# CONCEPUTAL DESIGN FOR A GULF COAST OXIDANT TRANSPORT AND TRANSFORMATION EXPERIMENT Workshop Proceedings and Recommendations

by

Walter F. Dabberdt William Viezee Hanwant B. Singh
Atmospheric Science Center
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

CONTRACT NO. 68-02-3752

Project Officer

Jason K. S. Ching
Meteorology and Assessment Division
Atmospheric Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

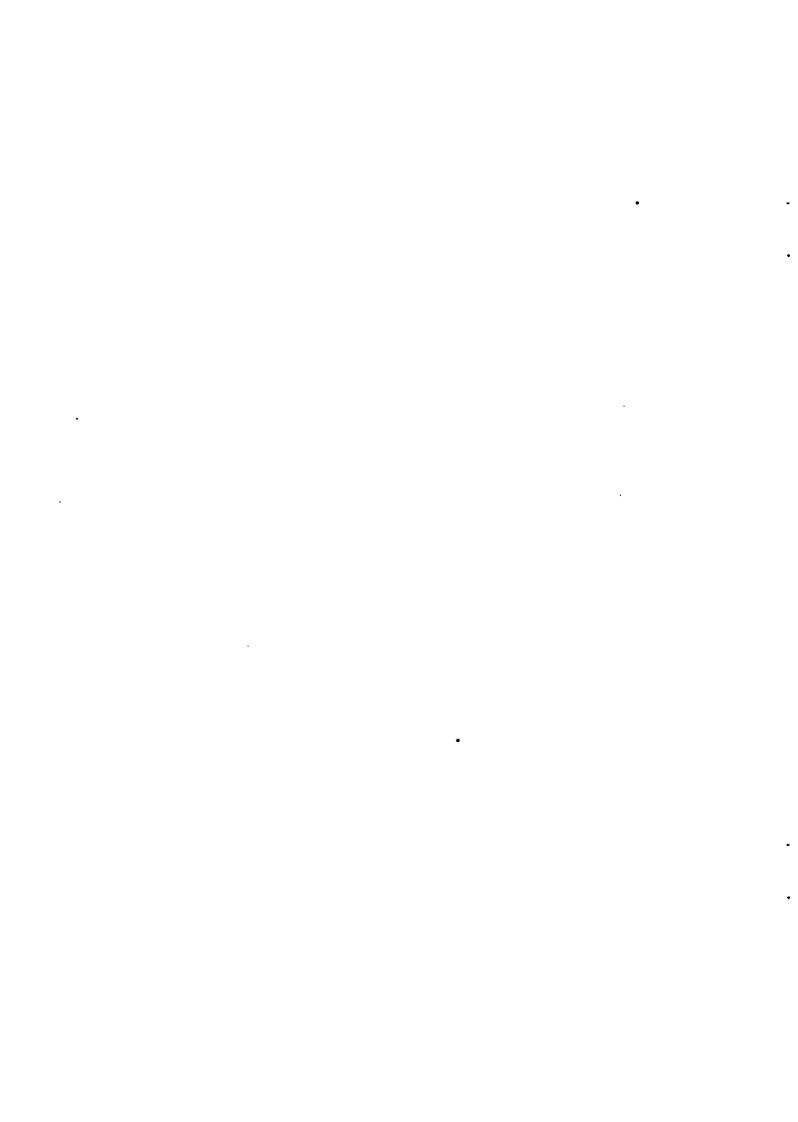
ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

# NOTICE

The information in this document has been funded by the United States Environmental Protection Agency under Contract No. 68-02-3752 to SRI International. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

### ABSTRACT

Thirty atmospheric scientists from government, industry, academia, and the private research sector participated in a workshop held during November 15-17, 1983, in Durham, North Carolina, to develop a conceptual design for a study of ozone transport and transformation in the western Gulf Coast area. The purpose of the study would be to better understand the unique meteorology and chemistry of the region, and to effectively adapt the EPA Regional Oxidant Model to that geographic area. Two working groups focused on the problems of meteorology and atmospheric chemistry, and measurement needs and methods. A conceptual design was developed for a five-year program that would include preparatory studies, the 3-month primary experimental program, and data analysis. The preparatory studies would consist of the collection and analysis of all existing data, simulation modeling, smog chamber studies, instrument development, and preliminary, limited field measurements. The primary experiment would consist of an enhanced routine monitoring network operated continuously, and frequent, intensive short-term experiments; the geographical domain of the study would be about 300 km east-west and 800 km north-south. The routine monitoring would include boundary-layer profiles (to 3000 m) of aerometric parameters by light aircraft, and enhanced radiosonde coverage. The intensive studies would rely heavily on sophisticated aircraft platforms such as doppler radar, UV and IR lidar, backscatter lidar, and in-situ gas concentration and flux measurements; gaseous and fluorescent particulate tracers would also be used. The cost of the total program was estimated at 9.5 to 12.4 million dollars.



# CONTENTS

																						_	
Absti	act	•	•	•		•		•	•	•	•	•	•	•	•	•		• (	•	•	•	. i	ii
Illus	trations								•	•									, ,				vi
	·s																						
	wledgements																						
		•	•		•	•	•	٠	٠	٠	•	•	٠	Ī	•	•					•	-	
1.	Executive Summary			•		•				•	•	•	•				•				•	•	1
	Introduction																						
	Working Group																						
	Recommendations	s f	or	a	Co	nc	en	tıı	a1	Pı	- ros	· Įr:	am	מ	es	i	m				•		10
2.	Introduction																						
	Objectives																						
	Background .																						
3.																							
٥.	Working Group Consider																						
	Chemistry	• •		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	23
	Chemicals																						
	Emissions																						
	Recommenda																						
	Meteorology.																						
	General .																						
	Identifica	tic	n	of	Re	le	va	nt	P	hei	noı	ne	na	•	•	•	•		•	•	•	•	59
	Design of 1	Mes	os	ca!	le	Se	a-	Br	ee	ze	E:	кр	er	ĺm	en	t	•	•	•	•	•	•	62
	Design of 1	Med	liu	m J	Ran	ge	T	ra	ns	po	rt	E	хр	er	im	e	nt	•	•	•	•	•	64
	Enhanced So	ıra	ce	aı	nd	Uр	pe	r	Ai:	r l	Mot	11	to	ri	ng	ı	Ve 1	two	r	k.	•		66
	Long-Range																						
4.	Recommendations For																						
5.	Conclusions and Rec																						
D . C																							0.0
	ences																						
List	of Participants								•			•			•		•				•		83

# ILLUSTRATIONS

Numt	<u>per</u>	Pag	<u>ge</u>
1	Projected area for intermediate transport experiment (dotted lines) showing location of vertical planes or "curtains" for horizontal flux measurements (dash-dot lines)	•	9
2	Conceptual program design and approximate costs	. 1	3
3	Workshop agenda	. 2	20
4	Example of typical synoptic-scale weather conditions along the U.S. Gulf Coast during summer	. 2	24
5	Mean number of thunderstorms—annual	. 2	25
6	Three-dimensional air-parcel trajectories near the surface and near 5000 ft predicted by LFM-II for the 24-hour period of 19 July, 18:00 CST to 20 July, 18:00 CST	. 2	27
7	Three-dimensional air-parcel trajectories near the surface and near 5000 ft predicted by LFM-II for the 24-hour period of 22 August, 18:00 CST to 23 August, 18:00 CST	. 2	29
8	Gridded annual emissions ( $10^4$ ton $y^{-1}$ ); values less than 40,000 ton $y^{-1}$ not shown	. 3	30
9	Ozone trends in Houston	. 3	32
10	Backward boundary-layer trajectories	. 3	35
11	Ozone concentrations (µg m <sup>-3</sup> ), air trajectories and sea level pressure distribution for October 20, 1975 flight	• 3	36
12	Air parcel trajectories during July 14-20, 1977, and ozone concentrations patterns	. 3	38
13	Schematic illustration of the "dynamic" layer structure of the regional scale model and the phenomena each layer is designed to treat	. 4	¥6
14	Schematic view of sea-breeze regime characteristic of Gulf Coast	. 6	50
15	Projected area for intermediate transport experiment (dotted lines) showing location vertical planes or "curtains" for horizontal flux measurements (dash-dot lines)	. 6	65
1.6	Conserval angular and communicate scale		, , 75

# TABLES

Nur	mber	Page
1	Trace chemicals in air	3
2	Trace chemicals in liquid water and particulate matter	4
3	Inert tracers of interest	4
4	Preparatory studies	11
5	Ozone (ppb) trends in Louisiana	33
6	NMHC/NO <sub>x</sub> ratio for ambient air	41
7	O <sub>3</sub> /PAN Ratios in Los Angeles, Hoboken, St. Louis, and Houston	42
8	Important trace chemicals to be measured	43
9	Platforms data centers operated during PEPE/NEROS	49
10	Air quality and meteorological parameters available for each platform	50
<b>l</b> 1	Schedule of missions flown	51
1 2	Trace chemicals in air	54
13	Trace chemicals in liquid water	55
14	Particulate matter	55
15	Inert tracers of interest	56
16	Preparatory studies	69

### **ACKNOWLEDGMENTS**

Dr. Jason Ching\*of the Meteorology and Assessment Division (MAD), U.S. Environmental Protection Agency contributed substantially through his enthusiastic encouragement and technical expertise. Dr. John Clarke\* and Dr. Fran Pooler\*, also of MAD, contributed significantly in the technical planning and execution of the workshop. Special thanks to Dr. William Pennell, Battelle-Pacific Northwest Laboratories, and Mr. Gary Tannahill, Exxon Company, U.S.A., who chaired the meteorology and chemistry working groups, respectively. Also, special thanks to Ms. Dorothy Sevela for helping with pre-conference arrangements and typing the report manuscript.

<sup>\*</sup>On assignment from National Oceanic and Atmospheric Administration (NOAA).

### SECTION 1

### EXECUTIVE SUMMARY

### INTRODUCTION

Regional-scale episodes of photochemical smog have been documented in the Northeast and Midwest United States. The transport of ozone and oxidant-precursor emissions from the industrial areas of the Gulf Coast to other areas of the United States, particularly the Northeast and Midwest, may exacerbate the smog problems in those areas. The extent of this transport is unknown.

This document presents the output of a workshop held in Durham, NC, November 1982, on a conceptual design for a Gulf Coast transport and transformation experiment. It outlines a field study designed to quantify the amounts of material injected into the large-scale flow and the amount remaining in the Gulf Coast area. Results of the field study will help to describe such transport, and aid in the application of the Regional Oxidant Model (ROM) to the Gulf Coast area to perform sensitivity studies on the regional transport of ozone and precursors.

The basic objective of such a Gulf Coast oxidant study would be to "investigate the unique meteorological and chemical processes in the Gulf Coast region that must be understood to effectively adapt the EPA Regional Oxidant Model to that geographic area." Some of the more important and relevant processes to be studied include:

- Three-dimensional transport by land- and sea-breeze circulations
- Transport and diffusion under near-stagnation conditions
- Ozone (and precursor) venting or mixing by precipitating and non-precipitating cumulus clouds

- Washout of nitrogeneous and oxygenated species and the impact on oxidant production
- Parameterization of the over-water atmospheric surface layer
- Large-scale inflow and outflow to/from the region
- Investigation of anomalously low values of the ratios of NMHC/NO<sub>x</sub> and PAN/O<sub>3</sub> and the concentration of PAN
- ullet Nocturnal NO $_{\mathbf{x}}$  removal and transformation mechanisms.

Thirty atmospheric scientists from government, industry, academia, and the private research sector participated in a three-day workshop to develop a conceptual design for the field study. Two working groups were formed, focusing on problems of meteorology and atmospheric chemistry, and measurement needs and methods. The conceptual design consisted of an interrelated series of studies that would have a high probability of: (1) determining which processes are most important in controlling regional oxidant concentrations, and (2) providing data to quantify the transport and transformation mechanisms involved, so that (3) a data base would be available for diagnostic evaluation of ROM, with subsequent improvements made to the model.

# WORKING GROUP CONSIDERATIONS

The atmospheric chemistry working group addressed and prioritized the trace chemicals that must be measured during any planned Gulf Coast oxidant study. The exact platforms to be employed, frequency of measurements, and spatial density of monitoring stations were issues which could not be considered by the working group since a detailed design of the Gulf Coast study did not exist. The group, therefore, focused on broader considerations dealing with trace chemical measurements and emissions data requirements.

Trace chemical measurements (both gas and liquid phases) were identified and ranked according to the importance and feasibility of the measurements. Tables 1-3 provide a listing of the species of interest and rank these by the above criteria. Among the nonchemical parameters,

TABLE 1. TRACE CHEMICALS IN AIR

Chemicals*	Ra	nk <sup>†</sup>
03	A	1
NO	A	
NO <sub>2</sub>	A	1
PAN	A	2
нио <sub>3</sub>	A	3
CH <sub>4</sub>	A	1
СО	A	2
ТНС	A	2
нс <sub>і</sub>	A	2
RCH=O	A	3
н <sub>2</sub> 0 <sub>2</sub>	A	3
HNO <sub>2</sub>	В	3
N <sub>2</sub> O <sub>5</sub>	В	3
но .	В	3
но <sub>2</sub>	В	3
$RO_{ ilde{2}}$	В	3
NO <sub>3</sub>	В	3
NH <sub>3</sub>	С	2
so <sub>2</sub>	С	1

\*Measurement of liquid water content and UV radiation (300-500 nm) were ranked as A2 and A1 respectively.

# <sup>†</sup>Key:

- A = important measurement
- B = desirable measurement
- C = optional measurement
- 1 = measurement technique
   is state-of-the-art
- 2 = measurement methods not
   yet fully developed or
   only applied with difficulty
- 3 = measurement methods
   currently unacceptable

TABLE 2. TRACE CHEMICALS IN LIQUID WATER AND PARTICULATE MATTER

		Rank			
Chemicals	Cloud <sub>*</sub> Water	Rain * Water	* Aerosols	Particulate Matter	Rank
NO <sub>3</sub>	В	В	В	Elements	C 1
ROH	С	С	С	s0 <sub>4</sub>	C 2
RCH=0	A	С	A	NO <sub>3</sub>	В 2
HC <sub>i</sub> (vac)	С	С	С	NH <sub>4</sub>	C 2
03	С	С	С		
H <sub>2</sub> O <sub>2</sub>	A	В	В		

 $<sup>\</sup>star$  Measurements are at levels of difficulty of 2-3.

TABLE 3. INERT TRACERS OF INTEREST

Tracer Type	Species	Ra	nk
Tracers of opportunity	7 Be	С	2
aradara ar apparauntu,	33 <sub>P</sub>	С	
	Fluorocarbons	A	1
	Elements	С	1
Injected tracers	Methane-21	A	2
	Perfluorocarbons	A	2
	SF <sub>6</sub>	A	1

liquid water content and ultraviolet radiation measurements were highly emphasized. It was generally believed that gas-phase processes provide the dominant source for ozone formation and hence constitute the most important measurements. The role of aldehydes and  $\rm H_{2}O_{2}$  in liquid phases is not well understood but may be potentially important (Table 2). Nitrate measurements in the aqueous phase (Table 2) were ranked high because of the sink potential of the aqueous phase for  $\rm NO_{2}$  and  $\rm HNO_{3}$ . Despite the recognized importance of gas-phase chemistry, the working group felt that liquid-phase processes may play a more important role in the wet and humid environment of the Gulf Coast as compared to relatively dry regions.

Tracers of opportunity were suggested, but only chlorofluorocarbons were considered high priority. <sup>7</sup>Be or <sup>33</sup>P stratospheric tracers were ranked low due, in part, to the complexity of data interpretation. Injected speciality tracers are unique tools to study long range transport, but are to be measured only when a planned tracer experiment is underway.

Recommendations and guidelines were developed for the emissions data required for input to ROM or other photochemical models; these included:

- (1) A 2-km x 2-km gridded inventory of emissions
- (2) Hourly temporal resolution, i.e., diurnal and seasonal emission patterns
- (3) Vertical resolution of emission sources
- (4) Source types (stationary, mobile, area, point, natural, etc.)
- (5) Natural VOCs on land
- (6) Gulf Coast water emissions.

It was felt that some sensitivity studies should be performed with existing models to get an idea of the importance of source emissions, particularly natural VOCs of land or water origin. One of the most pernicious problems is the very nature of the emissions inventory. In principle, emissions data (temporally and spatially resolved) should be available for individual species. This is not possible in practice. Current models can use groups of chemicals (alkanes, alkenes, and

aromatics) and this is a desirable speciation of emission data. It was felt, however, that carbon bond mechanisms may be employed in a future version of ROM. It does not appear feasible that emissions information can be obtained in a format directly applicable to the carbon bond model. It is assumed that some algorithms must be devised to solve this problem.

The meteorology working group discussed a wide range of atmospheric circulations and phenomena which were judged to be potentially important in determining oxidant concentrations in the Gulf Coast and interior regions downwind; these features included

- Land and sea-breeze circulations
- Convective cumulus cloud venting
- Synoptic-scale transport and disturbances
- Surface deposition and destruction
- Synoptic-scale subsidence
- Low-level jet
- Characteristics of planetary boundary layer over the Gulf of Mexico.

On the basis of these discussions, the working group made recommendations and developed conceptual designs for a mesoscale sea-breeze experiment, a medium-range transport study, and an enhanced routine monitoring network. However, a long-range transport (-1000 km) component was not recommended. Within the budgetary guidelines presented by EPA, it was concluded that the resources could more effectively be used to undertake the other components, and that long-range experiments would best be undertaken as an adjunct to or in conjunction with separate studies conducted by other agencies.

