution gases will be prepared in the laboratory using a zero air system. The zero air system generates pure air on site 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. Instrument response will be correlated with concentration for each hydrocarbon species. Linear or polynomial fits to the calibration will be determined for each hydrocarbon species and the correlation coefficient must be greater than 0.995 for the calibration to be acceptable.

Section B8 Inspection/Acceptance Requirements for Supplies and Consumables

There are no inspection/acceptance requirements for supplies or consumables for this project.

Section B9 Data Acquisition Requirements (Non-direct Measurements)

All data obligated under the contract for this project are expected to be direct measurements so there are currently no specifications for data from non-direct sources. Meteorological data from the National Weather Service may be collected during data analysis, **but** this data collection is outside the scope of the contract.

Section B10 Data Management

DATA MANAGEMENT

The data management system for continuous and non-continuous data collection is outlined below.



Section CI Assessment and Response Actions

ASSESSMENT AND RESPONSE ACTIONS

Instruments will be audited before and after placement in the field using methods described elsewhere in this Plan and in the TNRCC (TACB) Quality Assurance Manual. A Quality Assurance Report will be prepared by the Project Manager (David Allen) at the end of the sampling period.

Section C2 Reports to Management

REPORTS TO MANAGEMENT

Beyond the monthly measurement and quality control data summaries, there will be only the final project report.

Section D1 Data Review, Validation and Verification

DATA REVIEW, VALIDATION AND VERIFICATION

Data Generation

Data generated at field sites or analytical laboratories will undergo initial validation at the site/lab of origin. The project director or Quality Assurance Officer will flag all data as deemed appropriate. The data points determined to not meet validation criteria may be flagged "SUSPECT" to indicate suspect data. Data points that are partially or wholly composed of values below the method detection limit will also be flagged as "BELOW DET". In addition to these standard data flags the project director may assign other alphanumeric characters as data flags. After on-site validation of the results, the initial validation will be forwarded with the corresponding data to the project sponsors. All data and appropriate data flags and any accompanying text will be loaded into a database.

Data Validation

Initial data validation at the site/lab of origin will allow the site/lab QA coordinator to assess the quality of the data being generated. If operational problems arise which affect the quality of data, the site/lab manager will initiate appropriate corrective action. Validation of data requires the evaluation of the accuracy, precision, completeness, comparability and representativeness of the data versus the DQOs listed in Section A7 of this Plan and the use of data quality indicator flags to document those data points not meeting the DQOs

Section D2 Data Validation and Verification Methods DATA VALIDATION AND VERIFICATION METHODS

Accuracy

The accuracy will be determined from performance audits of the individual instruments. The audit will assess the instrument performance by examining the instrument response to known standards (at least five points) which encompass the operational range of the instrument. A linear regression of the form

$$y = mx + b$$

where the standard value is the independent (x) value, the instrument reading is the dependent (y) variable, m is the slope, and b is the y intercept.

will be used to determine the measurement accuracy. The percent accuracy determined by the performance audit will be determined by the equation:

$$\%$$
 accuracy = *m x* 100

where m is the slope of the linear regression.

◆ All data associated with a performance audit yielding a slope outside the required acceptable range will be flagged to indicate that the data does not meet requirements for accuracy.

Precision

Precision will be determined from instrument span check standard and/or precision check standard data. A minimum of seven data points should be used to calculate the precision. Precision will be determined from the standard deviation using the following equations:

Standard Deviation.(s) =
$$\sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}}$$

where x is the experimentally determined value for the i^{th} measurement. n is the number of the measurements performed, and x is the mean of the experimentally determined values.

The precision will be determined as a percentage of the average concentration of the span check standard and/or precision check standard using the following equation,

$$Precision = 100 \frac{3s}{x}$$

where x is the average of the span or precision measurements. s is the standard deviation of the replicate span check standard or precision check standard data.

The precision should be reported for data periods between instrument calibrations or other major instrument operational changes that may effect changes in the operational performance of the instrument.

◆ ALL data associated with a relative standard deviation outside the required limits for precision should be flagged to indicate that the data does not meet precision requirements.

All span and precision check standards should be evaluated for percent difference (%D) using the following equation:

$$\%D = \frac{x - x_i}{\overline{x}}$$

where x is the result of the span or precision check standard and x is the actual concentration or the span or precision check standard.