The working group considered two possible experimental designs for a mesoscale sea-breeze experiment, finally integrating the two into a single study; the two designs are as follows:

- (1) A spatially fixed (Eulerian) box-budget study to quantify the net transport into or out of the sea breeze/emission area
- (2) A tracer (Lagrangian) experiment to study the role of the sea breeze in recirculating pollution.

The Eulerian box-budget experiment would be carried out in a rectangular area, 300 km north-to-south, and 200 to about 400 km east-to-west. This area would include the sea-breeze circulation and coastal emission sources. The Houston-Galveston-Lake Charles area was considered most suitable for this program. The box would be 3 km deep (the average depth of the sea-breeze).

A wide variety of in situ and remote measurement systems were considered necessary for successful completion of the study; these included airborne backscatter and differential-absorption laser radar (lidar) systems, airborne doppler radar and ground-based doppler sodar, in situ aerometric sampling aircraft, and meteorological profiling systems. Even with these systems, it was concluded that a budget study of the box cannot be readily done by closing the box with observations. It was, therefore, recommended that available observations be used in conjunction with a modeling approach to estimate pollutant fluxes within and through the box.

The release of multiple tracers for a sea-breeze experiment was also considered. Tracers should be released near ground-level on the coastal side of the convergence zone and inside the convergence zone. Injection of tracers in cumulus clouds should be carried out to study recirculation of pollutants by the sea-breeze, and cloud venting in the sea-breeze front.

The sea breeze program should also include studies of venting by cumulonimbus and cumulus congestus clouds that form in the afternoon inland along the sea breeze convergence zone. Because of the lengthy extent of the zone roughly parallel to the coastline and its high frequency, it may be an effective mechanism for transport of ozone precursors out of the Gulf Coast emissions source region, thereby possibly minimizing local ozone formation and impacting regions further downwind. It was recommended that inert gas tracers would provide a useful method for quantifying the effects of cumulus-cloud venting. One or more tracers released at or near the surface in the convergence zone would be measured aloft by aircraft, both in the boundary layer and at

the level of outflow near the cloud tops. For practical reasons, cumulus congestus or small cumulonimbus clouds would be preferable as their tops are within the capabilities of available research aircraft.

An intermediate-range oxidant transport experiment would involve a total time of 30-48 hours for atmospheric measurements, and would cover a horizontal distance of 400-500 km from the Gulf Coast emissions source. This distance would take the experiment from the Houston-Galveston area northward into Oklahoma and Arkansas, and would focus on ozone and its precursors, and on released tracers. The intermediate transport experiment would take place under conditions of synoptic-scale southerly flow, preferably during the occurrence of a nocturnal low-level jet.

During daytime and possibly during nighttime, convective cumulus clouds can be expected to develop in the southerly flow of warm, moist (mT) air. Thus, cumulus convective transport will be part of the experiment. Figure 1 shows the projected area (stippled boundaries) for an intermediate range (high-level and low-level) transport experiment. Measurements are recommended across three vertical planes or "curtains" (dash-dot lines in Figure 1). Tracers and tetroons should be released at a low level (e.g., 1500 m in the mixed layer under the clouds), and at a high level (e.g., at the level of the cumulus clouds). Measurements would be made for the purposes of

- Computing fluxes out of the mixed layer and out of the cloud layer
- Validating parametric schemes for cumulus convection transport in ROM.

Tracer releases in the low-level jet were also recommended in order to define the transport characteristics of this phenomenon. It was agreed, however, that more knowledge and information on the occurrence, location, and spatial extent of the low-level jet is needed before a detailed plan can be designed.

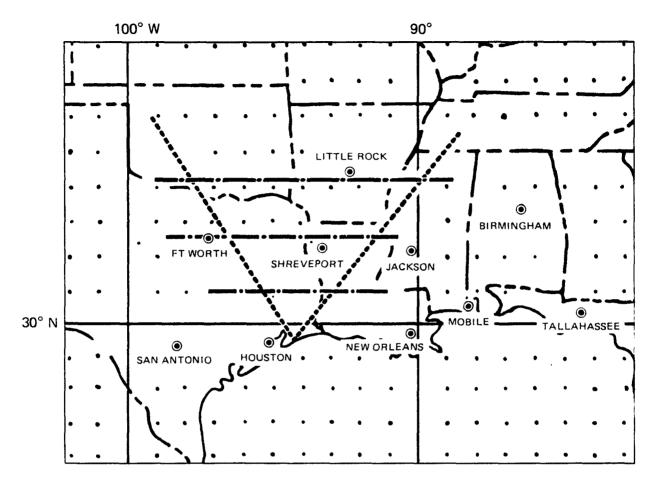


Figure 1. Projected area for intermediate transport experiment (dotted lines) showing location of vertical planes or "curtains" for horizontal flux measurements (dash-dot lines).

The work group recommended that an enhanced network of surface and upper-air observations be operated throughout the time period that the mesoscale sea-breeze and intermediate transport programs are conducted. The network area was outlined as extending from Fort Worth, Texas, eastward to the Alabama border (about 300 km), and then 600 km southward to a point approximately 200 km offshore. The existing National Weather Service (NWS) radiosonde stations within the network area (about 6) would be enhanced by 5-6 additional stations, including two stations offshore to double the spatial resolution of the NWS network. Vertical profiles of ozone would be obtained to 700 mb (10,000 ft msl) by single-engine aircraft at each of 12 available radiosonde locations. The network would be operated for a 3-month period.

The benefits of the enhanced observational network would be:

- Provision of offshore data
- 6-hour resolution on radiosonde ascents
- Vertical profiles of air quality obtained three to four times per day.

An important element of the routine monitoring network should be the acquisition of satellite, radar, and lightning data from existing systems for the purposes of enhancing the definition of mesoscale circulations and convective phenomena. Although these systems (for the most part) are in place and operating, special attention should be devoted to the archiving of these data (not routinely done). Satellite data should include visible and infrared observations from both geostationary and polar-orbiting satellites. High-resolution, false-color radar displays are available from several commercial sources using data from National Weather Service radars.

Operational lightning detection networks (e.g., the lightning position and tracking system available from Atlantic Scientific Corp., Melbourne, FL) already cover most of the Gulf Coast area and should blanket the study region on the time frame of the Gulf Coast oxidant program.

## RECOMMENDATIONS FOR A CONCEPTUAL PROGRAM DESIGN

The two working groups recommended that some preparatory research and development efforts should be undertaken in addition to the principal components of the major study itself. As summarized in Table 4, the preparatory efforts comprise both modeling and data analysis studies, and experimental studies or hardware development. In some cases, these efforts are not unique to the Gulf Coast oxidant study or are already being actively pursued, and these efforts are not included in the conceptual experimental design presented later. In many cases the study would be seriously affected in the event the efforts are either unsuccessful or not completed in time. The working groups provided subjective cost estimates which should be considered indicative of the order of magnitude of each effort. Each preparatory study is

TABLE 4. PREPARATORY STUDIES

Description	Estimate of Cost (\$000) <sup>†</sup>	Priority*
Modeling and Data Analysis:		
- collection, analysis and interpretation of existing air quality and meteorological data	200-300 (p)	Н
- application of Urban Airshed Model to Houston - evaluation of Regional Oxidant Model‡ (being	50-100 (g) nc	M H
done by USEPA for northeastern states) - ROM sensitivity study to evaluate impact of natural hydrocarbon emissions‡	ne	L
• Experimental Studies and Hardware Development:		
- develop gaseous aldehyde measurement techniques (surface and airborne) †	100 <b>-200</b> (p)	Н
- hydrogen peroxide instrument development (work ongoing elsewhere)	50 (p)	М
- smog chamber studies of Gulf Coast atmospheres	300 (p)	М
- in-cloud chemistry studies (coordinate with on-going studies) †	≤500 (p)	М
- continued development/improvement of airborne wind-finding doppler radar (work on-going elsewhere) †	nc	М-Н
<ul> <li>improvements in tracer technology, e.g.</li> <li>fluorescent dye, perfluorocarbons, tetroons,</li> </ul>	ne	M-H
reactive tracers (work on-going elsewhere) - improvements in remote measurement of ozone, profiles by UV and IR DIAL (ongoing elsewhere) †	nc	Н
- exploratory, limited-duration mobile (air-borne) aerometric measurement program and	500-1000	Н
data analysis (limited) - enhanced routine monitoring network for ozone, hydrocarbons, and PBL structure	1250-1500	L-H**

 $_{\rm H}^{\star}$  = high; M = medium, L = low priority

p = contract research; g = USEPA study

Study is not unique to Gulf Coast

<sup>\*\*</sup> Priority is constrained by availability of funds.

also given a subjective priority ranking. In general, the high-priority efforts are essential for a high-quality Gulf Coast oxidant study, while the moderate-priority efforts are highly desirable. A low priority indicates that the results would be very useful, but not essential.

The overall conceptual program design (Figure 2) is divided into four elements:

- (1) Preparatory analyses
- (2) Preparatory measurement studies
- (3) Gulf Coast regional oxidant transport study
- (4) Reporting.

In the preparatory-analysis phase, currently available air quality and meteorological data from the study region would be compiled to create a comprehensive data base. The data would be analyzed to provide a better understanding of temporal and spatial variations of oxidant throughout the region, and to develop an improved understanding of the importance of (for example) moisture, synoptic-scale wind flow, long range transport, land-sea breeze circulation, and low-level jet in the formation of high oxidant concentrations. Additionally, a photochemical simulation model would be applied to the Houston metropolitan area as a test of the hypothesis that oxidant concentrations are anomalous or that the combination of relatively high HC-to-NO<sub>X</sub> ratio, high ambient humidity, and intense sunlight result in chemical conditions that are different from other regions.

As part of the preparatory measurement/study phase, an enhanced routine monitoring network would be established and operated for three months to provide a comprehensive Eulerian aerometric data base. The purpose would be to gain an improved understanding of oxidant formation and transport, and to develop a detailed research plan for the primary experimental program. The ERN\* would include aerometric soundings by light aircraft at each of 12 radiosonde locations. An exploratory mobile sampling and data analysis task is also recommended to refine and coordinate mobile sampling methods and to provide a limited data base

<sup>\*</sup>ERN - Enhanced Routine Monitoring Network.

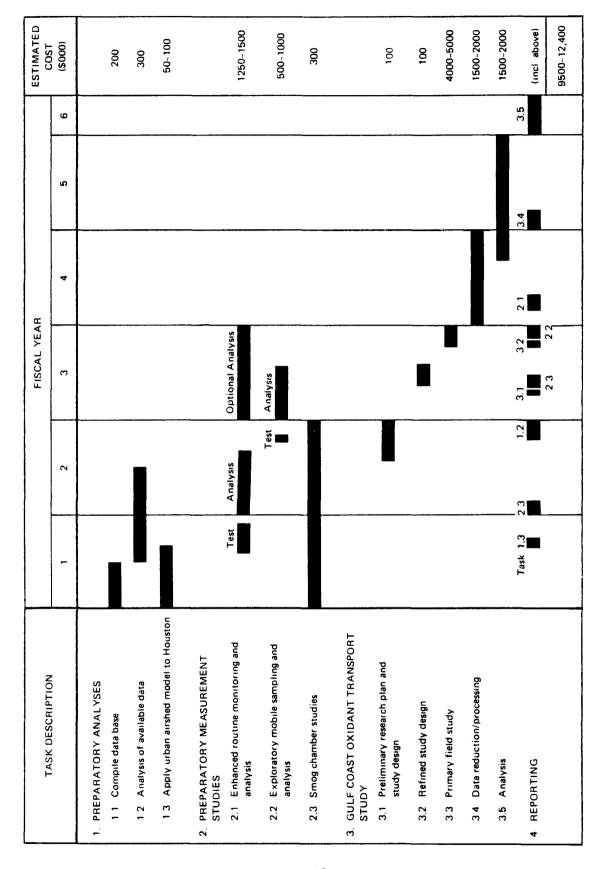


Figure 2. Conceptual program design and approximate costs.

for the purpose of optimizing the use of the various aircraft in the primary study. This limited sampling program would focus on developing sampling strategies, and on obtaining limited data for the mesoscale land/sea breeze, cloud venting, and medium-range transport experiments that are anticipated to be conducted later during the primary field study. Lastly, smog chamber studies would be conducted to simulate photochemical oxidant production unique to the precursor mixture of the Gulf Coast, and to explore the possible effects of high relative humidity.

A preliminary, detailed research plan and study design would be developed for the experimental and analysis phases of the principal Gulf Coast oxidant transport and transformation study. The plan would specify numbers and types of airborne platforms, instrumentation specifications, and sampling strategies and protocols. Also specified would be comprehensive specifications for the surface aerometric network, including parameters for measurement, analytical methods, site locations, sampling frequency, data processing and so forth. aspects of tracer applications in the mesoscale and medium-range transport studies would also be delineated, such as tracer-types, and release, sampling and analysis methods. Scheduling of the intermediate range transport case-studies would also be addressed, including definition of criteria for determining when or where experiments are to be conducted, and for contingency plans in the event meteorological conditions are not optimum for the fulfillment of the primary study objectives.

The three-month primary field study of oxidant transport and transformation would have two major aspects: (1) operation of the enhanced routine monitoring network, and (2) short-term case studies of mesoscale and medium-range transport and transformation. The short-term case studies would consist of (1) mesoscale studies of pollutant transport and oxidant production within the domain of the land/sea breeze circulation and (2) medium-range (ca 400-500 km) studies of oxidant transport out of the Gulf emissions source region. Cloud venting studies would be an integral component of the mesoscale

experiments. The mesoscale studies would constitute the majority of the 10 case studies recommended, and would rely heavily on a full complement of airborne platforms in addition to the use of gas tracers with airborne and surface in situ sampling. Each study would cover a 30-hr period. On the order of three medium-range transport experiments are contemplated. Analysis of the processed data would address several basic issues: (1) relation of ozone formation to the precursor mix of the region, (2) impact of high humidity, (3) role and significance of cumulus clouds in venting ozone or precursors out of the boundary layer, (4) nature and significance of medium-range oxidant and precursor transport into and out of the region, (5) role of land/sea breeze circulation in production of locally high ozone concentrations, and (6) three-dimensional spatial distribution of ozone on episodic days.

The overall program could be accomplished in about five years at an estimated cost that ranges between 9.5 and 12.4 million dollars. In the event that the preparatory field studies (i.e., ERN and exploratory mobile sampling) are deleted from the program, the estimated cost range would decrease to about 7.75 to 9.9 million dollars; the schedule might be compressed by approximately six months. The working groups did not, however, recommend the deletion of the preparatory field studies. On the contrary, they were highly recommended as necessary to the ultimate success of the program.

Finally, the Gulf Coast oxidant study should seek to integrate and coordinate its activities with those of other major atmospheric studies planned for the same time frame and geographic domain. The multi-agency national STORM program (STormscale Operational and Research Meteorology) appears to be one such potentially viable mesoscale study. STORM has been proposed by a steering committee composed of 13 representatives of member institutions of the University Corporation for Atmospheric Research (UCAR), and would be supported at an annual cost of 60 to 120 million dollars per year for 10 years, (UCAR, 1983). A second candidate program is a projected 100 million dollar acid precipitation study (MATEX) of long-range atmospheric transport and transformation being considered by the Electric Power Research Institute. A MATEX design and

feasibility study is currently underway, and should be completed later this year. Preliminary indications are that it could overlap the geographical domain and schedule of the Gulf Coast oxidant study. Integration of the Gulf Coast oxidant study with programs like STORM and MATEX should be pursued because of the benefits of technical synergism and cost savings that would result.

### SECTION 2

### INTRODUCTION

### **OBJECTIVES**

As stated by the U.S. Environmental Protection Agency (EPA), the basic objective of a Gulf Coast oxidant transport and transformation experiment would be "to investigate the unique meteorological and chemical processes present in the Gulf Coast region that must be understood to effectively adapt the EPA Regional Oxidant Model (ROM) to that geographic area." Examples of the more important, relevant processes that require study include the following:

- Three-dimensional transport by land- and sea-breeze circulations
- Transport and diffusion under near-stagnation conditions
- Ozone (and precursor) venting or mixing by precipitating and non-precipitating cumulus clouds
- Washout of nitrogeneous and oxygenated species and its impact on oxidant production
- Parameterization of the over-water atmospheric surface layer
- Large-scale inflow and outflow to/from the region
- Investigation of anomalously low values of the ratios of  $NO_X/NMHC$  and  $PAN/O_3$  and the concentration of PAN
- Nocturnal NO, removal and transformation mechanisms.

### **BACKGROUND**

### General

The western portion of the U.S. Gulf Coast has several unique meteorological and (air pollutant) emissions characteristics that must be better understood in order to project or control atmospheric concentrations of ozone. The high concentration of refining and petrochemical industries along the Louisiana and northeastern Texas coasts results in a higher-than-normal ratio of atmospheric concentration of hydrocarbons to oxides of nitrogen; at the same time, PAN (peroxyacetylnitrate) concentrations are significantly less than those found in other source regions around the country. High ozone concentrations are infrequent in Houston and Baton Rouge and, when present, do not persist for extended periods as is common elsewhere (e.g., Los Angeles; northeast corridor, Washington-New York). There are conflicting views as to whether the western Gulf Coast is a significant regional exporter of ozone or precursors, or whether it is itself adversely impacted by the advection of pollutants into the region.

Perhaps the most unique aerometric feature of the region is not any one of the meteorological or chemical (emissions) characteristics, but rather the fact that many occur simultaneously in combination. densities are greatest near the coastline, and (except for Dallas) decrease markedly inland. The diurnal land-sea breeze regime encompasses most of the significant source regions. In addition to the diurnal reversal of wind flows, convergence along the sea breeze front induces afternoon and evening cumulonimbus development. This in turn, can cut off photochemical ozone production in the boundary layer while transporting ozone and precursors out of the boundary layer into the free troposphere. A further complication occurs at night when a low-level nocturnal jet is frequently formed between the top of the surface-based nocturnal radiation inversion and the bottom of the subtropical high-pressure subsidence inversion. On the larger scale, the location of the source region at the northerly edge of the subtropical easterly waves makes regional-scale advection poorly defined and difficult to simulate in numerical models. The lack of upper-air meteorological data in the western Gulf is an added complication. On the regional scale, the role of the nocturnal midwestern low-level jet (created by the slope of the Great Plains) is largely unknown insofar as its effectiveness and importance in transporting coastal emissions to the upper Mississippi Valley.

In developing a conceptual design for a Gulf Coast oxidant transport and transformation experiment, the working groups considered the potential significance of these aerometric characteristics or processes, and developed an outline for an interrelated series of studies that would have a high probability of: (1) determining which processes are most important in controlling regional oxidant concentrations, and (2) providing data to quantify the transport and transformation mechanisms involved, so that (3) a data base would be available for diagnostic evaluation of ROM with subsequent improvements made to the model.

The approach to the development of a conceptual design at the workshop involved a sequence of introductory, informal lectures followed by a series of meetings of small working groups. The workshop agenda is given as Figure 3. The lecture topics included: background profiles of regional meteorology, chemistry and emissions; overview of ROM; and summaries of relevant previous and future experimental studies. Two working groups were established: Group A was chaired by Mr. Gary Tannahill of Exxon Company, U.S.A., with Dr. Hanwant B. Singh, SRI International, and Dr. Fran Pooler, USEPA, serving as vice-chairmen. Group A focused on atmospheric chemistry measurement needs and resources. Group B was chaired by Dr. William Pennell of the Battelle-Pacific Northwest Laboratories, with vice-chairmen Dr. John Clarke\*, USEPA, and Mr. William Viezee, SRI International. Group B directed its efforts toward the identification and prioritization (relative) of atmospheric processes and development of a framework for the design of a series of experiments.

<sup>\*</sup>On assignment from the National Oceanic and Atmospheric Administration (NOAA).

	TUESDAY, 15 NOVEMBER 1983
08:00 - 09:00 a.m.	Registration
09:00 - 09:15	Welcome, K. Demerjian, Director, Meteorology and Assessment Division, Environmental Sciences Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency
09:15 - 09:30	EPA Goals and Objectives, J. Ching, MAD, ESRL, U.S. Environmental Protection Agency
09:30 - 10:15	Summary of Synoptic Meteorological Features and Transport Characteristics of the Region, W. Viezee, SRI International
10:15 - 10:35	BREAK
10:35 - 11:15	Summary of Emissions and Ambient Ozone Features of the Region, W. Dabberdt, SRI International
11:15 - 12:00 p.m.	Overview of Photochemical Features and Processes, H. Singh, SRI International
12:00 - 1:30	LUNCH
1:30 - 2:00	Overview of the EPA Regional Oxidant Model, K. Shere, MAD, ESRL, U.S. Environmental Protection Agency
2:00 - 2:30	Review of the PEPE/NEROS Experimental Program. J. Clarke, MAD, ESRL, U.S. Environmental Protection Agency
2:30 - 3:00	Preview of Other Prospective Atmospheric Studies in the Region, F. Pooler, MAD, ESRL, U.S. Environmental Protection Agency
3:00 - 3:20	BREAK
3:20 - 4:00	Conceptual Framework for a Gulf Coast Regional Oxidant Transport and Transformation Study, W. Dabberdt, SRI International
4:00 - 4:30	Group Discussion of the Proposed Conceptual Framework

Figure 3. Workshop agenda.

4:30 - 4:45 p.m.	Charge to the Working Groups
4:45 - 5:15	Initial Working-Group Meetings:
	Group A G. Tannahill, Chairman F. Pooler, Vice Chairman H. Singh, Vice Chairman
	Group B W. Pennell, Chairman J. Clarke, Vice Chairman W. Viezee, Vice Chairman
	WEDNESDAY, 16 NOVEMBER 1983
08:00 - 09:00 a.m.	Plenary Session
09:00 - 10:00	Working Group Sessions
10:00 - 10:20	BREAK
10:20 - 10:00	Working Group Sessions
12:00 - 1:15 p.m.	LUNCH
1:15 - 2:00	Plenary Session
2:00 - 3:00	Working Group Sessions
3:00 - 3:20	BREAK
3:20 - 5:00	Working Group Sessions
6:00 - 8:00	DINNER
8:00 - 9:30	Working Group Sessions
L	

Figure 3. (continued)

THURSDAY, 17 NOVEMBER 1983
Plenary Session
Working Group Sessions
BREAK
Working Group Sessions
LUNCH
Final Working Group Sessions
Final Plenary Session
ADJOURNMENT

Figure 3. (concluded)

The following subsection summarizes the lectures, while Chapter II of this report summarizes the discussions of the two working groups. Chapter III contains recommendations for a conceptual program design, while Chapter IV summarizes the workshop and its recommendations. The Appendix provides names and addresses of the workshop participants, and identifies the working group in which each participated.

### Summary of Presentations

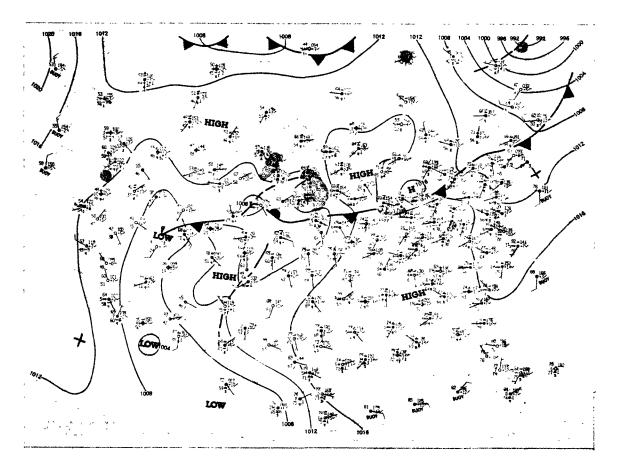
The following discussions are summaries of five technical presentations given at the beginning of the workshop. They represent three limited summaries of background conditions in the region as well as the scope of several local significant experimental studies; also included are overviews of (1) EPA's Regional Oxidant Model, which may be applied to the Gulf Coast region, and (2) an earlier, major aerometric-oxidant study conducted in the northeast, which in some respects might be similar to various aspects of a Gulf Coast oxidant

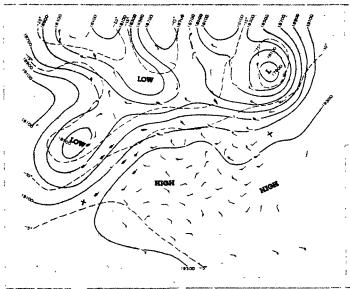
study. The five presentations were originally given to familiarize the workshop attendees with the region and its characteristics and problems; the summaries are given here with a similar purpose—to orient the reader. It should, however, be reemphasized that these discussions do not necessarily constitute any of the recommendations of the working groups; they are simply an assemblage of background information presented by the organizers of the workshop.

# Synoptic Meteorological Features and Transport Characteristics of the Gulf Coast Region (W. Viezee, SRI International)--

The meteorological conditions that prevail along the Gulf Coast during the summer months of June, July, August, and September were reviewed. Summertime weather conditions are unique with respect to those in other regions of the United States for the following reasons:

- The Gulf Coast is under the influence of a maritime-tropical (mT) air mass of large vertical extent. This air mass is associated with a westward extension of the quasi-stationary subtropical high pressure system centered at 30°N latitude over the Atlantic Ocean (also called "high of the Azores" or "Bermuda high"). Horizontal pressure gradients are weak, and winds are light and variable from ground level to 500 mb (18,000 ft MSL) and above. No persistent "steering" currents exist. Figure 4 shows an example of some operational weather maps (surface weather map and 500-millibar height-contour chart) that illustrate the typical pressure distribution found in the Gulf Coast area during summer.
- Over the Gulf of Mexico, the average sea surface temperature (83°F) is higher than the average air temperature, which accounts for large values of relative humidity in the air mass. The average air temperature inland over the coastal plain is higher than that over the water from June to August. This land/water air-temperature difference is most evident along the Gulf Coast of northeast Texas and Louisiana. Significant sea-breeze circulations are observed in these areas.
- Along the Texas and Louisiana coasts, the daily maximum temperature can reach and exceed 100°F. The 24-hour values of relative humidity rarely fall below 60 percent.





SOURCE: Dept. of Commerce, NOAA, 1983

Figure 4. Example of typical synoptic-scale weather conditions along the U.S. Gulf Coast during summer (18 July 1983, 07:00 EST).

• In the warm, moist, and uniform air mass with light and variable wind flow, local and regional weather conditions are frequently controlled by diurnal radiative heating and cooling. Convective showers and thunderstorms during the day, fog, and low-level stratus clouds at night, and local land— and seabreeze circulations are very much evident. High speed winds near the top of the boundary layer (low-level jet), and the persistent occurrence of the sea-breeze front or convergence zone can be considered as unique features of the Gulf Coast meteorology. Figure 5 shows the annual mean number of thunderstorm days for the United States. The maximum occurrence along the flat Gulf Coast area, which coincides with the mean position of the sea-breeze front, exemplifies a unique meteorological feature.

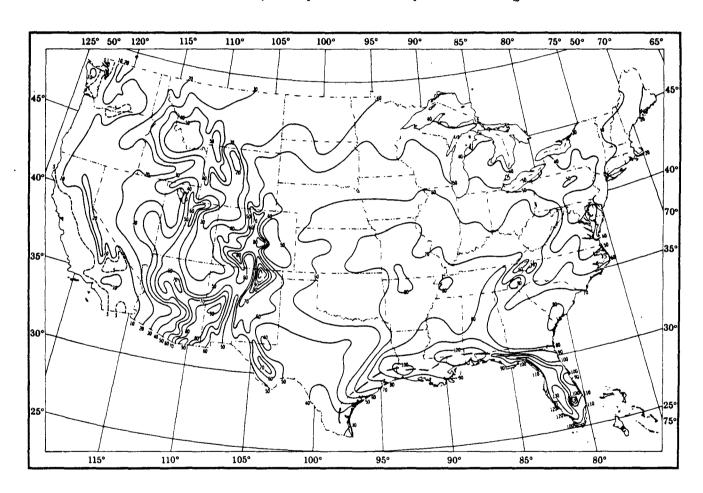


Figure 5. Mean number of thunderstorms — annual.

Synoptic-scale, three-dimensional air parcel trajectories near the surface and 5000 ft (1500 m) were presented for the periods 19-21 June and 22-24 August 1983, when high ozone concentrations were observed in the Houston, Texas area. These data were presented for the purpose of identifying typical summertime air transport characteristics.

During the afternoon of 20 July, 1-hour average  $0_3$  concentrations in the Houston area ranged from 140 to 210 ppb. No elevated readings were recorded near Baton Rouge and New Orleans, Louisiana. Figure 6 shows the three-dimensional air parcel trajectories near the surface and 5000 ft (1500 m) generated by the Limited Area Fine-Mesh (LFM-II) numerical prediction model of NOAA\* for the 24-hour period of 18:00 CST, 19 July to 18:00 CST, 20 July. Thus, the trajectories are the predicted paths of air parcels that terminate at the indicated locations during the late afternoon of 20 July near the times of elevated  $0_3$  readings at Houston. The mean 24-hour vertical motion of the air parcels, expressed in units of cm per second, is printed at the trajectory end-points; mean descending motions are negative, ascending motions are positive. [The LFM-trajectories, however, are subject to considerable uncertainty, particularly in the Gulf Coast region and within the planetary boundary layer. Much of this uncertainty derives from the weak pressure gradients at these low latitudes and the effects of secondary circulations and migratory easterly waves. As a consequence, these trajectories should be viewed as only a general indication of multi-day atmospheric transport.] The trajectories are typical of those found during the summer. The air parcels move anti-cyclonically around the prevailing high-pressure system with a general downward (subsiding) motion. On the west side of the high-pressure system, air parcels are transported by southerly winds from locations over the Gulf of Mexico, across the Texas coast, and toward Oklahoma, Arkansas, and northern Louisiana. Depending on the position of the prevailing high pressure system and the strength of the horizontal pressure-gradient field, this general area can be one of northward transport of Gulf Coast emissions.

<sup>\*</sup>Trajectory data were supplied by Ronald M. Reap, Techniques Development Lab. (TDL)/NOAA, Silver Spring, Maryland.

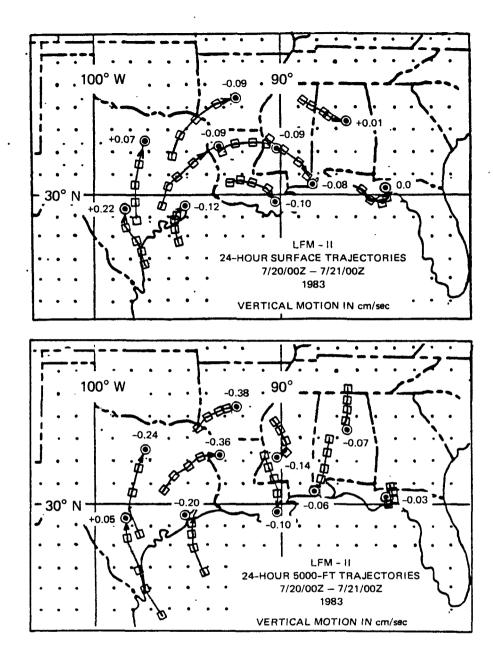


Figure 6. Three-dimensional air-parcel trajectories near the surface and near 5000 ft predicted by LFM-II for the 24-hour period of 19 July, 18:00 CST to 20 July, 18:00 CST.

Air parcel positions are indicated at 6-hour time intervals (squares). 24-hour mean vertical motion is printed at end of trajectory with downward motion shown as negative.

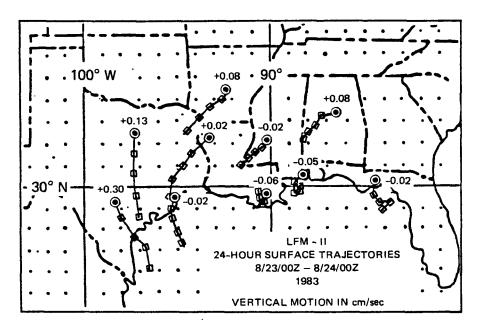
In southern Louisiana and Mississippi, air parcels move from the coastal area southward over the Gulf of Mexico. Figure 6 strongly suggests that air parcels recirculate from land to water and back to land.

During the period 22-24 August, hourly 0<sub>3</sub> concentrations as high as 130 to 210 ppb were recorded in the Houston area during daytime. Near Baton Rouge, Louisiana, occasional readings of 107 and 112 ppb occurred, while in New Orleans the highest concentration for the month was only 85 ppb on 23 August. Figure 7 shows the LFM-II air parcel trajectories predicted for the 24-hour period of 18:00 CST, 22 August, to 18:00 CST, 23 August. The general anticyclonic flow of the air parcels associated with the high pressure system is evident. The speed of the air parcels both near the surface and near 5000 ft, however, is much less than on 20 July (Figure 6). In fact, the flow field near the 5000-ft level is close to stagnation. Southerly transport of air is seen along the Texas coast. Southern Louisiana and Mississippi show little air movement. Except perhaps for the Texas area, no defined large-scale transport out of the Gulf Coast region is evident.

A look at other days throughout the summer of 1983 showed characteristics of air-parcel transport quite similar to those of Figures 6 and 7. Under such conditions of low wind speed (i.e., small pressure gradients), the presence or absence of high-oxidant events may be controlled primarily by local circulations associated with: the sea breeze and the sea-breeze convergence zone; daytime convective clouds (e.g., fair weather cumulus, towering cumulus, and thunderstorms); and the nighttime land breeze and/or low-level jet.

# Summary of Emissions and Ambient Ozone Features of the Region (W. Dabberdt, SRI International)--

The major source areas for hydrocarbon and nitrogen oxides emissions along the western Gulf Coast are the Houston-Galveston-Port Arthur and Baton Rouge-New Orleans corridors; secondary source areas are Lake Charles (LA), Dallas, Fort Worth, Corpus Christi, San Antonio, and Oklahoma City-see Figure 8, adapted from Clark (1980). Point-source hydrocarbon emissions in the Port Arthur (250,000 tons  $y^{-1}$ ) and Houston



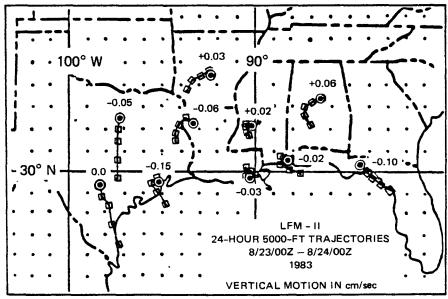
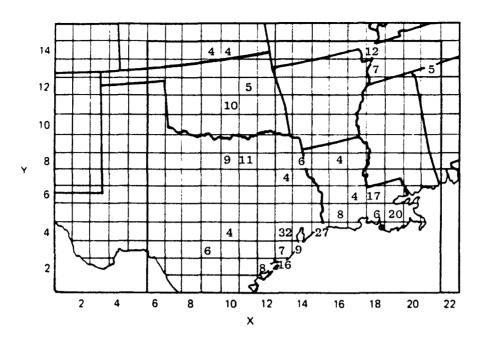
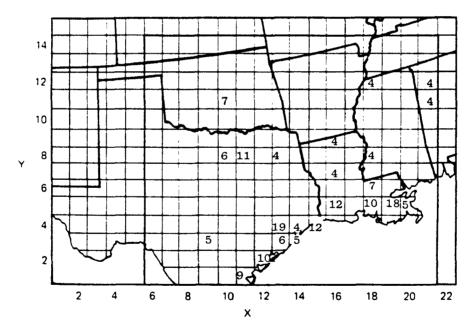


Figure 7. Three-dimensional air-parcel trajectories near the surface and near 5000 ft predicted by LFM-II for the 24-hour period of 22 August, 18:00 CST to 23 August, 18:00 CST.

Air parcel positions are indicated at 6-hour time intervals (squares). 24-hour mean vertical motion is printed at end of trajectory with downward motion shown as negative.



#### (a) HYDROCARBONS



#### (b) OXIDES OF NITROGEN

Figure 8. Gridded annual emissions ( $10^4$  ton  $y^{-1}$ ); values less than 40,000 ton  $y^{-1}$  not shown.

(190,000 tons  $y^{-1}$ ) grid squares (approximately 125 km on a side) are greater than those of any similar grid in the eastern two-thirds of the United States, while Baton Rouge, Galveston and New Orleans (about 140,000 tons  $y^{-1}$ ) are comparable to the emissions in New Jersey and Delaware (130,000 tons  $y^{-1}$ ). Area-source hydrocarbon emission densities in New Orleans and Houston are comparable to those of St. Louis, but are a factor of four less than New York and Chicago. Together, area- and point-source emission densities in the New Orleans-Baton Rouge and Houston-Port Arthur-Galveston areas are nearly comparable to the major source regions of the upper midwest and northeast. Emission densities of nitrogen oxides are generally less than those in the major midwestern and northeastern source regions. As seen in Figure 8, NO, emissions are fairly uniform all along the coast from Bay City, TX (southwest of Galveston) to New Orleans. A significant feature of both hydrocarbon and nitrogen oxides emissions along the Gulf Coast is the high concentration in two major source regions and the very low concentration in most of the surrounding areas. This contrast is highlighted in Figure 8 by the omission of emission-values that are less than 40,000 tons  $y^{-1}$ .

Ozone concentrations at ground level in Houston and southern
Louisiana are infrequently high and spatially variable. Trijonis (1979)
summarized ozone levels during the period 1974-78 at two locations in
Houston; three indicators were used, as shown in Figure 9: (1) average
daily peak-hour concentration during the smog season; (2)
95th-percentile.of daily peak-hour concentrations during smog season;
and (3) second-highest hourly concentration for the year. The Mae Drive
location (Figure 9a) shows little interannual variation of the
smog-season average concentration (Item 3 above) of about 70 ppb, while
the 95th-percentile value varies from 140 to 175 ppb and the
second-maximum values vary from 200 to 265ppb, with the peak
second-maximum value recorded in 1976. Ozone concentrations at Aldine
(Figure 9b) are generally similar, except that the second-maximum peak
of 300 ppb occurred in 1975. Ozone trends in southern Louisiana are
tabulated in Table 5 for the period 1976-81 from data compiled by the

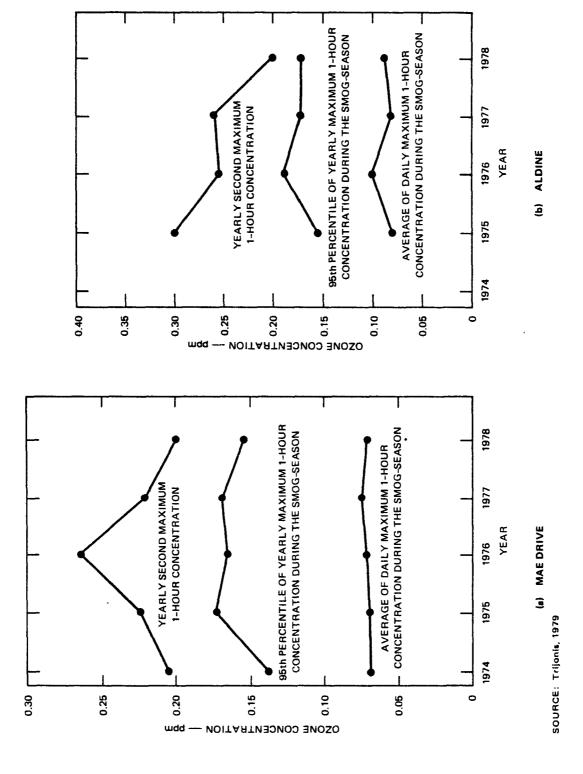


Figure 9. Ozone trends in Houston.

Louisiana Department of Natural Resources. Mean annual concentrations are lowest at New Orleans and highest at Baton Rouge. New Orleans had only four days (in six years) with hourly concentrations in excess of the 120-ppb ambient air quality standard; Lake Charles averaged about five days per year, and Baton Rouge averaged 13 days. While annual maximum hourly concentrations averaged 190 ppb in Baton Rouge, they were only 152 ppb in Lake Charles and 121 ppb in New Orleans.

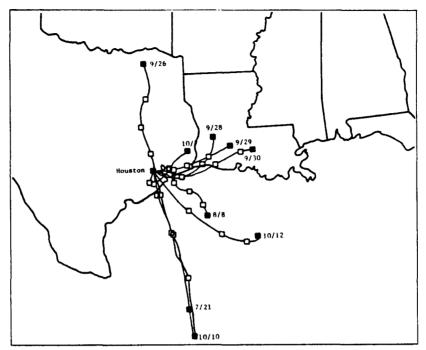
TABLE 5. OZONE (ppb) TRENDS IN LOUISIANA

	<b>'</b> 76	<b>'</b> 77	<b>'</b> 78	<b>'</b> 79	'80	'81
Baton Rouge						
Maximum Mean Days >120	201 28 16	188 25 11	214 24 28	140 19 2	218 21 13	179 22 10
Lake Charles						
Maximum Mean Days >120	144 25 14	145 16 1	167 17 5	117 17 0	187 22 4	- - -
New Orleans						
Maximum Mean Days >120	118 16 0	120 14 0	137 16 2	122 15 1	126 14 1	104 14 0

Of the many specialized aerometric studies conducted over the past 10 years in the region, two relevant experimental studies of regional oxidant distribution in Louisiana and eastern Texas were reviewed: the 1975 Gulf Coast oxidant study conducted by Research Triangle Institute, RTI (Decker et al., 1976) and the 1976 southern Louisiana oxidant study by Radian Corporation (Lambeth, 1978). The RTI study provides: (1) 48-hr backward trajectory-estimates from Houston, DeRidder and Nederland

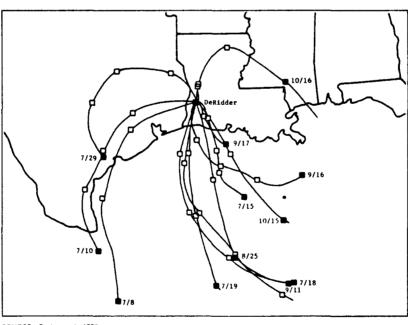
for the upper- and lower-decile days of the 1975 ozone "season"--July-October 1975; and (2) ozone concentrations along extended aircraft flight tracks (usually a rectangular pattern), together with backward air trajectories for selected points on the track (e.g., corners). There is no unambiguous distinction between the trajectories associated with the upper-decile ozone cases and those of the lower-decile cases. In general, however, the high days have more of an eastward component to them and are somewhat shorter (i.e., lower wind speed). Figure 10 illustrates: (a) high-ozone days at Houston, and (b) low-ozone days at DeRidder, LA. Figure 11 is typical of the "high-ozone" aircraft tracks from the RTI study: background concentrations for this low-level flight (225 m) appear to be in the 60-80 ppb (120-160 g m<sup>-3</sup>) range with peak values of 125 and 143 ppb at different locations. Along the Louisiana coast, morning (triangles) and evening (squares) trajectories diverge little, while there is significant divergence in the northern part of the state. However, quantitative analysis of the aircraft data is limited by sampling difficulties associated with the use of a single aircraft in the large area of the sampling domain.

In the Radian study, continuous surface measurements of ozone were made from July 17 through October 17, 1976, at nine sites in southern Louisiana--an area about 500 km (E-W) by 200 km (N-S). Lambeth (1978) concludes that the data indicate that dense precursor emissions from the Baton Rouge area result in high ozone levels downwind; the effect was most prominent 15-25 km downwind, although "still quite noticeable" 50-80 km downwind. Similar results were observed downwind of New Orleans. Comparison of ventilation conditions during each of several multi-day case studies generally indicated that widespread high ozone in southern Louisiana is associated with poor ventilation, and low ozone with good ventilation. There is also evidence to imply that ozone is depleted" less rapidly over the Gulf of Mexico and unpopulated coastal areas compared to the normal decline in ozone after sunset in inland areas of southern Louisiana." Also, increased cloud cover and improved dispersion near "large rain areas" may explain the low ozone levels observed in areas of extensive shower activity.



SOURCE Decker et al., 1976

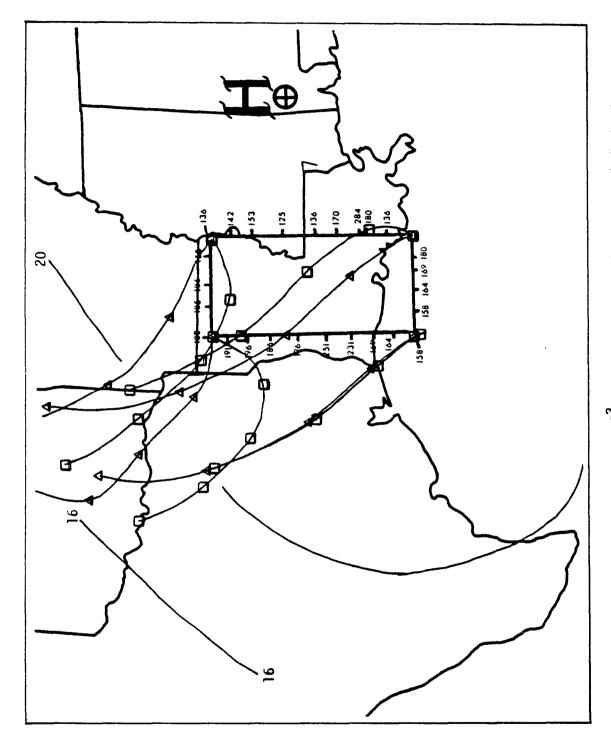
(a) UPPER DECILE OZONE MAXIMA (03 > 278  $\mu g$  m  $^{-3}$ ) FOR HOUSTON



SOURCE Decker et al 1976

(b) LOWER DECILE OZONE MAXIMA (0  $_3 < 75~\mu g~m^{-3})$  FOR DeRIDDER

Figure 10. Backward boundary-layer trajectories.



Ozone concentrations ( $\mu gm^{-3}$ ), air trajectories and sea level pressure distribution for October 20, 1975 flight. Figure 11.

On a larger spatial scale, Wolff and Lioy (1980) and Wolf et al. (1977) examined the possibility of regional-scale ozone transport from the western Gulf Coast to the northeast corridor. Their analyses are primarily qualitative and involve the interpretation of daily synoptic maps of peak-hour ozone distribution and corresponding multi-day, boundary-layer air trajectories; an example is given as Figure 12. conclusion is made that "under certain meteorological conditions, high ozone concentrations were transported from the western Gulf Coast area to the Midwest and the Northeast... The circulation around the high-pressure systems which caused these episodes traveled northward from the Texas-Louisiana Gulf Coast to the Midwest and then eastward to the Northeast and the Middle Atlantic Coast. Ozone concentrations within this river averaged ~120-130 ppb and were as high as 328 ppb in Connecticut... The ozone produced is undoubtedly supplemented by emissions into the ozone river en route through the Mississippi and Ohio Valleys to the Northeast."

The concept of a cross-country "ozone river," however, is open to substantial question as to whether it indeed reflects the long-range transport of ozone, or is the result of a continuum of source regions and associated downwind areas where ozone production and destruction occur on the mesoscale. This countercontention has been suggested by Niemeyer (1977) who states that "an alternative analysis would show that in regions of limited dispersion (associated with the weak gradient region of the high pressure cell) conditions are optimum for the limited dilution of ozone precursors and that the elevated ozone levels observed are due to precursors emitted not too far distant from the point of measurement."

The obvious conclusion would appear to be that the potential significance of an actual "ozone river", which transports ozone in high concentrations for thousands of kilometers, is sufficiently great to warrant further study to document the extent and magnitude of ozone transport away (or toward) the high emission areas of the Gulf Coast.

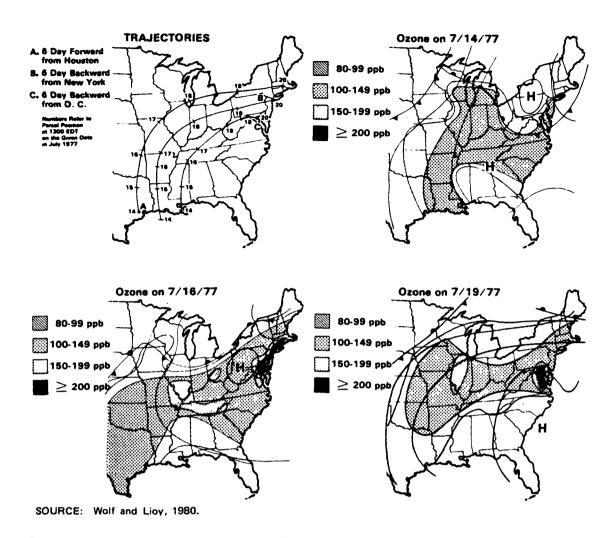


Figure 12. Air parcel trajectories during July 14-20, 1977, and ozone concentrations patterns.

#### Atmospheric Oxidant Chemistry: Features and Measurement Technologies (H. Singh, SRI International)—

The existing literature was reviewed with two objectives in mind:

- What are the typical or atypical features of the Gulf Coast area as far as oxidant formation is concerned?
- What new measurement technologies are likely to be available to the planned Gulf Coast oxidant study?

One of the key features of the Gulf Coast region is its somewhat unique meteorology. Typical weather conditions are characterized by hot temperatures (daily maximum temperatures of 80-110°F for the year) and intense morning sunshine followed by afternoon thundershowers. While high temperatures and intense sunlight are likely to accelerate

 $0_3$ -forming processes, frequent showers most likely decelerate them. Direct knowledge of the effect of thundershowers on a pre-existing photochemical mix is limited, but it can be speculated that such processes would remove free radicals, aldehydes,  $NO_X$ , acids, and possibly, some nonmethane hydrocarbons.

The key photochemical processes that result in ozone formation were reviewed briefly. In addition, the principle processes that oxidize and ultimately remove nitrogen oxides from the atmosphere were also reviewed. It was pointed out that while nighttime and daytime removal of  $\mathrm{NO}_{\mathrm{X}}$  proceeds via substantially different processes, in both cases heterogeneous processes play an important role. This feature of  $\mathrm{NO}_{\mathrm{X}}$  removal is likely to be more important in the Gulf Coast region compared to other, drier regions. Indeed, the direct wet deposition rate of  $\mathrm{NO}_{2}$  can be as high as 25 percent of the nitrate aerosol rate (5 x 10  $^{-4}\mathrm{s}^{-1}$ ).

Review of precursor data from Houston indicated the following generalizations:

- Typical average nonmethane hydrocarbon concentrations are of the range 0.8 to 1.2 ppmC in the morning hours (6-9 AM) and about 40 percent lower in the afternoon.
- The NMHC mix is typically composed of 60-70 percent parafin, 10-20 percent olefin, and 15 to 25 percent aromatics.
- Mean hourly concentrations of nitrogen oxides (NO $_{\rm x}$ ) are 10 to 50 ppb with maximum (1-h) concentrations of 80 to 200 ppb.
- Average NMHC/NO<sub>x</sub> ratio (ppmC/ppm) is 10 to 20, but a range of 5-50 can be encountered.

The above precursor levels were compared with limited data from other cities to point out that ambient precursor concentrations in Houston were fairly typical of those encountered in other United States cities. Compared to data from other regions (Table 6), the  $\rm HC/NO_X$  ratio is slightly on the high side, and may reflect somewhat more rapid removal of  $\rm NO_X$  by wet processes in Houston or excess hydrocarbon sources from the nearby ship channel.

The behavior of secondary pollutants (ozone and PAN) was also examined. The highest average  $0_3$  levels are encountered during the summer (April-September). A limited analysis of  $0_3$  data from 4 stations

in Houston during July-September 1983, was used to make the following two observations:

- Although hourly 03 levels as high as 200-300 ppb are encountered in Houston, the frequency of such exceedences is very low.
- High 0<sub>3</sub> levels (>120 ppb) rarely occur on consecutive days or on days immediately following extensive shower activity.

There was no evidence that air from the Gulf contained high  $0_3$  or precursor concentrations. The Beasley  $0_3$  monitoring station (outside Houston) has collected data for a number of years. When days with winds from Houston are excluded,  $0_3$  levels (corrected) were typically in the 60 to 100 ppb range for 1977-1979. NMHC levels in the vicinity of this station with Gulf winds were 10 to 20 ppb.

Data from a number of stations from southern Louisiana also showed relatively low  $0_3$  levels. When the Louisiana data are corrected for calibration errors (by -18 percent), the  $0_3$  exceedences (>120 ppb) during August and October 1976, are virtually nonexistent. In addition, available PAN data from Houston show extremely low concentrations with 80 to 100 percent of data falling in the 0-2 ppb range. As Table 7 shows, not only are PAN levels low, but  $0_3$  to PAN ratios are exceedingly high. The precise reasons for this low PAN abundance have not been explored.

Available technology for measurement of trace chemicals from ground and airborne platforms was also reviewed. It was suggested that significant improvements in technology have occurred which could enhance the success of a Gulf Coast oxidant study. Table 8 summarizes the key species that must be measured and the status of technology that is likely to become available by 1985. It was also suggested that research efforts on some of these technologies could be accelerated to bring them on line by 1985.

In addition, the following observations were made:

- There is a significant body of existing data from the Gulf Coast that must be thoroughly analyzed.
- The precursor concentrations in Gulf Coast cities are not atypical of other urban centers.

TABLE 6. NMHC/NOX RATIO FOR AMBIENT AIR (Source: Cantrell, et al., 1982)

Location	Site Type	NMHC/NO <sub>x</sub> *	Comments	Reference
Chicago, IL	Urban	4.4	year long average	Horie et al. (1979)
Washington, D.C.	Urban	6.4	year long average	Horie et al. (1979)
New York City, NY	Urban	7.9	year long average	Horie et al. (1979)
Camden, NJ	Urban	7.5	year long average	Horie et al. (1979)
Los Angeles, CA	Urban	10.0	year long average	Horie et al. (1979)
Denver, CO	Urban	14.3	year long average	Horie et al. (1979)
Baltimore, MD	Urban	18.4	year long average	Horie et al. (1979)
Houston, TX	Urban	21.4	High NMHC emissions	Horie et al. (1979)
Austin, TX	Urban	33.1		Horie et al. (1979)
Tulsa, OK		10.9		Eaton et al. (1979)
Philadelphia, PA	Suburban/ Impaction/ Rural	10-20		Chan et al. (1979)
Huber Heights/ New Carlisle, OH	Suburban/ Impaction/ Rural	27		Spicer et al. (1976a)
Phoenix, AR	Suburban/ Impaction/ Rural	10	Ground Station	Spicer et al. (1978)
Phoenix, AR	Suburban/ Impaction Rural	~15	Urban Plume Aircraft Measurement	Spicer et al. (1978)
Jetmore, KA	Rural	10		Martinez and Singh (1977)
Liberty Mounds, OK	Rural	45		Eaton et al. (1979)
Wynona, OK	Rural	170		Eaton et al. (1979)
General Rural Area	Rural	<30:1		U.S. EPA (1977)
Beverly, MA	Rural	13		Spicer et al. (1981)

 $<sup>^{\</sup>star}$ Average value for 6 a.m. to 9 a.m. period.

TABLE 7.  $\rm O_3$ /PAN RATIOS IN LOS ANGELES, HOBOKEN, ST. LOUIS, AND HOUSTON

Location	Range of PAN Levels (ppb)	0 <sub>3</sub> /PAN Ratio*	Number of Samples
Los Angeles, California <sup>†</sup>	0-10 10-20 20-30 30-40 40-50 50	9.1 <sup>‡</sup> 7.6 6.0 5.2 4.5 4.9	19 59 27 6 5
Hoboken, New Jersey <sup>†</sup>	0-2 2-4 4-6. 6-8 8-10	28.0 25.3 24.0 22.8 25.1	14 15 4 8 2
St. Louis, Missouri <sup>†</sup>	0-2 2-4 4-6 6-8 8-10 10-12 ≥12	16.3 16.2 10.0 7.4 5.4 5.0 3.2	3 31 60 31 14 5
Houston, Texas Aldine Site	0-2 2-4 4-6	96.4 31.9 20.2	78 10 3
Crawford Site	0-2 2-4	76.3 32.8	60 7
Fuqua Site	0-2	237.3	20

<sup>\*</sup>Ratio is for (average O<sub>3</sub>)/(average PAN), the averages corresponding to the specified PAN range.

<sup>&</sup>lt;sup>†</sup>Adapted from Lonneman et al., (1976)

<sup>&</sup>lt;sup>‡</sup>For Los Angeles, the ratio is for (average total oxidants)/(average PAN).

TABLE 8. IMPORTANT TRACE CHEMICALS TO BE MEASURED

Comments	Regional coverage	At very low (ppt) concentrations, some H <sub>2</sub> O interference	Interference from PAN, HNO3,	Available as a research tool	PAN, organic nitrate interference; only a research tool	Unreliable TNMHC data for TNMHC <0.5 ppm	1 to 3 hr average whole air samples collected and analyzed for alkanes, alkenes, alkynes and aromatics $(C_2^-C_{12}^-)_{12})$	Analytical methodology in a develop- mental stage (critically important chemical group)		Possible interferences due to aerosol	neutralization PAN, organic nitrates as possible interferents	Method currently being tested	Long cycle time; unsuited for airborne operation		Instrument is being tested Instrument is being tested	Instrument is being tested Untested with possible interferences	Instrument is being tested; important for nighttime chemistry		
Mode of Operation	Cont. Cont. Cont.	Cont	Cont.	Cont.	Cont.	Semi-Cont.	Discrete	Discrete	Discrete	Discrete		Discrete Cont.	Semi-Cont. Semi-Cont.	Discrete	Cont. Semi-Cont	Semi-Cont.	Semi-Cont.		
Platform*	A, G	А, G	A,6	А, G	9	9	A, G	<sub>U</sub>	9,A	9	o o	o, A,G	A,G	А, G	A, G	99	A,G		
Availability (year)	1983 1983 1983	1983	1983	1983	1983	1983	1983	1985	1983	1983	1984	1985 1985	1983	1983	1986 1985	1985 1985	9861	· · · · · · ·	
Power/w.t. Requirements	Excessive Nominal Nominal	Nominal	Nominal	Nominal	Nominal	Nominal	Nominal	Nominal	Nominal	Nominal	Nominal	Nominal Nominal	Nominal Nominal	Nominal	Excessive Nominal	Excessive Nominal	Excessive		
Sensitivity	≈1 ppb (1 km) ≤1 ppb ≤1 ppb	<0.1 ppb	s5 ppb	<0.1 ppb	<0.1 ppb	0.1 рряпС	1 ppbC	<1 ppbc	<0.1 ppb	0.1 ppb	0.1 ppb	0.1 ppb 1 ppb	0.1 ppb 3 ppb	0.01 ppp	5x10 <sup>5</sup> molec cm <sup>-3</sup> 5x10 <sup>5</sup> molec cm <sup>-3</sup>	10 <sup>7</sup> molec cm <sup>-3</sup> 10 <sup>7</sup> molec cm <sup>-3</sup>	l ppb		
Analysis Technique	UV DIAL Chemiluminescence UV absorption	Chemiluminescence	Catalytic conversion to NO, then chemiluminescence	Photolytic conversion to NO, then chemiluminescence	Luminal chemiluminescence	Flame detection	GC - FID	Derivative HPLC	BC - GC	Filter pack/ion chromatography	Chemiluminescence with converter	Dual enzyme-PHOPAA fluorescence Tunable diode laser absroption	Flame photometry Pulsed fluorescence	BC - 6C	Laser-induced fluorescence 14CO oxidation	Matrix isolation/electron spin Chemical amplifier technique	Tunable diode laser	No methods available	No methods available
Species	°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°°	NO	NO <sub>2</sub>	NO.2	NO <sub>2</sub>	CH <sub>4</sub> /CO/TNMHC	Hydrocarbon species	Aldehydes	PAN	HNO3	ноз	H202 H202	202 202	Synthetic tracers (F11,F12,CH <sub>3</sub> CC <sub>13</sub> , C <sub>2</sub> Cl <sub>4</sub> ,C <sub>2</sub> HCl <sub>3</sub> , etc )	Ю	RO <sub>2</sub> RO <sub>2</sub>	NO <sub>3</sub>	HNO <sub>2</sub>	N205

\* A = alrborne G = ground-based

43

- Based on a cursory analysis of data, it appears that Gulf Coast air is typically characterized by low ozone and PAN levels with interspersed high-ozone events.
- The high frequency of thundershowers (one every 2 or 3 days) is a feature that is unique to the Gulf Coast and impacts photochemical processes in a way that cannot be defined clearly at present.
- Significant new technologies involving remote sensing and optical techniques can be brought to bear on the successful conduct of a Gulf Coast oxidant study.

#### Overview of the EPA Regional Oxidant Model (K. Schere, U.S. EPA)-

A theoretical framework for a multi-day 1000-km scale simulation model of photochemical oxidant has been developed. It is structured in a highly modular form so that eventually the model can be applied through straightforward modifications to simulations of particulates, visibility and acid rain. The regional oxidant model (ROM) is currently being completed for application to the upper midwest and northeast section of the United States.

The model structure is based on phenomenological concepts and consists of three and one-half layers. The interface surfaces separating the layers are functions of both space and time that respond to variations in the meteorological phenomena that each layer is intended to treat. Among the physical and chemical processes affecting passage and distribution of photochemical concentrations that the model is designed to handle are: horizontal transport; photochemistry; nighttime wind shear and the nocturnal jet; cumulus cloud effects; mesoscale vertical motion; mesoscale eddy effects; terrain effects; subgrid-scale chemistry processes; natural sources of hydrocarbons, NO<sub>X</sub>, and stratospheric ozone; and wet and dry removal processes, e.g., washout and deposition.

Lamb (1982) also has considered the predictibility of pollutant concentrations at long range, along with such related problems as the parameterization of "mesoscale" diffusion and the design of model "validation" experiments. A basis is established for estimating quantitatively the levels of uncertainty associated with dispersion model predictions.

Figure 13 is a schematic illustration of the layered structure of the ROM, and describes the function of each layer; Part (a) considers daytime phenomena and Part (b), nighttime phenomena.

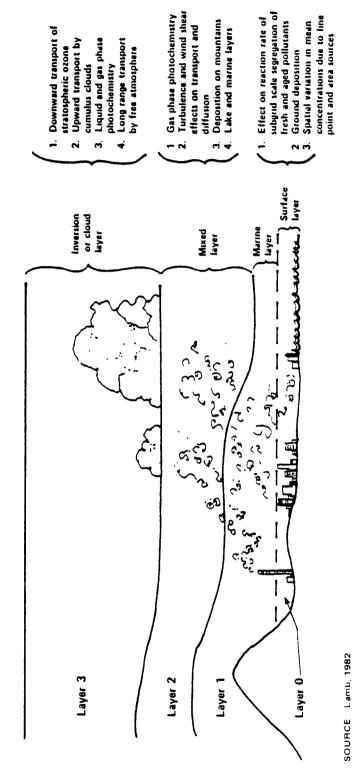
## Review of the PEPE/NEROS\* Experimental Program J. Clarke, U.S. EPA)--

Together, the PEPE and NEROS\* studies included three or four (depending how they are tallied) separate and coordinated programs. The first NEROS study (e.g., see Ruff, Gasiorek, and Shigeishi, 1979) was designed to provide a semi-quantitative understanding of the nature and extent of ozone in the northeast. A regional air mass characterization study was conducted in the summer of 1979; the objective was to provide data to substantiate or refine assumptions or parameterizations of the ROM. A regional-scale urban plume study and regional oxidant studies were conducted in summer 1980. Urban plume studies were conducted out of Baltimore, while regional and urban plume studies were conducted out of Columbus, Ohio. The following discussion describes the scope of the latter effort and is extracted from a summary article by Vaughan, Chan, Cantrell and Pooler (1982).

The Regional Field Studies Office (RFSO) of the United States Environmental Protection Agency (EPA) sponsored a field study in July-August 1980, to examine the transport and chemical transformation of polluted air masses extending over hundreds of kilometers. EPA's Meteorology Division was a cosponsor of the field study. It desired to examine the dynamics of oxidant formation, transport, and removal in developing a data base for the regional oxidant model. Its focus was on regional characterizations as well as detailed understanding of urban plume dynamics for providing various parameters to the model. The Meteorology Division's activities were organized as the Northeast Regional Oxidant Study (NEROS).

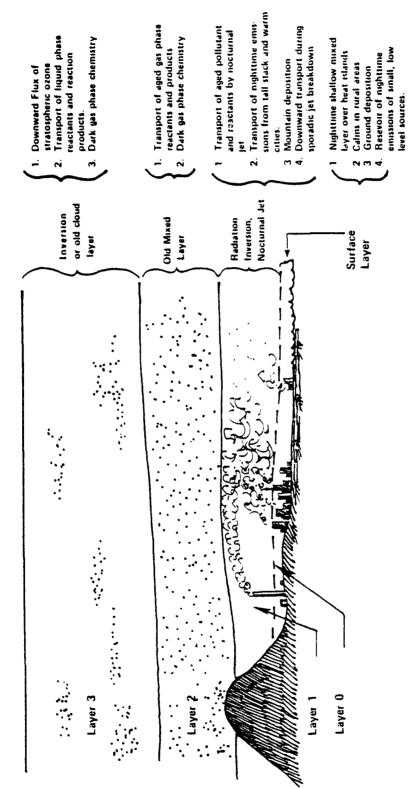
<sup>\*</sup>PEPE - Persistent Elevated Pollution Episodes
NEROS - Northeast Regional Oxidant Study





(a) DAYTIME

Schematic illustration of the "dynamic" layer structure of the regional scale model and the phenomena each layer is designed to treat. Figure 13.



SOURCE Lamb, 1982

(b) NIGHTTIME

Figure 13. (concluded)

Air quality and meteorological measurements were carried out from surface platforms (fixed, mobile, and moving) and airborne platforms; Table 9 provides a summary of the measurement platforms and data centers.\* Within the collection of measurements from PEPE/NEROS is information on gaseous pollutants (particularly  $SO_2$ , NO,  $NO_x$ ,  $O_3$ , and hydrocarbons); aerosol indicators (b<sub>scat</sub>, SO<sub>4</sub>, Aitken nuclei count, aerosol filters, chemical analyses, and particle size distribution); and meteorological parameters, multiple tetroon trajectories, temperature, wind speed, dew point, and mixing height (from various lidar measurements)]. Vertical profiles of these parameters exist from spiral flights and ramping flights, while horizontal gradients are available on a large scale for regional missions and on an intermediate scale for urban plume missions. A total of 353 flight hours were logged by the CHEM-1, CHEM-2, SCOUT, and CHOPPER aircraft in 100 missions. Table 10 indicates which air quality and meteorological parameters were recorded by each platform.

The NEROS missions for urban and regional studies involved release of small tetroon clusters at various altitudes and a large tetroon (tracked by FAA radars). Once the transport field was marked with tetroons, the aircraft and mobile platforms were deployed to document the air quality and mixing conditions in the air mass. CHOPPER and NOAA-Turbulence were fairly heavily dedicated to urban plume surveys. EPA Lidar carried out mostly plume-oriented studies, but occasionally conducted regional studies outside Ohio. Moving Lab conducted frequent ground-level surveys near Columbus, but also was deployed to West Virginia and Kentucky for PEPE-oriented regional surveys. NEROS regional measurements were carried out to characterize the northeastern grid used in the regional oxidant model between the 70°W and 85°W longitude, and 38°N and 45°N latitude. SCOUT, CHEM-1, and CHEM-2

<sup>\*</sup>It should be noted that EPA, through the Office of Air Quality Planning and Standards, operated the Northeast Corridor Regional Monitoring Program (NECRMP) during the summer of 1980 from Baltimore to Boston. The program involved augmented air quality and meteorological measurements. These data are valuable in characterizing the eastern edge of the study grid.

#### TABLE 9. PLATFORMS AND DATA CENTERS **OPERATED DURING PEPE/NEROS**

#### Airborne Laboratories

CHEM-1 (Chemistry aircraft) CHEM-2 (Chemistry aircraft) SCOUT (Chemistry aircraft) ELECTRA (Lidar system)

CHEM-3 (Chemistry aircraft) LAS\* Queenair EPA-Lidar Turbulence aircraft Cloud chemistry aircraft

Surface-based laboratories

Moving laboratory Doppler Sodar 1 and 2 Aerosol laboratory Lidar van Small tetroon tracking Large tetroon tracking GC laboratory Special photochemistry precursors Tethered balloon NO, Ozone network Bertin sodar Dry deposition experiment MARS\* Sunphotometry Data center Weather center

source: Vaughan et al., 1982.

\*UV-DIAL = Ultraviolet-Differential Adsorption Lidar.

HSRL = High Spectral Resolution

Lidar.

LAS = Laser Adsorption Spectrometer.

MARS = Microwave Atmospheric Remote Sensor.

TABLE 10. AIR QUALITY AND METEOROLOGICAL PARAMETERS AVAILABLE FOR EACH PLATFORM (Source: Vaughan, et al., 1982)

	Platforms													
Airborne	West, Then	. (v. 6g	å,	Š	o. 5.	201	14°C	Y S	Fillers:	No see see see see see see see see see se	en de la companya de	Ten Hear	A STATE OF THE STA	And Marie
CHEM-1° CHEM-2	2-8 12	X X	X X	X X	X X	X X	X X	X X	X X	x	X X	,	ς	
Scout Electra	0.4 1-60	x			X PRO	X PRO		x	х	x	х	,	ζ	
CHEM-3 LAS	10 10-30				X	HTD				х	х			
Turbulence Chopper	<1 5	·		x	X X	x		x	***************************************	x	х	,	x x	х
EPA Lidar						PRO*						•		
Surface-based Moving lab	8-15	X +INT	x	x	x	x		x	x					
Sodar ! Sodar 2	300 <sup>4</sup>							<del></del>	•	PRO PRO			PRO PRO	PRO PRO
Aerosol lab* Lidar van		X INT	x	х	х	X PRO*	x							
Special Photochemical				x	x			x				x		•
Tethered balloon	30				х					PRO	PRO		PRO	PRO
Network		******		х	х							х		
Bertin sodar	300°												PRO	PRO
Dry dep. MARS	600	x			x					PRO PRO	PRO PRO		х	х

provided frequent in situ surveys across various parts of this NEROS They were usually vectored back to the location of the large EPA tetroon, in order to follow the aging of the air mass in the vicinity of this specific marker. Moist air masses moving in from the west and southwest, and Canadian polar air masses were characterized by these flights. ELECTRA was deployed for its regional surveys out of Wallops Island, VA., in support of NEROS and PEPE regional objectives. CHEM-3 provided correlative in situ measurements at selected locations below

X - Point measurement available.
 PRO - Profile showing variations with altitude.
 HTD - Heated nephelometer.

SO<sub>4</sub> - Continuous readings from a modified Meloy 285 INT - Integrated burden (for SO<sub>2</sub> these measurements were from correlation spectrometers)

a = Acrosol size distribution measurements were round correlation spectrometers)
 b = Hydrocarbon cannisters were analysed in EPA's GC Laboratory in Columbus, Ohio.
 c = Filters were collected with a 3.5 μm cut point and analysed for SO<sub>4</sub> and NO<sub>5</sub>
 d = Seven second readings reported as 15 min averages.
 e = The Indar signal is not a true profile of the parameter "b<sub>max</sub>" but is related to it, since it records the backscatter of light from layers of atmospheric aerosol. It gives a good indication of mixing depth.

ELECTRA's flight path (as it had done earlier in the program for LAS-Queen Air flights).

PEPE regional surveys were less restricted, and involved flights into stagnant air masses (two to five days old) or into moving air masses that experienced regional visibility degradation, as reported by FAA and NWS wire services and by satellite imagery. These regional surveys extended into New York and New England during the first week in August 1980, following development of large-scale haziness in the area. In the middle of the second week in August, several flights into Tennessee, Alabama, and Arkansas were carried out to characterize a maritime tropical air mass associated with an extension of the Bermuda high that had stagnated over Georgia and Tennessee for four days. Measurements also were made as this aged air mass swept out to the Atlantic. On two occasions. 25 July and 11 August, tetroons were placed in or near power plant plumes, and flights were made to characterize the mixing of these plumes into the general air mass. A summary of the types of missions flown during the study period is shown in Table 11.

TABLE 11. SCHEDULE OF MISSIONS FLOWN (Source: Vaughan, et al., 1982)

		July							August												
	20	23	24	25	26	29	30	31	1	2	4	5	6	7	8	9	10	11	12	13	15
Urban Plume Limited Full scale	Х	Х		X		Х	Х	X	Х	х	В	Х	x	Х	х		Х	Х	Х	х	(X)
Regional																					,
PEPE			P						Х			X	X	X	X	Х	P	P			
NEROS				P			P			X					X						X

It is obvious that with the resources available to the project, only limited urban plume flights could be carried out while regional surveys were in progress.

#### SECTION 3

#### WORKING GROUP CONSIDERATIONS

#### CHEMISTRY

The working group addressed and prioritized trace chemicals that must be measured during any planned Gulf Coast oxidant study. The exact platforms to be employed, frequency of measurements, and spatial density of monitoring stations were issues which could not be considered by the working group since a detailed design of the Gulf Coast study did not exist. The group, therefore, focused on broader considerations dealing with trace chemical measurements and emissions data requirements. The working group strongly felt that a number of mini-studies should be completed and their results employed to design a major Gulf Coast study. The following sections briefly describe the working group recommendations.

#### Chemicals of Interest

Trace chemical measurements (in gas and liquid phases) were identified and ranked according to their importance and feasibility of the measurements. These rankings were as follows:

# Importance of Measurement: A. Important 1. Methods well defined and applied with ease B. Desirable 2. Methods not fully developed and applied with difficulty C. Optional 3. Methods unacceptable

Tables 12-15 provide a listing of the species of interest and rank these by the above criteria. Among the nonchemical parameters, liquid

TABLE 12. TRACE CHEMICALS IN AIR

Chemicals *	Rank <sup>†</sup>
03	A 1
NO	A 1
NO <sub>2</sub>	A 1
PAN	A 2
HNO <sub>3</sub>	A 3
CH <sub>4</sub>	A 1
co	A 2
тнс	A 2
HC <sub>i</sub>	A 2
RCH=O	A 3
н <sub>2</sub> о <sub>2</sub>	A 3
HNO <sub>2</sub>	в 3
N <sub>2</sub> O <sub>5</sub>	в 3
но	в 3
но <sub>2</sub>	в 3
RO <sub>2</sub>	в 3
NO <sub>3</sub>	в 3
NH <sub>3</sub>	C 2
so <sub>2</sub>	C 1

\*Measurement of liquid water content and UV radiation (300-500 nm) were ranked as A2 and A1 respectively.

### <sup>†</sup>Key:

- A = important measurement
- B = desirable measurement
- C = optional measurement
- 1 = measurement technique
   is state-of-the-art
- 2 = measurement methods not
   yet fully developed or
   only applied with difficulty
- 3 = measurement methods
   currently unacceptable

TABLE 13. TRACE CHEMICALS IN LIQUID WATER

	Rank*								
Chemicals	Cloud Water	Rain Water	Aerosols						
NO <sub>3</sub>	В	В	В						
ROH	С	С	С						
RCH=O	A	С	A						
HC <sub>i</sub> (vac)	С	С	С						
03	С	С	С						
H <sub>2</sub> O <sub>2</sub>	A	В	В						

<sup>\*</sup>Measurements are at levels of difficulty of 2-3.

TABLE 14. PARTICULATE MATTER

Туре	Ra	nk
Elements	C	1
so <sub>4</sub>	С	2
sо <sub>4</sub> nо <sub>3</sub>	В	2
NH <sub>4</sub>	С	2

TABLE 15. INERT TRACERS OF INTEREST

Tracer Type	Species	Ra	nk
Tracers of opportunity	7 Be 33 <sub>P</sub>		2
	Fluorocarbons	A	1
	Elements	С	1
Injected tracers	Methane-21 Perfluorocarbons <sup>SF</sup> 6	A A A	2 2 1

water content and ultraviolet radiation measurements were highly emphasized. It was generally felt that gas-phase processes provide the dominant source term for ozone formation and hence constitute the most important measurements. The role of aldehydes and  $\rm H_{2}O_{2}$  in liquid phases are not well understood but may be potentially important (Table 13). Nitrate measurements in the aqueous phase (Table 13 and 14) were ranked high because of the sink potential of the aqueous phase for  $\rm NO_{2}$ ,  $\rm HNO_{3}$ , and nitrate aerosols. Despite the recognized importance of gas-phase chemistry, the working group felt that liquid-phase processes may play a more important role in the wet and humid environment of the Gulf Coast compared to relatively dry regions.

Tracers of opportunity were suggested, but only chlorofluorocarbons were considered high priority. <sup>7</sup> Be or <sup>33</sup>P stratospheric tracers were ranked low in part due to the complexity of data interpretation. Injected speciality tracers are unique tools to study long range transport, but are to be measured only when a planned tracer experiment is underway.

#### Emissions Data

It is anticipated that ROM or other models would be employed in the Gulf Coast region. The working group provided guidance on what is

highly desirable and what must be obtained at a minimum. The following general guidelines were suggested:

- (1) A 2-km x 2-km gridded inventory of emissions.
- (2) Hourly temporal resolution, i.e., diurnal and seasonal emission patterns
- (3) Vertical resolution of emission sources
- (4) Source types (stationary, mobile, area, point, natural, etc.)
- (5) Natural VOCs on land
- (6) Gulf Coast water emissions.

It was felt that some sensitivity studies should be performed with existing models to get an idea of the importance of source emissions, particularly natural VOCs of land or water origin. One of the most pernicious problems is the very nature of the emissions inventory. In principle, emissions data (temporally and spatially resolved) should be available for individual species. This is not possible in practice. Current models can use groups of chemicals (alkanes, alkenes, and aromatics) and this is a desirable speciation of emission data. It was felt, however, that carbon bond mechanisms may be employed in a future version of ROM. It does not appear feasible that emissions information can be obtained in a format directly applicable to the carbon bond model. It is assumed that some algorithms must be devised to solve this problem.

#### Recommendations

For all surface and aircraft sampling, all chemicals ranked "A" must be measured. Those ranked "B" should be attempted when possible. Prior to the Gulf Coast study a number of mini-studies are recommended. These would provide many of the answers that are needed to better design the Gulf Coast oxidant studies. The following mini-studies were recommended:

 Analyze all existing air quality and meteorological data to critically examine the oxidant problems in the Gulf Coast and the relationship of ozone concentrations to meteorological and emissions conditions.

- (2) Fully analyze the data from the NEROS experiment to focus on the strengths and weaknesses of the ROM model as applied to the Northeast. Also, a sensitivity analysis of emission sources to better gauge the role of natural VOCs and the effect of the inherent uncertainties in the emissions data base needs to be undertaken.
- (3) Efforts should be initiated now to ensure a reliable field measurement capability by 1985, particularly for aldehydes and  $\rm H_2O_2$ .
- (4) Employ an existing airshed model in the Houston area to see if Houston ozone levels are less than those predicted by existing knowledge.
- (5) Conduct smog chamber/fog chamber irradiation studies to simulate the Gulf Coast air precursor mixtures.
- (6) Because of the humid and cloudy environment of the Gulf Coast, a better knowledge of in-cloud processes--especially as a sink mechanism--is desirable.

Item Nos. 1 to 3 were rated as necessary. Other suggestions were considered highly desirable but contingent on resource availability. The working group felt that suggestions 2-6 can be implemented with a budget of 0.7 to 1.3 million dollars. It was assumed that recommendation No. 1 would be performed by EPA at no cost to this proposed study.

#### **METEOROLOGY**

#### General

After background material had been presented, and after some preliminary discussion by the workshop attendees on the objectives and rationale for a Gulf Coast Oxidant Transport and Transformation Experiment, the Chairman of Work Group B, William Pennell, presented the following meteorological topics for discussion by the group:

- Land and sea breeze circulations
- Convective cumulus cloud venting
- Synoptic-scale transport and disturbances
- Surface deposition and destruction

- Synoptic-scale subsidence
- Low-level jet
- Characteristics of planetary boundary layer over the Gulf of Mexico.

The above meteorological features were judged to possibly play important roles in determining events of high and low oxidant concentration along the Gulf Coast area of the United States.

Walter Lyons then presented the major weather categories relevant to the Gulf Coast area for consideration by the work group members throughout the discussions:

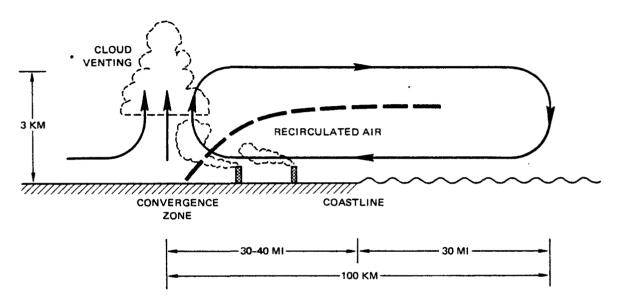
- Tropical disturbances (easterly waves, tropical depressions, tropical storms, and hurricanes)
- Frontal disturbances (infrequent and weak during summer, but strong and followed by cold northerly winds during winter)
- Strong onshore flow of southerly and southeasterly winds
- Sea breeze regime without showers or thunderstorms ("dry" sea breeze) or accompanied by rainshowers or thunderstorms along the on-land convergence zone under conditions of weak synoptic-scale wind flow (weak horizontal pressure gradients).

#### Identification of Relevant Phenomena

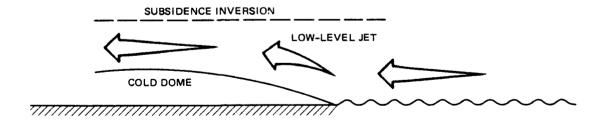
Mesoscale and regional scale atmospheric transport are determined by three-dimensional circulations that vary in scale from local or micro to intermediate or meso, and synoptic. Included are mesoscale convective systems and land/sea breeze circulations as well as the low-level coastal jet and the mid-continental nocturnal jet. Not only can these circulations significantly impact mesoscale advection, but convective phenomena may be important for their role in the two-way exchange of polluted boundary-layer air and clean mid-to-upper tropospheric air (and possibly stratospheric air). Accordingly, the Gulf Coast oxidant transport and transformation study must seek to measure and analyze three-dimensional, unsteady transport phenomena.

Shih-Ang Hsu characterized the land- and sea-breeze regime as it has been studied on the upper Texas Gulf Coast. Under conditions of weak

"Bermuda High" southerly (onshore) flow of about 5-10 knots (2.5 - 5 m/s), a fully developed sea breeze extends from about 30 miles (50 km) offshore to 30-40 miles (50-65 km) inland between noon and 6 p.m. The dimensions are 60-70 miles (100 km) in the horizontal (perpendicular to the coast) with half over land and half over the Gulf, and 3 km in the vertical. The mean wind speed for the sea breeze is about 6 m/s (12 knots). Figure 14(a) shows a schematic sea-breeze circulation in the vertical plane perpendicular to the coast line. The convergence zone is



(a) FULLY DEVELOPED SEA-BREEZE CIRCULATION (NOON TO 6 PM)



(b) LOW-LEVEL JET ASSOCIATED WITH SEA BREEZE (9 PM TO 3 AM)

Figure 14. Schematic view of sea-breeze regime characteristic of Gulf Coast.

located 30-40 miles (50-65 km) inland. It has front-like characteristics and is often identified by a distinct line of cumuliform clouds. Near the time of maximum surface temperature in the afternoon, convective showers and thunderstorms can develop.

On the basis of his experience with the Lake Michigan sea-breeze, Walter Lyons noted that the convergence zone can be like a chimney 1-2 km wide with updrafts of over 1 m/s. When the sea breeze overlies an area of pollutant emmissions (such as can be the case in the Houston, Galveston, Lake Charles and New Orleans regions) it can recirculate pollutants from land to water and back to land. At the same time, the convergence zone and cumulus clouds can vent pollutants upward to higher levels, and thunderstorm downdrafts along the sea-breeze front can transport clean air from high levels in the troposphere to the ground. Under such conditions, a "pollution front" can develop between recirculated old polluted air and clean downdraft air as indicated in Figure 14(a) by the heavy dashes. The persistence of this front may provide a prevalent and important mechanism for transport of anthropogenic pollutants to the free troposphere, thereby constituting a pseudo emissions line source of sufficient vertical and horizontal extent to be a potentially important contributor to global tropospheric air quality.

Shih-Ang Hsu pointed out that a shallow cold-air dome (100-200 m in depth) frequently develops over land near 9 p.m. when radiational cooling of the land surface begins. When this process intensifies, a low-level jet-type windflow is observed above the cold dome over land from about 9 p.m. to 3 a.m. the next morning, as illustrated in Figure 14(b). Around 6 a.m., the windflow reverses to a land breeze. Offshore heavy cumulus clouds and light rainshowers produced by the land breeze convergence over the water can then be observed.

The potential role of the land- and sea-breeze circulation in the local and regional transport and redistribution of pollutants in the Gulf Coast area was recognized by all working group members. It was agreed, however, by the workshop at large that the existing data base of meteorological and air quality observations (e.g., HAOS aircraft and ground data) should be examined and analyzed to provide better evidence

that a mesoscale experiment involving the sea-breeze front, and nighttime low-level jet winds have pollution implications that are related to high and low ozone events\*.

Intermediate transport out to a distance of about 400 km, and long-range transport out to 1000 km were also identified as meteorological phenomena relevant to a summertime Gulf Coast oxidant study. The area where transport of pollutants from Gulf Coast emission sources may be important lies on the west side of the subtropical "Bermuda High" (see Section 2B, Figures 6 and 7). It includes Texas and Louisiana, under conditions of relatively large horizontal pressure gradient and southerly winds. When southerly winds extend over the western Great Plains, as is the case when the western end of the "Bermuda High" covers the Mississippi Valley, a low-level jet can develop between midnight and sunrise at about 1500-2500 ft (500-800 m) above ground level; wind speeds of 25-30 knots (12-15 m/s) are common. Some work group members suggested that emissions from the Texas-Louisiana coastal region can be transported northward into Missouri and even Minnesota by such southerly wind flow.

No measurements currently exist that conclusively demonstrate long-range ozone transport events out of the Gulf Coast region. It was agreed that an intermediate and, possibly a long-range transport experiment, should be considered in the Gulf Coast oxidant experiment design study.

#### Design of Mesoscale Sea-Breeze Experiment

After having identified the sea breeze as a significant meteorological phenomenon, the work group proceeded to discuss a possible mesoscale experiment design. Two experiments were considered:

For example, some workshop members expressed the opinion that easterly and northeasterly windflow along the Gulf Coast is more important to high ozone in Houston than the sea breeze. This wind flow regime is frequent during spring and fall on the southside of a continental polar high-pressure system.

- A spatially fixed (Eulerian) box-budget study to quantify the net transport into or out of the sea breeze/emission area
- A tracer (Lagrangian) experiment to study the role of the sea breeze in recirculating pollution.

The Eulerian box-budget experiment would be carried out in a rectangular area, 300 km north-to-south and 200 to about 400 km east-to-west. This area would include the sea-breeze circulation and coastal emission sources. The Houston-Galveston-Lake Charles area was considered most suitable for this program. The box would be 3 km deep (the average depth of the sea-breeze).

After lengthy discussion of the measurement systems and platforms, and their use and deployment, it was concluded that a budget study of the box cannot be readily done by closing the box with observations. It was, therefore, recommended that available observations be used in conjunction with a modeling approach to estimate pollutant fluxes within and through the box.

The release of multiple tracers for a sea-breeze experiment was also considered. Tracers should be released near ground-level on the coastal side of the convergence zone and inside the convergence zone. Injection of tracers in cumulus clouds should be considered also. Ground-based and airborne tracer sampling should be carried out to study recirculation of pollutants by the sea-breeze and cloud venting in the sea-breeze front.

The sea breeze program should also include studies of venting by cumulonimbus and cumulus congestus clouds that form in the afternoon inland along the sea breeze convergence zone. Because of the lengthy extent of the zone roughly parallel to the coastline and its high frequency (see Figure 5), it may be an effective mechanism for transport of ozone precursors out of the Gulf Coast emissions source region, thereby possibly minimizing local ozone formation and impacting regions further downwind. It was recommended that inert gas tracers would provide a useful method for quantifying the effects of cumulus-cloud venting. One or more tracers released at or near the surface in the convergence zone would be measured aloft by aircraft, both in the

boundary layer and at the level of outflow near the cloud tops. For practical reasons, cumulus congestus or small cumulonimbus clouds would be preferable, as their tops are within the capabilities of available research aircraft.

The work group recommended that a mesoscale sea breeze program include on the order of 10 intensive studies carried out over a time period of 10-12 weeks (3 months).

The following systems were considered necessary for the experiment:

- Aircraft with backscatter lidar for vertical profiling of ambient particle and injected fluorescent particle-tracer (Uthe, 1983; Ching et al., 1984)
- Aircraft with UV and IR DIAL (lidar) systems for vertical ozone profiles
- Airborne capability for remote wind sensing, i.e., airborne doppler radar (Hildebrand, 1983)
- Chemical aircraft with in-situ instrument measurement capability
- Scout aircraft for initial observations and atmospheric profiling
- Routine (ground-based) monitoring systems, such as the following:
  - Doppler sodar (5-6 units)
  - Doppler radar (1-2 units)
  - T.p-sondes (5-6 units)
  - Towers of opportunity
  - Portable Automated Mesonet (PAM) systems (30-40 units)
  - Rawinsondes (3 units)

#### Design of Medium Range Transport Experiment

An intermediate-range oxidant transport experiment would involve a total time of 30-48 hours for atmospheric measurements, and would cover a horizontal distance of 400-500 km from the Gulf Coast emissions source. This distance would take the experiment from the Houston-Galveston area northward into Oklahoma and Arkansas and would focus on ozone and its precursors, and on released tracers. The intermediate transport experiment would take place under conditions of synoptic-scale southerly flow, preferably during the occurrence of a nocturnal low-level jet.

During daytime and possibly during nighttime, convective cumulus clouds can be expected to develop in the southerly flow of warm, moist (mT) air. Thus, cumulus convective transport will be part of the experiment. Figure 15 shows the projected area (stippled boundaries) for an intermediate range (high-level and low-level) transport experiment. Measurements are recommended across three vertical planes or "curtains" (dash-dot lines in Figure 15). Tracers and tetroons should be released at a low level (e.g., 1500 m in the mixed layer under the clouds) and at a high level (e.g., at the level of the cumulus clouds). Measurements would be made for the purposes of:

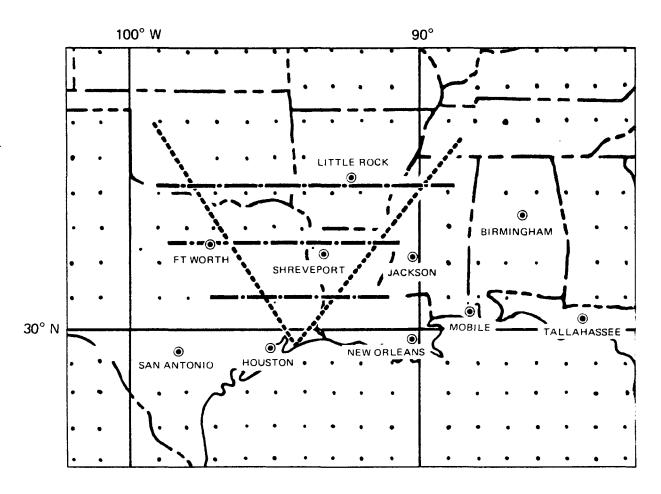


Figure 15. Projected area for intermediate transport experiment (dotted lines) showing location of vertical planes or "curtains" for horizontal flux measurements (dash-dot lines).

- Computing fluxes out of the mixed layer and out of the cloud layer
- Validating parametric schemes for cumulus convection transport in ROM.

Tracer releases in the low-level jet were also recommended in order to define the transport characteristics of this phenomenon. It was agreed, however, that more knowledge and information on the occurrence, location, and spatial extent of the low-level jet is needed before a detailed plan can be designed.

## Enhanced Surface and Upper-Air Monitoring Network

The work group recommended that an enhanced network of surface and upper—air observations be operated throughout the time period that the mesoscale sea—breeze and intermediate transport programs are conducted. The network area was outlined as extending from Fort Worth, Texas, eastward to the Alabama border (about 300 km), and then 600 km southward to a point approximately 200 km offshore. The existing National Weather Service (NWS) radiosonde stations within the network area (about 6) would be enhanced by 5-6 additional stations, including two stations offshore to double the spatial resolution of the NWS network. Vertical profiles of ozone would be obtained to 700 mb (10,000 ft ms1) by single—engine aircraft at each of 12 available radiosonde locations. The network would be operated for a 3-month period.

The benefits of the enhanced observational network would be:

- Provision of offshore data
- 6-hour resolution on radiosonde ascents
- Vertical profiles of air quality obtained three-four times per day.

An important element of the routine monitoring network should be the acquisition of satellite, radar, and lightning data from existing systems for the purposes of enhancing the definition of mesoscale circulations and convective phenomena. Although these systems (for the most part) are in place and operating, special attention should be devoted to the archiving of these data (not routinely done). Satellite

data should include visible and infrared observations from both geostationary and polar-orbiting satellites. High-resolution, false-color radar displays are available from several commercial sources using data from National Weather Service radars. Operational lightning detection networks (e.g. the lightning position and tracking system available from Atlantic Scientific Corp., Melbourne, FL) already cover most of the Gulf Coast area and should blanket the study region on the time frame of the Gulf Coast oxidant program.

Some work group members raised the question whether or not the enhanced routine monitoring network should be operated during an entire summer prior to the mesoscale and intermediate transport experiments. This could provide the 3-month data base needed to better understand the impact of local and regional wind flow on high and low oxidant events (a better understanding from an analysis of already existing data was recommended by the workshop at large). Study of this special data base would also help design a more effective (non-redundant) mesoscale experiment.

The question of effects from stratospheric ozone was brought up also. Since the mesoscale sea-breeze experiment and the medium-range transport experiment are planned during the summer, upper tropospheric low-pressure troughs with stratospheric ozone intrusions are not expected to directly affect the Gulf Coast area. It was decided, however, that background ozone measurements should be made in the middle and upper troposphere to assess a possible stratospheric ozone influence. These measurements can be part of the enhanced routine monitoring network.

# Long-Range Transport Experiment

The working group recommended that a long-range transport ( $\sim 1000~km$ ) experiment not be conducted. Within the budgetary guidelines presented by EPA, it was felt that the resources would more effectively be used to conduct comprehensive mesoscale and intermediate-range studies. Long-range experiments would best be undertaken as an adjunct to or in

conjunction with separate programs such as long range acidic deposition, transport and transformation studies conducted as joint multi-agency or multi-organizational programs.

#### SECTION 4

## RECOMMENDATIONS FOR A CONCEPTUAL PROGRAM DESIGN

In their deliberations, the two working groups recommended that research and development efforts should be undertaken preparatory to the principal components of the major Gulf Coast oxidant study. As summarized in Table 16, the preparatory efforts comprise both modeling and data analysis studies, and experimental studies and hardware development. In some cases, these efforts are not unique to the Gulf Coast oxidant study or are already being actively pursued; these efforts are not included in the conceptual experimental design presented later, although in many cases the study would be seriously affected in the event they are either unsuccessful or not completed in time. working groups provided subjective cost estimates which should be considered indicative of the order of magnitude of each effort. Each preparatory study is also given a subjective priority ranking. general, the high-priority efforts are essential for a high-quality Gulf Coast oxidant study, while the moderate-priority efforts are highly desirable. A low priority indicates that the results would be very useful, but not essential. In one case, the priority would appear to be ambiguous: a preparatory effort involving the operation of the enhanced routine monitoring network (for a three-to-four-month period) one or two years before the primary study, is prioritized both low and high. In principle, the working groups suggested that operation of the network and analysis of the data would be extremely desirable, provided it did not jeopardize the overall study by excessively stretching the timetable or expanding the costs beyond those likely to be available. In essence,

TABLE 16. PREPARATORY STUDIES

	Description	Estimate of Cost (\$000) †	Priority*
•	Modeling and Data Analysis:		
	- collection, analysis and interpretation of existing air quality and meteorological data	200-300 (p)	н
	- application of Urban Airshed Model to Houston - evaluation of Regional Oxidant Model <sup>‡</sup> (being	50-100 (g) nc	M H
	<pre>done by USEPA for northeastern states) - ROM sensitivity study to evaluate impact of natural hydrocarbon emissions†</pre>	пс	L
·	Experimental Studies and Hardware Development:		
	<pre>- develop gaseous aldehyde measurement techniques (surface and airborne) †</pre>	100-200 (p)	н
	<ul> <li>hydrogen peroxide instrument development<sup>‡</sup></li> <li>(work ongoing elsewhere)</li> </ul>	50 (p)	М
	- smog chamber studies of Gulf Coast	300 (p)	М
	atmospheres - in-cloud chemistry studies (coordinate with	≤500 (p)	М
	<pre>on-going studies) † - continued development/improvement of airborne wind-finding doppler radar (work on-going elsewhere) †</pre>	nc	М-Н
	- improvements in tracer technology, e.g. fluorescent dye, perfluorocarbons, tetroons, reactive tracers (work on-going elsewhere)	nc	М-Н
	- improvements in remote measurement of ozone, profiles by UV and IR DIAL (ongoing elsewhere) #	nc	н
	<ul> <li>exploratory, limited-duration mobile (air- borne) aerometric measurement program and</li> </ul>	500-1000	н
	<pre>data analysis (limited) - enhanced routine monitoring network for ozone, hydrocarbons, and PBL structure</pre>	1250-1500	L-H**

 $<sup>{}^{\</sup>star}$ H = high; M = medium, L = low priority

p = contract research; g = USEPA study

Study is not unique to Gulf Coast

<sup>\*\*</sup> Priority is constrained by availability of funds.

the decision to retain or delete the preparatory ERN\* is a pragmatic one that must be addressed by the Agency. The conceptual experimental design that is presented below has retained the preparatory ERN.

The overall conceptual program design is summarized in Figure 16, which includes a description of the major tasks as well as the scheduling and estimated cost. The program is divided into four elements:

- (1) Preparatory analyses
- (2) Preparatory measurement studies
- (3) Gulf Coast regional oxidant transport study
- (4) Reporting

In the following, a brief description is given of each task:

- Tasks 1.1-1.2: All of the available and relevant air quality and meteorological data from the study region would be compiled to create a comprehensive data base. Both routine long-term monitoring programs and short-term case studies would be used. The data would be analyzed to provide a better understanding of temporal and spatial variations of oxidant throughout the region, and to develop an improved understanding of the importance of (for example) moisture, synoptic-scale wind flow, long range transport, land-sea breeze circulation, and low-level jet in the formation of high oxidant concentrations.
- Task 1.3: The SAI\*\* Urban Airshed photochemical simulation model, or another suitable model, would be applied to the Houston metropolitan area as a test of the hypothesis that oxidant concentrations are anomalous; or that the combination of relatively high HC-to-NO<sub>x</sub> ratio, high ambient humidity, and intense sunlight results in chemical conditions that are different from other regions.
- Task 2.1: The enhanced routine monitoring network would be established and operated for three months (July-September). It would provide a comprehensive

<sup>\*</sup>ERN - Enhanced Routine Monitoring Network.

<sup>\*\*</sup>Systems Applications, Inc., San Rafael, California.

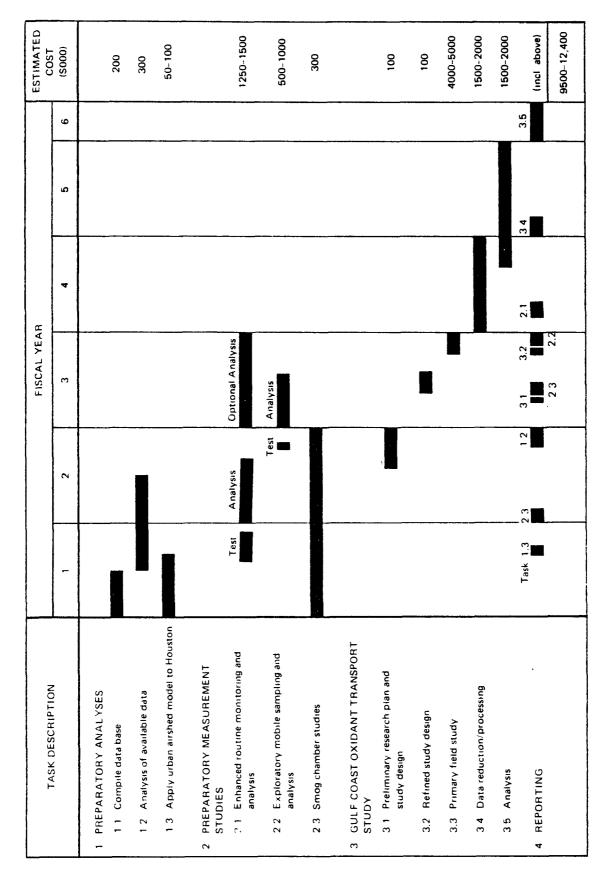


Figure 16. Conceptual program design and approximate costs.

Eulerian aerometric data base for the purpose of gaining an improved understanding of oxidant formation and transport, and of developing a detailed research plan for the primary experimental program. The ERN would include six-hourly light-aircraft soundings of temperature, humidity, aerosol backscatter, and ozone at each of 12 radiosonde locations; radiosondes would also be released at six-hourly intervals. A two-part analysis phase is suggested so that extended analyses might be conducted where indicated by the results of a basic analysis; e.g., in the event significant mesoscale ozone transport or production is observed.

- Task 2.2:
- An exploratory mobile sampling and data analysis task is recommended to refine and coordinate mobile sampling methods, and to provide a limited data base for the purpose of optimizing the use of the various aircraft in the primary study. The aircraft would include the following sensors or sampling technologies: wind-finding doppler radar, in situ ozone concentration and flux, remote ozone profiling by UV or IR DIAL (lidar), in situ gas tracer sampling and remote sensing of injected fluorescent particle tracers by backscatter lidar. This limited sampling program would focus on developing sampling strategies and obtaining limited data for the mesoscale land/sea breeze, cloud venting, and medium-range transport experiments that are anticipated to be conducted later during the primary field study.
- Task 2.3:
- Smog chamber studies would be conducted to simulate photochemical oxidant production unique to the precursor mixture of the Gulf Coast, and to explore the possible effects of high relative humidity.
- Task 3.1:
- A preliminary, detailed research plan and study design would be developed for the experimental and analysis phases of the Gulf Coast oxidant transport and transformation study. This preliminary plan would be based on the analysis of the historical aerometric data base (Task 1.2) and the preliminary analysis of the preparatory ERN effort (Task 2.1); preliminary qualitative inputs from the exploratory mobile sampling program (Task 2.2) would also be considered. The plan would specify numbers and types of airborne platforms, instrumentation specifications, and sampling strategies and protocols. Also specified would be comprehensive specifications for the surface aerometric network, including parameters for measurement, analytical methods, site locations, sampling frequency, data processing and so forth. All aspects of tracer applications in the mesoscale and medium-range transport

studies would also be delineated, such as tracer-types, and release, sampling and analysis methods. Scheduling of the intermediate range transport case-studies would also be addressed, including definition of criteria for determining when or where experiments are to be conducted, and contingency plans in the event meteorological conditions are not optimum for the fulfillment of the primary study objectives.

- Task 3.2: The preliminary research plan and study design would be refined and finalized based on the results of the analysis of the exploratory mobile sampling data (Task 2.2), and other available inputs.
- Task 3.3: Conduct the three-month primary field study of oxidant transport and transformation. The study would have two major aspects: (1) operation of an enhanced routine monitoring network, and (2) short-term case studies of mesoscale and medium-range transport and transformation. The ERN operation is described in Task 2.1. The short-term case studies would consist of (1) mesoscale studies of pollutant transport and oxidant production within the domain of the land/sea breeze circulation, and (2) medium-range (ca 400-500 km) studies of oxidant transport out of the Gulf emissions source region. Cloud venting studies would be an integral component of the mesoscale experiments. The mesoscale studies would constitute the majority of the 10 case studies recommended, and would rely heavily on a full complement of airborne platforms in addition to the use of gas tracers with airborne and surface in situ sampling. Each study would cover a 30-hr period. A minimum sample requirement would be three medium-range transport experiments. The number of sampling platforms would be reduced, and would consist primarily of two or three remote ozone-profiling aircraft, and two or three in situ ozone and gas tracer sampling aircraft. Multiple gas tracers would be used to document effects of altitude and release time-period on ozone transport; variation of the ratio of tracer release rates of multiple tracers with altitude or time would constitute a unique identification of the time of release, and would provide information on transport time and longitudinal diffusion.
- Task 3.4: The data collected during the primary study (Task 3.3) would be reduced and processed under this task.
- Task 3.5: Analysis of the processed data would occur under this task, and would address several basic issues: (1) relation of ozone formation to the precursor mix of the

region, (2) impact of high humidity, (3) role and significance of cumulus clouds in venting ozone or precursors out of the boundary layer, (4) nature and significance of medium-range oxidant and precursor transport into and out of the region, (5) role of land/sea breeze circulation in production of locally high ozone concentrations, and (6) three-dimensional spatial distribution of ozone on episodic days.

Task 4: Report the results of all preparatory, planning, data collection, and analysis tasks.

As illustrated in Figure 16, the overall program could be accomplished in about five years at an estimated cost that ranges between 9.5 and 12.4 million dollars. In the event that the preparatory field studies (i.e., ERN and exploratory mobile sampling) are deleted from the program, then the estimated cost range would decrease to about 7.75 to 9.9 million dollars; the schedule might be compressed by approximate— ly six months. The working groups did not, however, recommend the deletion of the preparatory field studies. On the contrary, they were highly recommended as necessary to the ultimate success of the program.

Finally, the Gulf Coast oxidant study should seek to integrate and coordinate its activities with those of other major atmospheric studies planned for the same time-frame and geographic domain. In particular, the multi-agency national STORM program (STormscale Operational and Research Meteorology) appears to be one such potentially viable mesoscale study. STORM has been proposed by a steering committee composed of 13 representatives of member institutions of the University Corporation for Atmospheric Research (UCAR). The National STORM Program would be supported at an annual cost of 60 to 120 million dollars per year for 10 years, and would involve major field programs in the east, midwest and west in 1987, 1991 and 1993 (UCAR, 1983). These field programs would be designed to obtain detailed observations of stormscale events and phenomena, and would utilize such sophisticated measurement methods as: digitized doppler and dual-polarized radar; advanced, densely spaced upper-air sounding systems; automated surface observational networks; instrumented aircraft; and geostationary and polar-orbiting satellite display and analysis systems.

A second candidate program is a projected 100 million dollar acid precipitation study (MATEX) of long-range atmospheric transport and transformation being considered by the Electric Power Research Institute. A MATEX design and feasibility study is currently underway and should be completed later this year, although preliminary indications are that it could overlap the geographical domain and schedule of the Gulf Coast oxidant study. Integration of the Gulf Coast oxidant study with programs like STORM and MATEX should be pursued because of the benefits of technical synergism and cost savings that would result.

#### SECTION 5

## CONCLUSIONS AND RECOMMENDATIONS

The two working groups recommended that some preparatory research and development efforts should be undertaken in addition to the principal components of the major study itself. The overall conceptual design is outlined in Figure 1.

In the preparatory-analysis phase, currently available air quality and meteorological data from the study region would be compiled to create a comprehensive data base. The data would be analyzed to provide a better understanding of temporal and spatial variations of oxidant throughout the region, and to develop an improved understanding of the importance of (for example) moisture, synoptic-scale wind flow, long range transport, land-sea breeze circulation, and low-level jet in the formation of high oxidant concentrations. Additionally, a photochemical simulation model would be applied to the Houston metropolitan area as a test of the hypothesis that oxidant concentrations are anomalous or that the combination of relatively high HC-to-NO<sub>X</sub> ratio, high ambient humidity, and intense sunlight result in chemical conditions that are different from other regions.

As part of the preparatory measurement/study phase, an enhanced routine monitoring network (ERN) would be established and operated for three months to provide a comprehensive Eulerian aerometric data base. The purpose would be to gain an improved understanding of oxidant formation and transport, and to develop a detailed research plan for the primary experimental program. This limited sampling program would focus on developing sampling strategies, and on obtaining limited data for the mesoscale land/sea breeze, cloud venting, and medium-range transport

experiments that are anticipated to be conducted later during the primary field study.

A preliminary, detailed research plan and study design would be developed for the experimental and analysis phases of the principal Gulf Coast oxidant transport and transformation study. The plan would specify numbers and types of airborne platforms, instrumentations specifications, and sampling strategies and protocols. Also specified would be comprehensive specifications for the surface aerometric network, including parameters for measurement, analytical methods, site locations, sampling frequency, data processing and so forth. All aspects of tracer applications in the mesoscale and medium-range transport studies would also be delineated, such as tracer-types, and release, sampling and analysis methods. Scheduling of the intermediate range transport case-studies would also be addressed, including definition of criteria for determining when or where experiments are to be conducted, and for contingency plans in the event meteorological conditions are not optimum for the fulfillment of the primary study objectives.

The three-month primary field study of the oxidant transport and transformation would have two major aspects: (1) operation of the enhanced routine monitoring network, and (2) short-term case studies of mesoscale and medium-range transport and transformation. The short-term case studies would consist of (1) mesoscales studies of pollutant transport and oxidant production within the domain of the land/sea breeze circulation and (2) medium-range (ca 400-500 km) studies of oxidant transport out of the Gulf emissions source region. Cloud venting studies would be an integral component of the mesoscale experiments. The mesoscale studies would constitute the majority of the 10 case studies recommended, and would rely heavily on a full complement of airborne platforms in addition to the use of gas tracers with airborne and surface in situ sampling. Each study would cover a 30-hour period. On the order of three medium-range transport experiments are contemplated. Analysis of the processed data would address several basic issues: (1) relation of ozone formation to the precursor mix of

the region, (2) impact of high humidity, (3) role and significance of cumulus clouds in venting ozone or precursors out of the boundary layer, (4) nature and significance of medium-range oxidant and presursor transport into and out of the region, (5) role of land/sea breeze circulation in production of locally high ozone concentrations, and (6) thee-dimensional spatial distribution of ozone on episodic days.

The overall program could be accomplished in about five years at an estimated cost that ranges between 9.5 and 12.4 million dollars. In the event that the preparatory field studies (i.e. ERN and exploratory mobile sampling) are deleted from the program, the estimated cost would range between 7.75 and 9.9 million dollars and the schedule might be compressed by approximately six months. The working groups did not, however, recommend the deletion of the preparatory field studies. On the contrary, they were recommended highly as necessary to the ultimate success of the program.

Finally, the Gulf Coast oxidant study should seek to integrate and coordinate its activities with those of other major atmospheric studies planned for the same time frame and geographic domain. The multi-agency national STORM program (STormscale Operational and Research Meteorology) appears to be one such potentially viable mesoscale study. STORM has been proposed by a steering committee composed of 13 representatives of member institutions of the University Corporation for Atmospoheric Research (UCAR), and would be supported at an annual cost of 60 to 120 million dollars per year for 10 years, (UCAR, 1983). A second candidate program is a projected 100 million dollar acid precipitation study (MATEX) of long-range atmospheric transport and transformation being considered by the Electric Power Research Institute. A MATEX design and feasibility study is currently lunderway, and sould be completed later this year. Preliminary indications are that it could overlap the geographical domain and schedule of the Gulf Coast oxidant study. Integration of the Gulf Coast oxidant study with programs like STORM and MATEX should be pursued because of the benefits of technical synergism and cost savings that would result.

## REFERENCES

- Cantrell, B.K., F.L. Ludwig, and H.B. Singh, 1982: "A Review of the Fate of NO, and Its Role in Rural Ozone Formation," Revised Task Report, SRI Project 3643, U.S. Environmental Protection Agency, CR 809330010 Research Triangle Park, NC.
- Ching, J.K.S., E.E. Uthe, B.M. Morley, and W. Viezee, 1984:
  "Observational Study of Transport in the Free Troposphere," Paper presented at Fourth Joint Conference on Applications of Air Pollution Meteorology with APCA, October 16-19, Portland, OR.
- Clark, T.L., 1980: "Annual Anthropogenic Pollutant Emissions in the United States and Southern Canada east of the Rocky Mountains, "Atmos. Env., Vol. 14, pp. 961-970.
- Decker, C.E., L.A. Ripperton, J.J.B. Worth, F.M. Vukovich, W.D. Bach, J.B. Tommerdahl, F. Smith, and D.E. Wagoner, 1976: "Formation and Transport of Oxidants Along Gulf Coast and in Northern U.S.," Contract No. EPA-450/3-76-033, U.S. Environmental Protection Agency, Research Triangle Park, NC.
- Eaton, W.C., C.E. Decker, J.B. Tommerdahl, and F.E. Dimmock, 1979:
  "Study of the Nature of Ozone, Oxides of Nitrogen and Nonmethane
  Hydrocarbons in Tulsa, Oklahoma," EPA Report No. EPA-450/4-79-008a.
- Horie, Y., M. Marians, J. Trijonis, P. Hurt, N. Chang, 1979: "Analysis of Oxidant for Precursor Emissions/Ambient Precursor Relationship," Final Report TSC-PD-A196-5, Technology Service Corp., Santa Monica,
- Lamb, R.G., 1982: "A Regional Scale (1000 km) Model of Photochemical Air Pollution -- Part 1. Theoretical Formulation," Paper, U.S. Environmental Protection Agency, NC.
- Lambeth, B.W., 1978: "Detailed Case Studies of Summer Ozone Events in Southern Louisiana," Technical Note, Contract No. 68-02-1383, U.S. Environmental Protection Agency, Research Triangle Park, NC.

- Lonneman, W.A., J.J. Bufalini, and R.L. Seila, 1976: "PAN and Oxidant Measurements in Ambient Atmospheres," Env. Sci. & Technol., Vol. 10, p. 374.
- Martinez, J.R. and H.B. Singh, 1979: "Survey of the Role of NO in Nonurban Ozone Formation," SRI International, Menlo Park, CA., Final Report, SRI Project 6780-8.
- Niemeyer, L.E., 1977: "Long Range Transport of Ozone Across the Midwestern and Eastern United States," Atmos. Env., Vol 11, No. 11, pp. 1119-1120.
- Ruff, R.E., L.S. Gasiorek, and H. Shigeishi, 1977: "Master Data File from the Summer 1975 Northeast Oxidant Transport Study," User's Manual, SRI International Project 3570-29 for EPA Contract 68-01-2940 (Task 029), U.S. Environmental Protection Agency, Boston, MA.
- Spicer, C.W., D.W. Joseph, and G.F. Ward, 1976: Final Data Report on the Transport of Oxidant Beyond Urban Areas, Final Report EPA Contract 68-02-2441, 388 pp.
- Spicer, C.W., D.W. Joseph, and G.F. Ward, 1978: "Investigations of Nitrogen Oxides Within the Plume of an Isolated City,"
  Battelle-Columbus Report to CRC (CAPA-9-77) July.
- Spicer, C.W., J.R. Koetz, G.W. Keigley, G.M. Sverdrup, and G.F. Ward, 1981: "A Study of Nitrogen Oxides Reaction within Urban Plumes Transported over the Ocean," Report for EPA Contract 68-02-2957, Battelle Laboratories, Columbus, Ohio, 167 pp.
- Trijonis, J., 1979: "Historical Emission and Ozone Trends in the Houston Area," Proc. of Specialty Conf. on Ozone/Oxidants: Interactions with the Total Environment, (edited by the Air Pollution Control Association), October 14-17, 1979, Houston, Texas.
- U.S. EPA, 1977: "Effectiveness of Organic Emission Control Programs as a Function of Geographic Location," EPA, OAQPS, Research Triangle Park, NC.

- Spicer, C.W., J.R. Koetz, G.W. Keigley, G.M. Sverdrup, and G.F. Ward, 1981: "A Study of Nitrogen Oxides Reaction within Urban Plumes Transported over the Ocean," Report for EPA Contract 68-02-2957, Battelle Laboratories, Columbus, Ohio, 167 pp.
- Trijonis, J., 1979: "Historical Emission and Ozone Trends in the Houston Area," Proc. of Specialty Conf. on Ozone/Oxidants: Interactions with the Total Environment, (edited by the Air Pollution Control Association), October 14-17, 1979, Houston, Texas.
- U.S. EPA, 1977: "Effectiveness of Organic Emission Control Programs as a Function of Geographic Location," EPA, OAQPS, Research Triangle Park, NC.
- University Corporation for Atmospheric Research, 1983: The National STORM Program, A Call to Action, Boulder, CO, 34 pp.
- Uthe E.E., 1983: "Applications of Surface Based and Airborne Lidar Systems to Environmental Monitoring," J. Air Pol. Contrl. Assoc., Vol. 33, No. 12.
- Vaughan, W.M., M. Chan, B. Cantrell, and F. Pooler, 1982: "A Study of Persistent Elevated Pollution Episodes in the Northwestern United States, Bull. Amer. Meteorol. Soc., 63, pp. 258-266.
- Wolff, G.T., P.J. Lioy, G.D. Wight, R.E., Meyers, and R.T. Cederwall, 1977: "An Investigation of Long-Range Transport of Ozone Across the Midwestern and Eastern United States," Atmos. Env., 11, pp. 797-802.
- Wolff, G.T. and P.J. Lioy, 1980: "Development of an Ozone River Associated with Synoptic Scale Episodes in the Eastern United States," Env. Sci. and Tech., 14, pp. 1257-1260.

## LIST OF PARTICIPANTS

Dr. Al Bowman Institute for Storm Research 3600 Mt. Vernon Houston, TX 77006

Dr. Joseph Bufalini (MD-84) ASRL Office of Res. & Development U.S. EPA Research Triangle Park, NC 27711

Dr. Jason Ching (MD-80) ASRL Office of Res. & Development U.S. EPA Research Triangle Park, NC 27711

Dr. John Clarke (MD-80) ASRL Office of Res. and Development U.S. EPA Research Triangle Park, NC 27711

Dr. Timothy Crawford Tennessee Valley Authority Air Resources Program River Oaks Building Muscle Shoals, AL 35660

Dr. Kenneth Demerjian (MD-80) ASRL Office of Research and Devel. U.S. EPA Research Triangle Park, NC 27711

Dr. Basil Dimitriades (MD-59) ASRL Office of Research & Devel. U.S. EPA Research Triangle Park, NC 27711 Mr. Richard Haws Research Triangle Institute Research Triangle Park, NC 27709

Dr. S.A. Hsu Coastal Studies Institute Louisiana State University Baton Rouge, LA 70803

Dr. Donald Lenschow NCAR P.O. Box 3000 Boulder, CO 80307

Dr. Walter A. Lyons R-SCAN Corporation 511 Eleventh Avenue South Minneapolis, MN 55415

Dr. James L. McElroy AMI EMSL-LV EPA P.O. Box 15027

Dr. Edwin L. Meyer (MD-14)
Office of Air Qual. Plng.
and Standards
U.S. EPA
Research Triangle Park, NC 27711

Dr. William Pennell Battelle-PNL Atmospheric Science Department P.O. Box 999 Richland, WA 99352

Dr. Fran Pooler ASRL U.S. EPA Research Triangle Park, NC 2711 Dr. Jack Durham (MD-84)
ASRL
Office of Research & Devel.
U.S. EPA
Research Triangle Park, NC 27711

Dr. Marcia Dodge (NMD-84) ASRL Office of Research & Devel. U.S. EPA Research Triangle Park, NC 27711

Dr. Scott Shipley NASA Langley Research Center MS-401A Hampton, VA 23665

Mr. Eugene Start NOAA/ARL/Idaho Research Office Idaho National Engineering Lab. Idaho Falls, Idaho 83401

Dr. Fred M. Vukovich Research Triangle Institute Research Triangle Park, NC 27711

Dr. Stephen Wise Coordinating Research Council c/o Mobil Research and Development Research Department Paulsboro, NJ 08066 Mr. James Price Texas Air Control Board Control Strategy Division 6330 Highway 290 East Austin, TX 78723

Mr. Kenneth Schere ASRL Office of Res. & Devel. U.S. EPA Research Triangle Park, NC 27711

Dr. Jack Schreffler ASRL U.S. EPA Research Triangle Park, NC 27711

Dr. Gary K. Tannahill Exxon Company, USA 800 Bell Avenue P.O. Box 2180 Houston, TX 77001

Dr. Harry Walker Monsanto P.O. Box 711 Alvin, TX 77511

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)						
1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.				
4. TITLE AND SUBTITLE CONCEPUTAL DESIGN FOR A GU	5. REPORT DATE					
AND TRANSFORMATION EXPERIM Workshop Proceedings and R		6. PERFORMING ORGANIZATION CODE				
7. AUTHOR(S) Walter F. Dabberdt, William Hanwant B. Singh	8. PERFORMING ORGANIZATION REPORT NO.					
9. PERFORMING ORGANIZATION NAME AP SRI International	10. PROGRAM ELEMENT NO. CDWA1A/02 2064 (FY-85)					
333 Ravenswood Ave.		11. CONTRACT/GRANT NO.				
Menlo Park, CA 94025		68-02-3752				
12. SPONSORING AGENCY NAME AND ADD Atmospheric Sciences Resea	13. TYPE OF REPORT AND PERIOD COVERED					
Office of Research and Deve		14. SPONSORING AGENCY CODE				
U.S. Environmental Protect Research Triangle Park, No		EPA/600/09				

15. SUPPLEMENTARY NOTES

Thirty atmospheric scientists from government, industry, academia, and the private research sector participated in a workshop in November 1983, in Durham, NC to develop a conceptual design for a study of ozone transport and transformation in the western Gulf coast area. The purpose of the study would be to better understand the unique meteorology and chemistry of the region, and to effectively adapt the EPA Regional Oxidant Model to that geographic area. Working groups focused on the problems of meteorology and atmospheric chemistry and measurement needs and methods. A conceptual design was developed for a five-year program that would include preparatory studies, the 3-month primary experimental program, and data analysis. The preparatory studies would consist of the collection and analysis of all existing data, simulation modeling, smog chamber studies, instrument development, and preliminary, limited field measurements. The primary experiment would consist of an enhanced monitoring network operated continuously, and frequent, intensive short-term experiments; the geographical domain of the study would be about 300 km east-west and 800 km north-south. The routine monitoring would include boundary layer profiles of aerometric parameters by light aircraft and enhanced radiosonde coverage. The intensive studies would rely heavily on sophisticated aircraft platforms such as doppler radar, UV and IR lidar, backscatter lidar, and in-situ gas concentration and flux measurments; gaseous and fluorescent particulate tracers would also be used.

17.	KEY WORDS AND DOCUMENT ANALYSIS		
a	DESCRIPTORS	b.identifiers/open ended terms	c. COSATI Field/Group
		Į	
		<u>.</u>	
	,		
18. DISTRIBUTION STA	TEMENT	19. SECURITY CLASS (This Report)	21, NO. OF PAGES
	UNCLASSIFIED		
KELE	ASE TO PUBLIC	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

		•	
.•			
•			
·			
,			
•			