All data associated with a precision or span check standard outside the required limits should be flagged to indicate the data does not meet the precision requirements. An exception to this would occur in the instance where the concentration of the precision standard is less than the required method detection limit divided by the fractional precision limit. For example, if the MDL = 2.0 ppbv and the precision limit is \pm 10 % then the precision standard must be greater than or equal to 20 ppbv.

Comparability

The comparability **of** data collected by different sites is assured. where feasible. by the network wide adoption of the same protocols. QA Plan and auditing procedures. and by the network wide use of the same measurement techniques and equipment. All data generated by methods and/or equipment protocols that do not compare with those required will be flagged to indicate that caution must be exercised when using the data.

Completeness

Completeness will be determined for the data generated using the following equation:

$$Completeness, \% = \frac{100 \ D_r}{D_s}$$

where D is the number of samples for which valid results are reported and D is the number of samples which are scheduled to be collected and analyzed during the year.

Time periods for which there is no data due to the scheduled analysis of quality control samples have been accounted for when establishing the completeness requirement.

Corrective Actions

Specific corrective actions required will vary dependent upon the equipment deployed and parameters measured. The following corrective actions relate to required quality control activities and are required at all sites and laboratories generating and analyzing data.

1.) The slope of the unadjusted calibration is outside the control limits for accuracy.

◆ The instrument exhibits an excessive bias and must be recalibrated. If the instrument is unable to meet the accuracy requirement, the cause of this inaccuracy should be determined and rectified. Should the project director choose to collect ambient data under an invalid calibration then all data associated with a calibration that does not meet the accuracy requirements must be flagged to indicate this fact.

2.) The correlation coefficient (\mathbb{R}^2) for the calibration is less than 0.995.

◆ The calibration is not valid and must be rerun prior to collection of data. If a valid calibration can not be conducted, the cause of this problem should be determined and rectified. Should the project director choose to collect ambient data under an invalid calibration then all data associated with the invalid calibration must be flagged to indicate this fact.

3.) The span check standard of precision check standard is outside the percent difference (%D) limits.

◆ The span check standard is not valid and must be reanalyzed. If reanalysis does not yield an acceptable %D, the problem should be located and the situation rectified. The instrument must be recalibrated. All data associated with the out of range span check standard must be flagged to indicate this fact.

Section D3 Reconciliation with Data Quality Indicators

RECONCILIATION WITH DATA QUALITY INDICATORS

The quality of the data generated by the Study will be assessed for accuracy, precision and completeness and will be compared with the data quality objectives. The procedures and equations to be used in conducting these assessments are presented below.

Accuracy

The accuracy will be determined from performance audits of the individual instruments. The performance audit will challenge the instrument with standards from an independent source, encompassing the operational range of the instrument.

Precision

Precision will be determined from an instrument span check standard and/or precision check standard records. A minimum of 7 data points should be used for the precision to be calculated. Precision should be determined for data time periods between calibration or other major maintenance that may effect the operation performance of the instrument.

Method Detection Limit

The method detection limit for each analyte will be determined by the following equation

$$MDL = 0 + s t_{(n-1,1-\alpha = 0.99)}$$

where s is the standard deviation of the replicate zero analyses, t is the detection value appropriate at a 99% confidence level and a standard deviation estimate with n- 1 degrees of freedom.

Completeness

Completeness will be determined from the data generated using the following equation:

Completeness,
$$\% = \frac{100 D_r}{D_r}$$

where D is the number of samples for which valid results are reported and D is the number of samples which are scheduled to be collected and analyzed.

APPENDIX

Sample Chain of Custody Form

Canister Sampling רובוע שמום טווכבי (וטוסושט ט-וובוע.אוס)

A. GENERAL INFORMATION

sampling date:	leak check date:
project name:	pressure measurements in psi
site name:	pressure (0 min):
canister UT ID #:	pressure (1 min):
autosampler UT ID #:	leak rate (psi/min):
autosampler port #	

B. SAMPLING INFORMATION

	operator	date
setup ,		
removal		

	temperatu	re (deg C)	pressure	flowrate	sampling	time (tin)
	interior	ambient	(psi)	(cc/min)	local	metered
start						
stop						

comments:

C. LABORATORY INFORMATION

operation	date	operator	comments
sample discarded:			
canister cleaned:			
canister evacuated:			
canister shipped:			
canister receieved:			
canister diluted:			
analysis completed:			

initial pressure (psi)	
final pressure (psi)	
dilution factor	

data file name

analysis results/conclusions: