Report to the
Texas Commission on Environmental Quality (TCEQ)

from the

Rapid Science Synthesis Team (RSST) for the
Second Texas Air Quality Study (TexAQS II)

This report was prepared by the
Southern Oxidants Study Office of the Director (SOS-OD)
at
North Carolina State University

by

Ellis B. Cowling, Director of SOS
Cari Furiness, Research Associate
Basil Dimitriades, Adjunct Professor

and

David Parrish of the Earth System Research Laboratory,
National Oceanic and Atmospheric Administration

In cooperation with Mark Estes of TCEQ,
and 26 other members of the Rapid Science Synthesis Team (RSST)

Introduction

The Rapid Science Synthesis Team (RSST) for the Second Texas Air Quality Study (TexAQS II) has been charged to address a series of 12 High Priority SIP-Relevant Science Questions identified by leaders within the Texas Commission on Environmental Quality (TCEQ). Answers to these important questions (see list on pages 3 and 4) are needed by TCEQ in order to fulfill the Commission's responsibility to develop and submit to the US Environmental Protection Agency scientifically sound State Implementation Plans (SIPs) by which to attain the recently implemented 8-hour National Ambient Air Quality Standards (NAAQS) for Ozone and Related Photochemical Oxidants. SIPs for both the Houston-Galveston-Brazoria Ozone Non-Attainment Area (HGB) and the Dallas-Fort Worth Ozone Non-Attainment Area (DFW) are scheduled to be completed during the early months of 2007.

Approaches to addressing TCEQ's SIP-Relevant Science Questions are being developed by a series of RSST Working Groups established by mutual agreement among leaders in TCEQ and the Office of the Director for the Southern Oxidants Study (SOS-OD). The SOS-OD is headquartered at North Carolina State University and is led by Ellis Cowling, Director of SOS, Cari Furiness, Research Associate, and Basil Dimitriades, Adjunct Professor at NC State and former EPA Project Officer for SOS.

Each of the 12 RSST Working Groups consists of 7-10 expert persons, drawn from various university-, state-, federal-, and private-sector organizations (members of each Working Group are listed on pages 3 and 4, names and organizational affiliations are on page 5). Each of these individuals has specialized knowledge and insights in the realms of science that are essential to provide insight into one or more of TCEQ's High Priority SIP-Relevant Science Questions.

Answers to TCEQ's SIP-Relevant Science Questions are needed in order to develop the most up-to-date and scientifically sound State Implementation Plans (SIPs) for two very different and very large ozone non-attainment areas within the state of Texas:

1) The Houston-Galveston-Brazoria ozone non-attainment is a COASTAL city of about 4 million people. The HGB non-attainment area consists of eight counties in southeastern Texas and is subject to very distinctive coastal (sea-breeze) meteorological conditions and extraordinarily large petrochemical sources of industrial emissions within the ozone non-attainment area (especially the Houston Ship Channel and other nearby sources of industrial emissions).

2) The Dallas-Forth Worth ozone non-attainment area is an INLAND city, also of about 4 million people. The DFW non-attainment area includes 8 counties in north-central Texas, with relatively typical inland metropolitan meteorological conditions and only limited industrial sources within the non-attainment counties but with several power plants in upwind locations within northeastern Texas.

Technical Liaison within TCEQ for the science assessment functions of the RSST is provided by Mark Estes of TCEQ's Data Analysis and Modeling Section. David Parrish of the Earth System Research Laboratory (ESRL) within the National Oceanic and Atmospheric Administration (NOAA) has been designated by NOAA ESRL to provide leadership for NOAA scientists for RSST activities; he acts as leader or co-leader for 8 of the 12 RSST Working Groups.

31 July 2006

TCEQ's High Priority SIP-Relevant Science Questions and Leaders (L), Participants (P) and Observers (O) in Working Groups within the Rapid Science Synthesis Team

Description of ozone and PM formation mechanisms, as observed and inferred independent of regulatory modeling

A Which local emissions are responsible for the production of high ozone in Houston, Dallas, and eastern Texas? Are different kinds of emissions responsible for transient high ozone and 8-hour-average high ozone (i.e., ≥84 ppbv)?
L – David Parrish, P – Tom Ryerson, Joost deGouw, Basil Dimitriades, David Allen, Mark Estes, O – Noor Gillani

B How do the structure and dynamics of the planetary boundary layer and lower troposphere affect ozone and aerosol concentrations in Houston, Dallas, and eastern Texas?
Co-L – Robert Banta & John Nielsen-Gammon, P – Allen White, Christoph Senff, Wayne Angevine, Bryan Lambeth, Lisa Darby, Bright Dornblaser, Daewon Byun, O – Carl Berkowitz, Noor Gillani

C Are highly-reactive VOC and NO_x emissions and resulting ambient concentrations still at the same levels in Houston as they were in 2000? How have they changed spatially and temporally? Are there specific locations where particularly large quantities of HRVOC are still being emitted? Are those emissions continuous or episodic? How well do the reported emissions inventories explain the observed concentrations of VOC and NO_x?
L – David Parrish, P – David Allen, Joost deGouw, Tom Ryerson, Mark Estes, David Sullivan, John Jolly, Eric Williams, Barry Lefer, O – Yulong Xie, Carl Berkowitz, Noor Gillani. **Note:** To answer the last part of question C, TCEQ must define the inventory to which the observations must be compared.

D What distribution of anthropogenic and biogenic emissions of ozone and aerosol precursors can be inferred from observations?
Co-L – David Allen & David Parrish, P – Tom Ryerson, Charles Brock, Joost deGouw, David Sullivan, Mark Estes, John Jolly, Eric Williams, Barry Lefer, O – Yulong Xie, Carl Berkowitz, Noor Gillani

E Are there sources of ozone and aerosol precursors that are not represented in the reported emissions inventories?
L – David Parrish, P – Tom Ryerson, Charles Brock, Joost deGouw, David Sullivan, John Jolly, David Allen, Eric Williams, Barry Lefer

Sensitivity to VOC and NO_x emission reductions

F How do the mesoscale chemical environments (NO_x-sensitive ozone formation vs radical-sensitive ozone formation) vary spatially and temporally in Houston, Dallas and eastern Texas? Which mesoscale chemical environments are most closely associated with high ozone and aerosol?
Co-L – Basil Dimitriades & David Parrish, P – David Allen, Harvey Jeffries, William Vizuete, Daewon Byun, Mark Estes, Kenneth Schere, Barry Lefer, O – Yulong Xie, Carl Berkowitz

Background ozone and aerosol concentrations and the role of regional transport

G How do emissions from local and distant sources interact to determine the air quality in Texas? What meteorological and chemical conditions exist when elevated background ozone and aerosol from distant regions affect Texas? How high are background concentrations of ozone and aerosol, and how do they vary spatially and temporally?
Co-L – David Allen & David Parrish, P –Bryan Lambeth, David Sullivan, Basil Dimitriades, Charles Brock, Michael Hardesty, Steve Brown, Joost deGouw, Steve Brown

H Which areas within Texas adversely affect the air quality of non-attainment areas within Texas? Which areas outside of Texas adversely affect the air quality of non-attainment areas within Texas?
Co-L – David Allen & David Parrish, P – Mark Estes, Greg Yarwood, Basil Dimitriades, David Sullivan, Charles Brock, Michael Hardesty, John Jolly, Bryan Lambeth

Other SIP-Relevant science questions

I Why does the SAPRC chemical mechanism give different results than CB-IV? Which replicates the actual chemistry better?
Co-L – David Allen & Greg Yarwood, P – Harvey Jeffries, William Vizuete, Bill Carter, David Parrish, Stuart McKeen, Daewon Byun, Joost deGouw, Barry Lefer, O – Mark Estes, Noor Gillani

J How well do forecast air quality models predict the observed ozone and aerosol formation? What are the implications for improvement of ozone forecasts?
L – Stuart McKeen, P – Gregory Carmichael, Bryan Lambeth, Kenneth Schere, James Wilczak, Greg Yarwood, Daewon Byun, John Nielsen-Gammon, Michael Hardesty

K How can observation and modeling approaches be used for determining (i) the sensitivities of high ozone in the HGB non-attainment area to the precursor VOC and NOx emissions, and (ii) the spatial/temporal variation of these sensitivities?
Co-L – Basil Dimitriades & David Parrish, P – Ted Russell, Harvey Jeffries, William Vizuete, Mark Estes, David Sullivan, Tom Ryerson, Greg Yarwood, Barry Lefer, O – Noor Gillani

L What existing observational databases are suitable for evaluating and further developing meteorological models for application in the HGB area?
Co-L – Robert Banta & Lisa Darby, P – John Nielsen-Gammon, Daewon Byun, Wayne Angevine, Mark Estes, Bryan Lambeth, Stuart McKeen

Note: Letter designations are for convenience only and do not denote priority. Questions in blue have been designated by TCEQ to receive special emphasis.

Members and Email Addresses of the TexAQS II Rapid Science Synthesis Team:

Dave Allen, University of Texas — allen@che.utexas.edu
Wayne Angevine, NOAA Earth System Research Laboratory — wayne.m.angevine@noaa.gov
Bob Banta, NOAA Earth System Research Laboratory — robert.banta@noaa.gov
Carl Berkowitz, DOE Pacific Northwest Laboratory — carl.berkowitz@pnl.gov
Chuck Brock, NOAA Earth System Research Laboratory — charles.a.brock@noaa.gov
Steve Brown, NOAA Earth System Research Laboratory — steven.s.brown@noaa.gov

Daewon Byun, University of Houston — Daewon.Byun@mail.uh.edu
Greg Carmichael, University of Iowa — gregory-carmichael@uiowa.edu
Bill Carter, University of California Riverside — carter@mail.cert.ucr.edu
Ellis Cowling, North Carolina State University — ellis_cowling@ncsu.edu
Lisa Darby, NOAA Earth System Research Laboratory — lisa.darby@noaa.gov

Basil Dimitriades, North Carolina State University — basildi@hotmail.com
Mark Estes, Texas Commission on Environmental Quality — mestes@tceq.state.tx.us
Joost deGouw, NOAA Earth System Research Laboratory — joost.degouw@noaa.gov
Cari Furiness, North Carolina State University — cari_furiness@ncsu.edu
Noor Gillani, University of Alabama at Huntsville — gillani@nsstc.uah.edu
Mike Hardesty, NOAA Earth System Research Laboratory — mike.hardesty@noaa.gov

Harvey Jeffries, University of NC at Chapel Hill — harvey@unc.edu
John Jolly, Texas Commission on Environmental Quality — jjolly@tceq.state.tx.us
Bryan Lambeth, Texas Commission on Environmental Quality — blambeth@tceq.state.tx.us
Barry Lefer, University of Houston — blefer@uh.edu
Stu McKeen, NOAA Earth System Research Laboratory — stuart.a.mckeen@noaa.gov
John Nielsen-Gammon, Texas A&M University — n-g@tamu.edu

David Parrish, NOAA Earth System Research Laboratory — david.d.parrish@noaa.gov
Tom Ryerson, NOAA Earth System Research Laboratory — thomas.b.ryerson@noaa.gov
Ted Russell, Georgia Institute of Technology — trussell@ce.gatech.edu
Ken Schere, US Environment Protection Agency — schere.kenneth@epa.gov
Christoph Senff, NOAA Earth System Research Laboratory — christoph.senff@noaa.gov

Dave Sullivan, University of Texas, — sullivan231@mail.utexas.edu
Will Vizuete, University of North Carolina at Chapel Hill — vizuete@email.unc.edu
Allen White, NOAA Earth System Research Laboratory — allen.b.white@noaa.gov
Jim Wilczak, NOAA Earth System Research Laboratory — james.m.wilczak@noaa.gov
Eric Williams, NOAA Earth System Research Laboratory — eric.j.williams@noaa.gov
Yulong Xie, DOE Pacific Northwest Laboratory — yulong.xie@pnl.gov
Greg Yarwood, Environ Corp — gyarwood@environcorp.com

Major Recent Air Quality Studies in the State of Texas

During recent years, the State of Texas assembled scientific teams to work with TCEQ and Texas Environmental Research Consortium (TERC) to improve scientific understanding of ozone formation and accumulation in eastern Texas. These scientific studies have been focused around two major air-quality field research programs in the State of Texas.

First Texas Air-Quality Study (TexAQS 2000)
The first of these two major field-research programs – TexAQS 2000 – was a relatively short-term (six-week-long) intensive field measurement program conducted during the summer of 2000. This program of both aircraft-based and ground-based field measurements was organized under the scientific leadership of Dr. Peter Daum of Brookhaven National Laboratory, Drs. Jim Meagher and Fred Fehsenfeld of NOAA (in what was then called the Aeronomy Laboratory), the SOS Office of the Director at NC State University, Messrs. Jim Thomas, Jim Price, and others of the Texas Commission on Environmental Quality, Drs. David Allen, of the University of Texas, John Nielson-Gammon of Texas A&M University, Matt Fraser of Rice University, and many other university, federal agency, and private sector scientists in Texas and other parts of the US and abroad.

TexAQS 2000 was one of the most comprehensive and successful air-quality field research programs ever organized in the US. TexAQS 2000 provided a substantially increased and reliable (although still incomplete) understanding of the complex photochemical and meteorological processes of ozone accumulation in Houston-Galveston and other areas of eastern Texas.

The TexAQS 2000 field research results demonstrated that the *extraordinarily stringent decreases in NO$_x$ emissions* proposed in the 2000 State Implementation Plan (SIP) for the Houston-Galveston non-attainment area of Texas was not an optimal approach. TexAQS 2000 research results also demonstrated that a more realistic plan for attainment of the National Ambient Air Quality Standard (NAAQS) for ozone should involve decreases in emissions of *both VOC and NOx* – including emissions of highly reactive, low-molecular-weight VOC (HRVOC) in the industrial areas surrounding the Ship Channel and Galveston Bay in Houston.

Second Texas Air Quality Study (TexAQS II and TexAQS 2006)
The second major field research program in the state of Texas – TexAQS II – is a much longer-term (18-month-long) program of aircraft-based, research-vessel-based, and ground-based measurements and mathematical modeling of the photochemical and meteorological processes leading to the formation and accumulation of ozone and particulate matter air pollution in eastern Texas.

TexAQS II began during June of 2005 and will extend through September 2006. Like the First Texas Air Quality Study (TexAQS 2000), TexAQS II will be one of the largest and most comprehensive air quality field research studies undertaken in the United States.

As indicated above, the TexAQS II research study includes not only the 2005 and 2006 summer ozone seasons, but also the intervening fall, winter, and spring months of 2005 and 2006 when occasional exceedances of the recently promulgated 8-hour ozone standard may occur – together with or separately from – occasional episodes of high concentrations of airborne particulate matter.

TexAQS II study will culminate during the months of August and September 2006 with a very intensive and well-focused series of coordinated direct photochemical and meteorological measurements and modeling studies. In order to distinguish this relatively short-term but very intensive 2-month-long intensive study from the rest of TexAQS II, the 2006 summer intensive study has been dubbed TexAQS 2006 in much the same way that the First Texas Air Quality Study was named TexAQS 2000.

The measurement platforms planned for implementation in TexAQS 2006 will include:
1) Multiple aircraft-based instrument platforms in both the Houston/Galveston and Dallas/Fort Worth areas of Texas,
2) Continuing direct measurements of air chemistry at a series of carefully placed ground-based measurement sites, a network of ground-based wind profiler and rawinsonde measurement locations, and both aircraft-based and ship-based ozone and particulate matter LIDAR measurements throughout eastern Texas,
3) An impressive array of direct measurements mainly by NOAA scientists and engineers stationed on NOAA's Ronald H. Brown Research Vessel. This vessel will be positioned at locations within the Houston Ship Channel, Galveston Bay and other ports along the Texas Gulf Coast at various times during TexAQS 2006.
4) An intensive set of chemical and meteorological measurements specific to ozone, particulate matter, and secondary species formation, made from the 200-ft-tall Moody Tower at the University of Houston.

The multimillion-dollar 18-month-long term TexAQS II field research study and its embedded short-term intensive study (TexAQS 2006) is being conducted jointly by staff of TCEQ and by scientists and engineers working under contracts issued by TCEQ and the Texas Environmental Research Consortium (TERC) through the Houston Advanced Research Center (HARC).

These contract research projects are being conducted by scientists, engineers, graduate students, and postdoctoral fellows within the following research organizations:
1) David Allen, David Sullivan, and others within the University of Texas, and associated consultant James Thomas,
2) Daewon Byun, Barry Lefer, Bernhard Rappenglück, and others within the University of Houston,
3) John Nielsen-Gammon and others within Texas A&M University,
4) David Parrish, Michael Trainer, Tom Ryerson, Stuart McKeen, Michael Hardesty, Robert Banta, Lisa Darby, Wayne Angevine, Charles Brock, Joost DeGouw, Christoph Senff, Allen White, James Wilczak, and others within NOAA,
5) Johan Mellqvist, Chalmers University of Technology, Göteborg, Sweden
6) Carl Berkowitz and Yulong Xie of the Department of Energy's Pacific Northwest Laboratory,
7) Harvey Jeffries and William Vizuete of the University of North Carolina at Chapel Hill,
8) Greg Carmichael of the University of Iowa,
9) William Carter of the University of California in Riverside,
10) Ted Russell of the Georgia Institute of Technology,
11) Ellis Cowling, Cari Furiness, and Basil Dimitriades of North Carolina State University,
12) Kenneth Schere of the US Environmental Protection Agency, and
13) Greg Yarwood of Environ Corporation.

All the research studies and plans for analysis and interpretation of results obtained during TexAQS II and TexAQS 2006 have been undertaken with specific scientific research objectives

in mind. But many of these investigations also have been designed, undertaken, and funded by various federal, state, and private-sector organizations with specific policy purposes in mind – and most particularly in order to be used by TCEQ in developing State Implementation Plans that will be required by the US EPA in 2007 for various ozone non-attainment areas in eastern Texas.

Much time and intellectual energy will have to be applied in order to analyze, interpret, synthesize, and eventually translate the measurements obtained from the various field measurements platforms listed above and the modeling studies that will be performed during TexAQS II and TexAQS 2006, into carefully crafted statements of scientific findings and statements of policy implications deriving from these scientific findings. Also, much additional time and both organizational and intellectual energy will be needed to accomplish both the required and desirable public notices, public hearings, preparation of public comments, development of responses to public comments, and consideration of alternative approaches that should be considered or used in the final State Implementation Plan (SIP) that will be submitted to EPA Region 6 and later to USEPA's Office of Air Quality Planning and Standards (EPA-OAQPS).

The time available between completion of many of the TexAQS II scientific studies and the deadline for preparation and final submission of the SIPs required for eastern Texas is extraordinarily short. Thus, careful plans are being implemented in order to use the very limited time that is available with efficiency – and to take as full advantage as possible of the available data-analysis and scientific synthesis skills that can be mustered by the TexAQS II and TexAQS 2006 science teams, and by TCEQ and/or TERC and HARC. For this reason, the Rapid Science Synthesis Team was created and is now being implemented under the leadership of the Southern Oxidants Study Office of the Director at North Carolina State University.

Additional Sources of Data and Information of Value in Providing Reliable Answers to TCEQ's High Priority SIP-Relevant Science Questions

In addition to the chemical and meteorological measurements and mathematical modeling results from TexAQS II and TexAQS 2006, the leaders, participants and observers involved in the 12 RSST Working Groups will have access to several additional sources of data and information regarding ozone and particulate matter pollution in Texas and surrounding states. To facilitate ready access to these data and information resources and their use in developing approaches to TCEQ's 12 High Priority SIP-Relevant Science Questions, URLs for many of these documents will be provided to all RSST Working Group members. Thus, we hope that these resources will help make the RSST process as useful and valuable as possible to TCEQ – and both intellectually and professionally satisfying to all participants in the RSST scientific research and assessment processes.

Mark Estes has indicated his willingness to use his detailed familiarity with many of these TCEQ, HARC, open literature, and other data and information resources to assist in identifying sources that are most likely to be relevant and useful in developing answers to specific High Priority SIP-Relevant Science Questions. Appendix A contains a compilation of these additional data and information resources, defined in large part by Mark Estes of TCEQ and Ellis Cowling of the SOS-OD.

RSST Working Group Reports

The remainder of this Report from the Rapid Science Synthesis Team (RSST) consists of descriptions of the following:

1. Scientific Approach,
2. Key TexAQS II and Other Data Needs,
3. Timelines for Completion of Interim and Final Assessment Reports, and
4. Expected Deliverable Products

for each of TCEQ's High Priority SIP-Relevant Science Questions. Each question is identified by the same letter designations used on pages 3 and 4 of this Progress Report.

It should be emphasized that these Approaches represent best available plans for the development of products that will apply scientific understanding to aspects of the policy-relevant questions identified by TCEQ. The Approaches are subject to revision during the RSST process, as are the products that can be developed from available data and data collected during TexAQS II and TexAQS 2006 and the specific investigators who will perform the analyses and develop the products and reports.

Question A Approach

Question A (two parts)**:**
Which local emissions are responsible for the production of high ozone in Houston, Dallas, and eastern Texas?
Are different kinds of emissions responsible for transient high ozone and 8-hour-average high ozone (i.e., ≥84 ppbv)?

Question A Working Group:
Leader:
    David Parrish
Participants:
    David Allen
    Joost deGouw
    Basil Dimitriades
   Mark Estes
    Tom Ryerson
Observer:
    Noor Gillani

Analysis Approach:
        The first part of this question requires a continuation and extension of the analyses performed on the data collected during TexAQS 2000. The second part of the question highlights an important change that has occurred since 2006: the regulatory focus upon 8-hour average high ozone rather than 1-hour transient high ozone.
        The observation-based approach to addressing both parts of this question will utilize aircraft measurements of ozone, other secondary product species, their precursors, and other tracer species in plumes downwind of urban areas and different source types such as power plants and industrial sources. The TexAQS 2000 study included such measurements, and TexAQS 2006 will include an even more extensive measurement suite. Particularly important precursors and other tracer species to be measured are biogenic and anthropogenic VOC including industrial HRVOC, NO_x, NO_y, SO_2, CO and CO_2. Particularly important secondary product and intermediates to be measured are ozone, formaldehyde, acetaldehyde and other oxygenated VOC (particularly those from biogenic VOC), organic nitrates including PANs, NO_3, N_2O_5, HNO_3, H_2SO_4, and HO_x radicals. Measurements are required within the urban plumes from HGB and DFW, within industrial plumes from HGB and other industrial complexes, within urban and rural power-plant plumes, and over source regions in rural sections of east Texas. Particular industrial source regions of interest include the ship channel in east Harris County, Galveston County near Texas City, more distributed sources in Brazoria County, downtown and west Harris County, and north Harris County, which are all in HGB, plus facilities in the Beaumont/Port Arthur and the Corpus Christi areas. Particular source regions of interest in DFW include the 4-county metroplex, the surrounding five counties, NE Texas region, and the region SE of metroplex. Surface-based measurements on the NOAA Research Vessel Ronald H. Brown, an enhanced measurement site at the University of Houston, and regional ground monitoring stations will provide complementary information on the spatial and temporal distribution of many of these species. Aircraft measurements will provide information on emissions, allowing mapping of precursors and their influence in ozone production. The analysis will determine the ozone production rate and efficiency in the urban and point source plumes,

and the impact of emission changes between 2000 and 2006 upon these production rates and efficiencies. Ozone lidar measurements from the NOAA Twin Otter will help to define plumes from various sources.

A detailed analysis of plumes from identified sources will be the approach taken to address the first part of Question A. Ryerson et al. (2006) have examined measurements from the four Electra flights during TexAQS 2000 when ozone concentrations above 150 ppbv were observed. Figure 1 shows the flight track segments where the highest ozone was observed. In
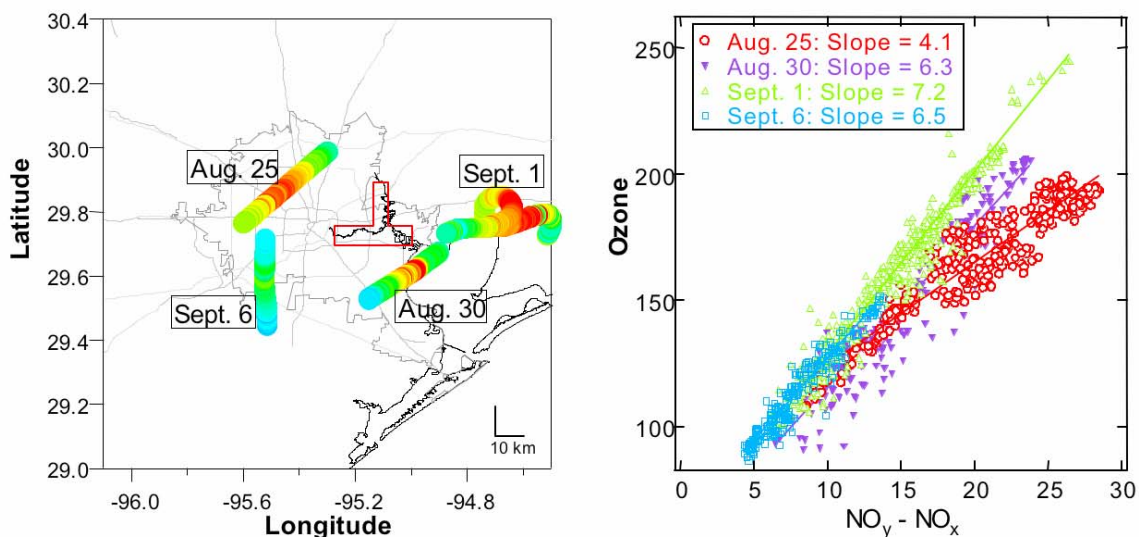
Figure 1. Highest ozone (red points) observed by the Electra aircraft during four flights in TexAQS 2000. In the left panel flight track segments are color-coded by observed ozone, and in the right panel the dependence of ozone on the products of NO$_x$ oxidation are shown with approximate ozone production efficiencies estimated from fitted slopes.

each case these plumes were traced back to emission sources in the Houston Ship Channel area by trajectory analysis. The relationship between the transport times derived from the trajectory analysis and the observed enhancements in ozone provided a measure of the average ozone production rates in the plumes. Figure 1 also shows the observed relationship between ozone and the products of NO$_x$ oxidation for those four flights; the slopes of these relationships provide an estimate of the ozone production efficiencies in these plumes. Ryerson et al. (2006) also treat ozone production in plumes from other regions within the HGB area. To comprehensively address the first part of question A, the Ryerson et al. analysis, or a related analysis, will be extended to other regions (Dallas and eastern Texas) and other flights of both the TexAQS 2000 and TexAQS 2006 studies. The Ryerson et al. analysis also will be supplemented with other related analyses (e.g., Daum et al., 2000; 2003; 2004; Gillani et al., 1998; Kleinman et al., 2002; 2003; Luria et al., 2000; Neuman et al., 2002; 2004; Nunnermacker et al., 2000; Ryerson et al., 1998; 2001; 2003.)

Addressing this second part of Question A will require new analyses that will determine the relative contributions of anthropogenic VOC (AVOV), biogenic VOC (BVOC), high reactivity VOC (HRVOC), other-than-HRVOC VOC (OVOC), and NO$_x$ to production of ozone in exceedance of the new ozone standard. This will be addressed primarily through one or more modeling studies supported by field data. Figure 2 exemplifies one approach. Here the WRF-Chem model was run with two sets of emissions: the 1999 NEI and those same emissions except with the power plant NO$_x$ emissions updated to 2004 to account for the emission controls that have been implemented recently. The output from both runs was examined to determine the 4th highest 8-hour average O$_3$ concentration for each model grid cell, and the corresponding 8-hour average NO$_2$. The plots show the percent decrease in these concentrations for the eastern U.S.

In eastern Texas, significant decreases in NO_2 are noted near the power plant locations. However, the 8-hour average O_3 decreases are limited to regions of relatively large biogenic VOC emissions. The qualitative conclusion that emerges is that power plant NO_x emissions in 1999 were responsible for elevating the 8-hour-average high ozone in forested regions of the state, but not, for example, in the HGB area. In that latter region, the model showed significant NO_2 decreases, but not O_3 decreases.

One specific planned modeling study, similar to those planned for Questions F and K, will entail application of traditional PAQM modeling of ozone production in the Houston area during a full ozone season, with a focus on 8-hour average ozone and its sensitivity to variation in the local AVOC, BVOC, HRVOC, OVOC, and NO_x emission components. If the modeling study covers a past ozone season, the requisite ambient conditions and emissions data inputs to the model will be available. Such a study would not have the benefit of comparisons with TexAQS 2006 data, but it has the advantage of providing timely input to the ongoing SIP-development process. If the modeling study is done for a future year, it would benefit from additional observational and other studies, namely:

(i) Observational studies to obtain reliable emission inventory inputs to the model. Existing emission inventory data for local AVOC, BVOC, HRVOC, OVOC, and NO_x emissions will be improved by comparing model-predicted ambient concentrations of the five emission components with respective concentrations measured by the aircraft during the 2006 ozone episode days.

(ii) Observational studies to obtain the boundary-conditions inputs to the model.

(iii) Optimization of chemical-mechanism input to the model (see Question I).

(iv) Observational studies to obtain data for assessing the credibility of the modeling results.

Resultant modeling data on relative sensitivities of 8-hour ozone to the five emission components, coupled with respective relative emission strength data, will indicate which emission group(s) contribute(s) most to the 8-hour episodic ozone.

Percent surface NO_2 change

Percent surface O_3 change
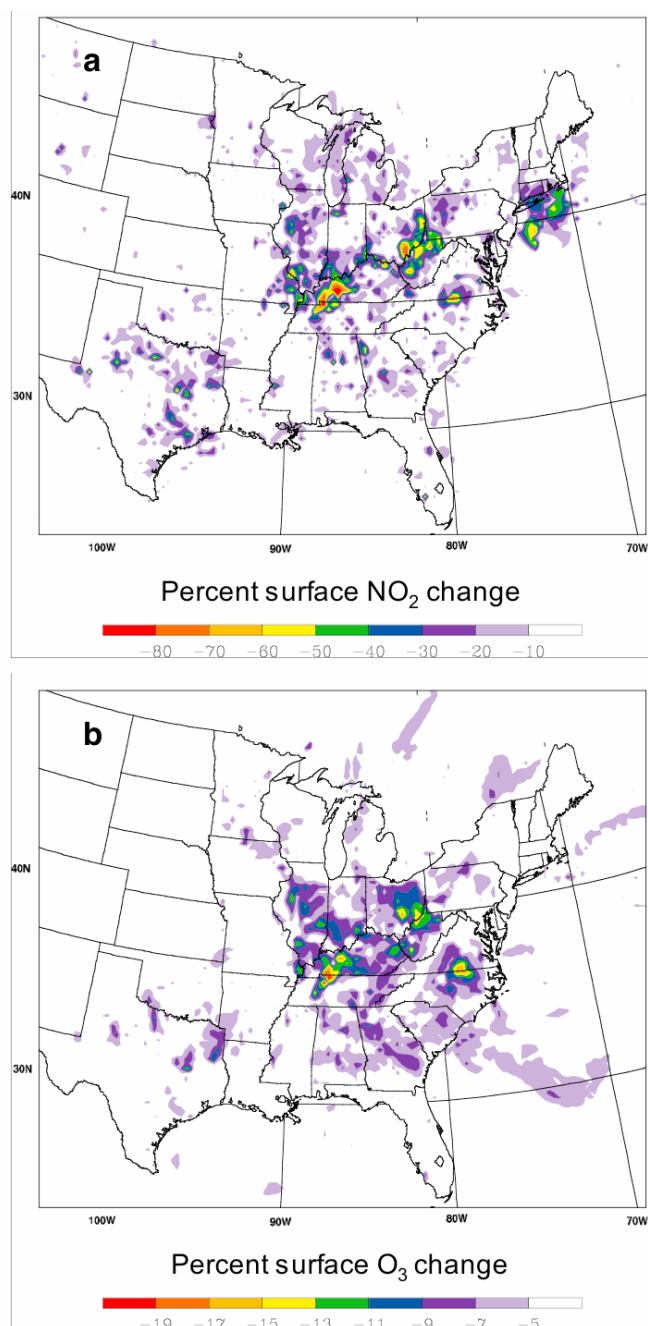
Figure 2. Modeled change in surface NO_2 and O_3 that resulted from the decrease in NO_x emissions from 1999 to 2004. Data are based upon 4th highest 8-hour average O_3.

Key TexAQS II or Other Study Data Needed:
1)   Aircraft measurements of ozone, other secondary product species, their precursors, and other tracer species in plumes downwind of urban areas and different source types such as power plants and industrial sources.
2)   Surface site and ship measurements of ozone, other secondary product species, their precursors, and other tracer species in plumes downwind of urban areas and different source types such as power plants and industrial sources.
3)   Ozone lidar measurements of plumes from various sources in coordination with the WP-3D flights.
4)   Emission inventory data for AVOC, BVOC, HRVOC, OVOC, and NO_x emissions in the Houston, Dallas, and eastern Texas.
5)   Traditional PAQM modeling with a focus on 8-hour average ozone and its sensitivity to variation in AVOC, BVOC, HRVOC, and NO_x emissions.

Suggested Deliverable Products, Timelines and Lead Contacts:
 1)   Process-oriented, observation-based analyses of ambient ozone production and its impact on transient high ozone and 8-hour-average high ozone;
        Preliminary Report - October 31, 2006; Final Report – August 31, 2007
        Tom Ryerson, Joost deGouw, David Parrish
 2)   Analysis through traditional PAQM modeling with a focus on 8-hour average ozone and its sensitivity to variation in AVOC, BVOC, HRVOC, and NO_x emissions.
        Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
        David Allen, Mark Estes, Basil Dimitriades, David Parrish

References:

Daum, P. H., et al. (2000), Analysis of the processing of Nashville urban emissions on July 3 and July 18, 1995, *J. Geophys. Res.*, *105*, 9155-9164.

Daum, P. H., et al. (2003), A comparative study of O_3 formation in the Houston urban and industrial plumes during the 2000 Texas Air Quality Study, *J. Geophys. Res.*, *108*, doi:10.1029/2003JD003552.

Daum, P. H., et al. (2004), Origin and properties of plumes of high ozone observed during the Texas 2000 Air Quality Study (TexAQS 2000), *J. Geophys. Res.*, *109*, doi:10.1029/2003JD004311.

Gillani, N. V., et al. (1998), Relative production of ozone and nitrates in urban and power plant plumes 1. Composite results based on data from 10 field measurement days, *J. Geophys. Res.*, *103*, 22,593-522,615.

Kleinman, L. I., et al. (2002), Ozone production rate and hydrocarbon reactivity in 5 urban areas: a cause of high ozone concentration in Houston, *Geophysical Research Letters*, *29*, 10.1029/2001GL014569.

Kleinman, L. I., et al. (2003), Correction to "Ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston", *Geophysical Research Letters*, *30*, doi:10.1029/2003GL017485.

Luria, M., et al. (2000), Influence of natural hydrocarbons on ozone formation in an isolated power plant plume, *J. Geophys. Res.*, *105*, 9177-9188.

Neuman, J. A., et al. (2002), Fast-response airborne in situ measurements of HNO_3 during the Texas 2000 Air Quality Study, *J. Geophys. Res.*, *107*, doi:10.1029/2001JD001437.

Neuman, J. A., et al. (2004), Nitric acid loss rates measured in power plant plumes, *J. Geophys. Res.*, *109*, doi:10.1029/2004JD005092.

Nunnermacker, L. J., et al. (2000), NO_y lifetimes and O_3 production efficiencies in urban and

power plant plumes: analysis of field data, *J. Geophys. Res.*, *105*, 9165-9176.

Ryerson, T. B., et al. (1998), Emissions lifetimes and ozone formation in power plant plumes, *J. Geophys. Res.*, *103*, 22,569-522,583.

Ryerson, T. B., et al. (2001), Observations of ozone formation in power plant plumes and implications for ozone control strategies, *Science*, *292*, 719-723.

Ryerson, T. B., et al. (2003), Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation, *J. Geophys. Res.*, *108(D8)*, doi:10.1029/2002JD003070.

Ryerson, T.B., et al., "Chemical and meteorological influences on extreme (>150 ppbv) ozone exceedances in the Houston metropolitan area", TCEQ Contract No. 582-4-65613, Draft report, 2006.

Question B Approach

Question B: How do the structure and dynamics of the planetary boundary layer and the lower troposphere affect ozone and aerosol concentrations in the Houston, Dallas, and eastern Texas?

Question B Working Group:
Co-Leaders:
    Robert Banta
    John Nielsen-Gammon
Participants:
    Bryan Lambeth
    Bright Dornblaser
    Allen White
    Christoph Senff
    Lisa Darby
    Wayne Angevine
    Daewon Byun
Observer:
    Carl Berkowitz
    Noor Gillani

Background:
      Major concerns that can be addressed with rapid turnaround after the completion of the TexAQS II intensive field campaign in August-September 2006 (TexAQS 2006) include: 1) the depth of the daytime mixed layer, 2) the role of winds and other meteorological factors (including the sea-breeze) vs. emissions in determining ozone concentrations in the Houston-Galveston Bay (HGB) area, 3) the role of horizontal transport in forming background concentrations of ozone in eastern Texas, and 4) the role of transport of background ozone from eastern Texas vs. local emissions in determining ozone concentrations in the Dallas-Ft. Worth (DFW) area.
      An important aspect of all these processes is how well they are represented in numerical weather prediction (NWP) chemical transport models. These models will be an important component of the air pollution forecasting process, and they are the primary tool in quantitatively evaluating the effects of pollution mitigation strategies. It is therefore important to establish their credibility and limitations in representing these meteorological processes by comparing them with all available measured data.

Analysis Approach:
1. The Depth of the Mixed Layer in Houston and Dallas
      The depth of the daytime mixed layer is an important quantity, because it defines the vertical dimension over which pollutants are diluted, and thus is one of the controlling factors in determining pollutant concentrations. An important concern is whether NWP models accurately determine daytime mixing heights, and whether the morning growth in mixing height is captured faithfully by models. If elevated layers of pollution are mixed downward (fumigated) to ground level, delays in the morning growth of the mixed layer may lead to the highest daily pollutant concentrations at a location. The fumigated pollution achieves high concentrations when it is first entrained into the growing mixed layer, but then it is diluted as the mixed layer continues to grow.

The regional behavior of the mixed layer height over rural areas in eastern Texas during pollution episodes is especially of interest, because these values form background concentrations for pollution that are transported into the nonattainment areas during the episodes. For example, a correlation between DFW total ozone concentrations and incoming background concentrations has been noted. Any relationship between mixed-layer height and these incoming concentrations, and the ability of models to predict this, would be important information.

The suppression of mixed-layer heights over Galveston Bay can keep pollutant concentrations at high levels, but this effect does not seem to be well handled by models. Airborne and shipboard measurements will provide important simultaneous profiles of pollutant concentrations and the mixed-layer inversion height z_i. Estimates based on preliminary data can be provided for model evaluation (*Senff, Banta*).

Study Plan: Preliminary data will be available from the profiler network during the course of the project. These data will be used to form histograms or other distribution plots of mixed-layer heights for each profiler for the entire project, and for selected periods of interest, such as stagnation or other pollution episodes. Daily time series of z_i will be available on web sites at the completion of the project for comparison with model output (*White, Angevine, Nielsen-Gammon, Byun*). Individual study days will be reviewed for cases when the morning transition is a factor in pollution concentration, and preliminary model intercomparisons will be described (*Dornblaser, Zhong, Byun, Nielsen-Gammon*). This will include measurements made from the Williams Tower in downtown Houston, where measurements at the top of the building will be compared with measurements near the surface to look for evidence of fumigation over the city (*Berkowitz, Darby*). Instrumented aircraft flights will provide data over eastern Texas that will be summarized for useful mixed-layer height and pollution information (*Senff, Darby, Banta, Angevine [P-3 representative]*).

2. Role of the Sea Breeze in the Houston, Ship Channel, Galveston Bay area

The role of light synoptic flow conditions and diurnal sea-breeze wind reversals in producing high pollutant concentrations in the HGB area are well recognized. Major questions include what kind of variability is seen in magnitude, timing, and location of high-pollutant-concentration occurrences on such wind-reversal days; what is the influence of larger-scale conditions such as gradient wind direction and speed; and are models able to capture this variability? It recently has been pointed out that even when the boundary-layer gradient winds are stronger (7-9 m/s or so), and no reversals occur, 1-hr ozone concentrations exceeding 150 ppb have been seen in the measurement network (6 September 2000), when a measurement site is judiciously located. This brings up the question, is there an exceedance at ground level *somewhere*, even if not in the measurement network, every sunny day because of the heavy emissions in the HGB area?

Study Plan: These questions are likely to be the subject of important longer-term research, but preliminary data will provide guidance as to whether the new dataset further verifies the association between diurnal wind reversals and high ozone, or if some cases potentially contrary to this model become evident (*Lambeth, Banta, Darby*). Flight legs designed to find the highest daily ozone even on days with stronger winds will be inspected to determine whether high ozone concentrations can be confirmed each day (*Banta, Senff, Darby, Hardesty*). Data from the *R/V Ronald Brown* will be available in the HGB area and will be monitored and inspected for key data addressing these issues (*Angevine*). In particular, the only surface-based lidar systems – an ozone DIAL and a Doppler lidar – will be operated from the deck of the Brown, which will be in the ship channel for extended periods during the TexAQS 2006 intensive.

3. The Role of Transport in Eastern Texas

Eastern Texas has many NO_x point sources, and is the recipient of pollution exported from other areas within and outside of Texas. Some current thinking is that the pollution becomes mixed and relatively homogeneous in the horizontal on a time scale of 24 hr in more rural areas of eastern Texas (TERC report). During episodes, eastern Texas becomes a reservoir of pollution forming the ozone background. This background increases through the episode, thus contributing to the even-higher ozone levels in non-attainment areas.

Study Plan: Ozone concentrations and mixed-layer heights in this area will be measured by airborne research flights. Data from these flights will be inspected for

- Mixed-layer heights and variability
- Horizontal smoothness or 'lumpiness' of ozone and aerosol concentrations
- Ozone in the lower free troposphere that will be entrained during the day
- Effects of advection by the nighttime winds, including low-level jets

Airborne ozone lidar research flights also will be carried out along the Texas-Louisiana border under easterly component wind flow, to measure pollution entering Texas from out of state. Other planned flights will document transport into this region from major sources in the state, especially the HGB area. Profiler data will provide information on the diurnal behavior of the mixing height, and the speed and direction of the boundary-layer winds, including the vertical structure *and* horizontal extent of the nocturnal LLJ (*White, Angevine, Nielsen-Gammon*). Research flight data will be inspected for periods of interest and summarized as described below.

4. The Role of Transport and Local Contributions in the Dallas-Ft. Worth area

Current thinking is that background ozone levels advected into the DFW area are highly correlated with – and an important component of – the total high ozone measured in the urban area. Under light wind conditions, local emissions from inside the DFW area add to the background and may remain in the urban area to produce exceedances. Recent analyses of 2005 data suggest that even though local emissions in the DFW area are relatively stable, the background concentrations and local contribution vary together. This suggests that synoptic-scale meteorology (probably wind speed and mixing height) plays a role in both the rural background and the local contributions. Thus, the studies of the eastern Texas rural background pollution levels and boundary layer properties previously outlined are important to understanding the DFW ozone problem.

Study Plan: Analysis of trajectories, including cluster analysis, will be performed to investigate these concepts, as well as the relationship between DFW pollution and properties of the boundary layer in eastern Texas (*Darby, White, Angevine, Nielsen-Gammon*). If scheduling and prioritizations permit, airborne missions will be flown in the DFW area to determine if the afternoon ozone maxima at the surface match the concentrations measured aloft, or if there is a surface-based gradient in DFW ozone concentrations. Measurements downwind of the urban core will evaluate whether the urban maximum is within the surface monitoring network, or if additional monitors are needed.

The procedure for reporting cases as described in the preceding paragraphs will be to provide the following:

- A list of case study days and flights that illustrate the effects of interest.
- Brief descriptions of the cases/flights, including testable hypotheses for the more detailed analyses to follow. This would include an assessment of whether the findings are apt to support current thinking, or especially, if important new information may contradict current views.

- Selected preliminary field data; in some cases model output, to illustrate a finding may be included, if appropriate.

Key TexAQS II or Other Study Data Needed:

A network of 5 existing and up to 4 new wind profilers and up to 4 new or existing rawinsonde measurement sites will be maintained across eastern Texas from July 2005 through September 2006. Meteorological and ozone and/or aerosol measurements also will be made at the 100+ ground-based NAMS, PAMS, SLAMS, EPA Region 6, municipal, and other air monitoring stations in eastern Texas, 38 TexAQS II Ozone Transport Monitoring Stations, and 11 TexAQS II Ozone Chemistry Monitoring Sites. These ground-based stations and monitoring sites will be maintained during this same 18-month TexAQS II study period. These ground-based wind-profiler and rawinsonde meteorological measurements, along with the surface networks of other ground-based ozone and aerosol-concentration measurements, will be supplemented with 1) a comprehensive array of shipboard air chemistry measurements complemented by Doppler and ozone lidar measurements aboard the *R/V Ronald H. Brown*, and 2) airborne ozone/ aerosol-backscatter lidar and air chemistry measurements, during the six-week-long TexAQS 2006 Intensive Study in August and September 2006.

More specifically:

1) Data for daytime mixed-layer measurements will include radar wind profiler estimates of the mixed-layer inversion height z_i from backscatter profiles, balloon soundings of temperature, humidity, and winds, shipboard profiles from lidar and profiler, and aircraft profiles from the P-3 and airborne ozone differential absorption lidar (DIAL). From these measurements, mixed-layer heights will be calculated. The lidar aircraft will make flights over eastern Texas and Galveston Bay to address these issues, and an indication of the results will be available soon after the flights, and can be compiled at the end of the project.

2) Research flights with the airborne ozone lidar will be aimed at finding out what the highest concentrations of ozone are on any given day, even if the boundary layer winds are 5 m/s or more. The aircraft will be directed to the likely location of the peak daily ozone using predicted trajectories from forecast models, and using the real-time trajectory tool (see next paragraph) with the radar wind profiler array. These measurements will provide a first look at whether high concentrations exist somewhere each day.

3)-4) The profiler array in Eastern Texas will provide important data on boundary-layer heights and winds, including the LLJ, and the origin of polluted or clean air using the real-time trajectory tool developed by NOAA/ESRL. The trajectory tool uses hourly profiler wind data to construct trajectories of the air flow, and it will be available in real time for TexAQS 2006. NWP model output will provide a picture of how meteorological processes create the mix of pollution in the region. Airborne ozone lidar flights will provide an immediate picture of how well mixed the ozone and aerosols are in the vertical and horizontal, and the contribution of ozone entering the state or originating from sources within the state that contribute to pollution levels in eastern Texas.

Suggested Deliverable Products, Timelines and Lead Contacts:
1) Analysis of the depth of the mixed layer in Houston and Dallas;
   Preliminary Report –October 31, 2006; Final Report – August 31, 2007;
   Christoph Senff, Robert Banta, Lisa Darby, Wayne Angevine, John Nielsen-Gammon, Daewon Byun, Bright Dornblaser
2) Analysis of the role of the sea breeze in the Houston, Ship Channel, Galveston Bay area;
   Preliminary Report –October 31, 2006; Final Report – August 31, 2007;

Robert Banta, Christoph Senff, Lisa Darby, Wayne Angevine, Bryan Lambeth
3) Analysis of the role of transport in Eastern Texas;
     Preliminary Report –October 31, 2006; Final Report – August 31, 2007;
     Allen White, Wayne Angevine, John Nielsen-Gammon
4) Analysis of the role of transport and local contributions in the Dallas-Ft. Worth area;
     Preliminary Report –October 31, 2006; Final Report – August 31, 2007;
     Lisa Darby, Allen White, Wayne Angevine, John Nielsen-Gammon

Question C Approach

Question C (five parts)**:**
Are highly-reactive VOC and NO$_x$ emissions and resulting concentrations still at the same levels in Houston as they were in 2000?
How have they changed spatially and temporally?
Are there specific locations where particularly large quantities of HRVOCs are still being emitted?
Are those emissions continuous or episodic?
How well do the reported emissions inventories explain the observed concentrations of VOCs and NO$_x$?

Question C Working Group:
Leader:
    David Parrish
Participants:
    David Allen
    Joost deGouw
    Mark Estes
    John Jolly
    Tom Ryerson
    David Sullivan
    Eric Williams
    Barry Lefer
Observers:
    Carl Berkowitz
    Yulong Xie
    Noor Gillani

Analysis Approach:
    The TexAQS 2000 study showed that the highly reactive VOC and NO$_x$ emissions were predominately associated with the emissions from petrochemical industrial facilities in the Houston area. Particularly important source regions are the Ship Channel area in east Harris County, Texas City in Galveston County, and more distributed sources in Brazoria County. There are several factors that determine the magnitude of the emissions from these facilities, as well as their spatial and temporal variation. One general approach to be taken here is to recognize the relevant factors and to define a specific analysis to investigate the influence of changes in each factor utilizing data from the TexAQS 2000 and 2006 intensive studies. A second general approach is to use more routine, longer-term data sets to identify temporal trends over a decadal scale, and to place the 2000 and 2006 intensive studies into a longer-term context.

Economic Factors:
    Demand for petrochemical products is expected to determine the total production level in the Houston area, and the fraction of total capacity at which the plants operate. Emissions from the petrochemical facilities are expected to rise and fall with production level, and emissions may rise more than proportionally if production capacity is stretched to its maximum. Considering the national economic trends, the summer of 2000 may well have been a time of high demand, and the summer of 2006 may well be period of lower demand, with a consequent lower level of industrial activity.

Economic Factors Analysis Approach:

Production statistics for the petrochemical industry in Houston should indicate the production activity of the Houston petrochemical facilities. These statistics will be examined to determine the Houston production level as a whole, and if possible for specific petrochemical facilities.

Comparison of the flux of CO_2 from specific petrochemical facilities during the two summers will provide a complementary approach, Since this flux is proportional to the fuel burned in the facility during the production process, the comparison will give an indication of any differences in production level. Such changes in production level could reflect plant capacity (new production units added, or older units closed down) changes as well as changing fraction of capacity actually in operation.

Emission Controls:

Since 2000, it is expected that significant emission control improvements have been implemented.

Emission Controls Analysis Approach:

Measurements in emission plumes from specific petrochemical facilities or from larger agglomerations of facilities will provide quantitative characterization of emission fluxes. In favorable situations absolute emission fluxes can be determined from plume transects combined with wind and boundary layer height data. In less favorable situations the relative fluxes of two emitted species (e.g. NO_x/CO_2, VOC/CO_2, VOC/NO_x, etc.) can still be determined from measurements made in plumes.

During TexAQS 2000 the NOAA-operated Electra aircraft characterized the species emitted in a wide variety of industrial plumes. The aircraft continuously measured with 1 second or 100 m resolution the absolute concentrations of NO_x, SO_2, CO and CO_2. These measurements were supplemented by similar measurements of NO_y (a more nearly conserved tracer of NO_x emissions) and canister measurements of VOC. During TexAQS 2006 the NOAA WP-3D aircraft will make the same measurements, and in addition will make continuous measurements of ethylene. The measured ethylene will be combined with much less frequent canister-based VOC measurements to evaluate the species that make up the total HRVOC emissions. The comparison between the 2000 and 2006 data sets will determine how the highly reactive VOC and NO_x emissions have changed spatially and temporally over the intervening 6 years. Aircraft transects across the entire Houston industrial regions will determine if there are specific locations where particularly large quantities of HRVOCs are still being emitted.

A wider spatial coverage of industrial emissions will be a goal of the TexAQS 2006 study. Emissions from industrial facilities in the Beaumont/ Port Arthur and Corpus Christi areas will be examined to see if there are underestimates in the emission inventory similar to those found in TexAQS 2000 for the facilities in Houston.

Surface-based measurements giving longer-term views of industrial plumes will provide critical complements to the snapshots given by the aircraft observations. In this regard, the measurements on the NOAA Research Vessel Ronald H. Brown will provide much longer-term plume measurements in the vicinity of the Houston Ship Channel and other coastal facilities and the Solar Occulation Flux (SOF) measurements will provide a comprehensive picture of the temporal pattern of the total ethylene flux from one or more specific industrial complexes. These measurements, as well as repeated aircraft transects of plumes, will be ideal to determine if those emissions are continuous or episodic.

Emissions data and meteorological measurements, coupled with dispersion models, will be used to predict pollutant concentrations on days when the aircraft, ship or SOF measures the plumes. These predictions will be compared to both absolute concentrations and the observed

concentration ratios. As a result it will be determined how well the reported emissions inventories explain the observed concentrations of VOC and NO_x.

Long-term Data Sets:

In the Houston area there have been extensive VOC measurements made by as many as eight auto-GC systems and by canister-based methods. Measurements were begun at some sites as early as 1997, giving temporal coverage over one decade by the end of 2006. Figure 1 presents results from two sites near the Ship Channel: 9 years of data from Clinton (on the western end) and 8 years of data from Deer Park (on the eastern end.). The medians at both sites indicate decreasing trends ambient HRVOC levels (PRELIMINARY ANALYSIS – DO NOT CITE OR DISTRIBUTE BEYOND THE RAPID SYNTHESIS TEAM).
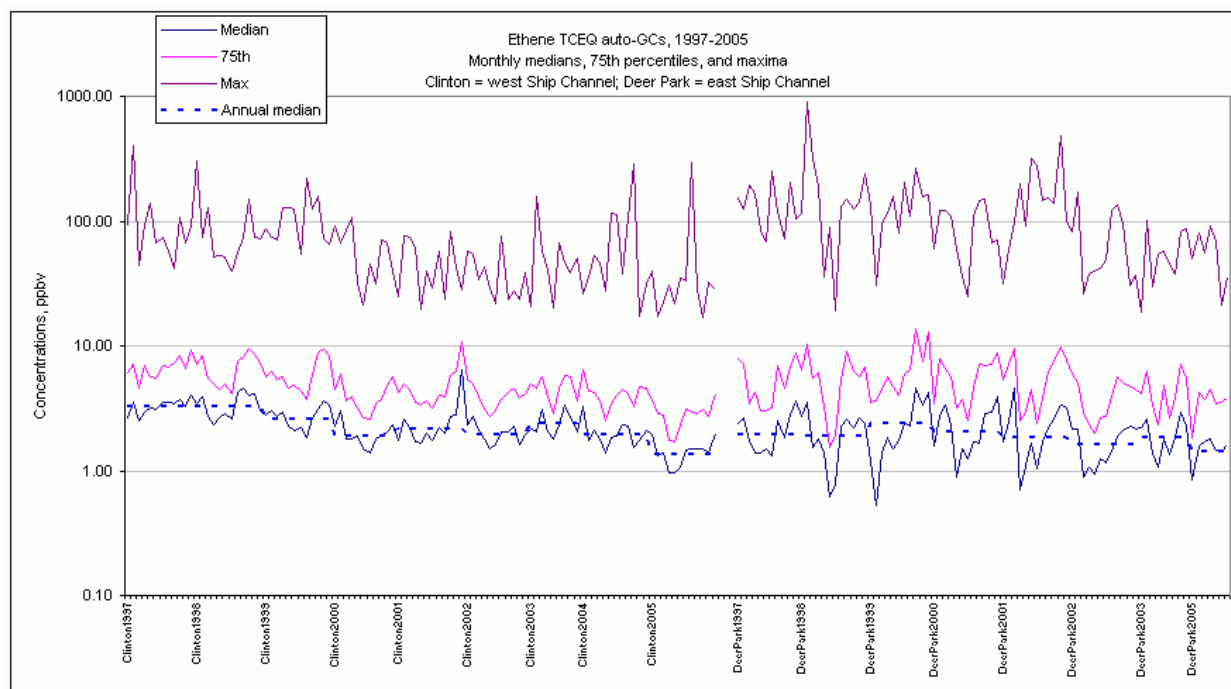
Further analysis of these results will include the addition of the 2006 data, control for meteorological variability and possible instrumental changes during the measurement period, and the comparison of the trend determined from ambient measurements with the temporal trend expected from emission inventories for the corresponding years. This analysis should help to determine how these emissions have changed temporally over the past decade.

Key TexAQS II or Other Study Data Needed:
1) Production statistics for the petrochemical industry in Houston; disaggregated to specific petrochemical facilities if possible.
2) Emissions inventories for highly-reactive VOC and NO_x for 2000, 2006 and all years from 1997 to present.
3) Continuous emission monitoring system (CEMS) data for petrochemical facilities for the period of the 2006 field intensive.
4) Aircraft measurements of NO_x, NO_y, SO_2, CO, CO_2, VOC, and ethylene in plumes from petrochemical facilities.
5) Shipboard measurements of NO_x, NO_y, SO_2, CO, CO_2, and VOC in plumes from petrochemical facilities.

6)   Solar Occultation Flux measurements of ethylene from specific petrochemical industrial complexes.
7)   Meteorological data sets for the Houston area from radar wind profilers, aircraft, sondes, surface sites, etc.
8)   Dispersion modeling of petrochemical plumes.
9)   Long-term HRVOC measurements and corresponding meteorological data sets for 1997-2006.

Suggested Deliverable Products, Timelines and Lead Contacts:
1)   Analysis of temporal trends in petrochemical production statistics in the Houston region;
      Preliminary Report - July 15, 2006; Final Report – August 31, 2007
      David Parrish
2)   Analysis of temporal trends in CO_2 emission fluxes from petrochemical facilities as an indicator of trends in petrochemical production activity;
      Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
      Tom Ryerson, David Parrish
3)   Analysis of temporal trends in NO_x and NO_y emission fluxes and NO_x/CO_2 and NO_y/CO_2 emission ratios from petrochemical facilities as an indicator of changes in NO_x emissions from these facilities, and comparison with CEMS data and emission inventories.
      Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
      Tom Ryerson, David Parrish
4)   Analysis of temporal trends in VOC emission fluxes and VOC/CO_2 and VOC/NO_y emission ratios from petrochemical facilities as an indicator of changes in VOC emissions from these facilities
      Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
      Joost deGouw, David Parrish
5)   Analysis of temporal trends of ambient HRVOC levels in the Ship Channel region as an indicator of changes in HRVOC emissions, and comparison with emission inventories.
      Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
      John Jolly**,** David Sullivan, Mark Estes
6)   Analysis of 2006 spatial variability of HRVOC emissions, comparison to 2000, and identification of specific locations where particularly large quantities of HRVOCs are still being emitted. Comparison with emission inventories.
      Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
      Joost deGouw, Eric Williams, David Parrish
7)   Analysis of temporal variability of HRVOC emissions: Are they continuous or episodic?
      Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
      Joost deGouw, Eric Williams, David Parrish

Question D Approach

Question D:
What distribution of anthropogenic and biogenic emissions of ozone and aerosol precursors can be inferred from observations?
(**Notes**: Question C specifically addresses highly-reactive VOC and NO_x emissions in the Houston area, so these will not be considered here. Question D will address all other ozone and aerosol precursor emissions, biogenic as well as anthropogenic, that are included in emission inventories. Question E will address evidence for additional, unrecognized sources of precursor emissions.)

Question D Working Group:
Co-Leaders:
      David Allen
      David Parrish
Participants:
      Chuck Brock
      Joost deGouw
      Mark Estes
      John Jolly
      Tom Ryerson
      David Sullivan
      Eric Williams
      Barry Lefer
Observers:
      Carl Berkowitz
      Yulong Xie
      Noor Gillani
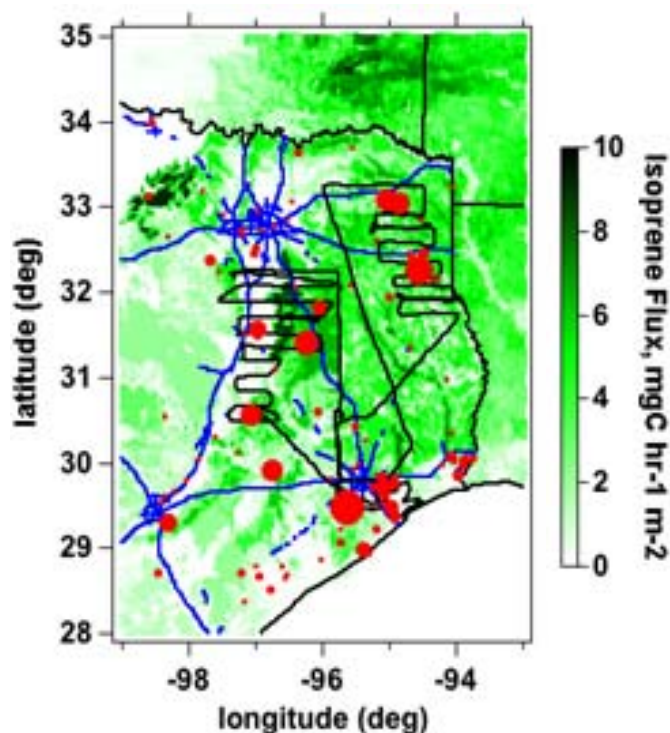
Figure 1. Location of major point sources of NO_x(red) and the distribution of biogenic emissions from forested regions of East Texas color coded in shades of green according to the emission intensity. Superimposed are two tracks flown by the Electra aircraft during TexAQS 2000.

Analysis Approach:
      The highly-reactive VOC and NO_x emissions, which are particularly important in the Houston area, have received special attention over the years. However, other classes of emissions also contribute importantly to air quality degradation in the East Texas region, and their importance may be greater when 8-hour average ozone is considered rather than 1-hour exceedances. Here we address sources that are believed to be particularly important contributors to ozone and aerosol formation, including urban and rural point sources, on-road and off-road vehicles, and biogenic emissions. It should be noted that the distribution of emissions implies definition of both the spatial and temporal variation of the emissions. The temporal variation will include diurnal, weekly and long-term (e.g. 2006 compared to 2000) scales.

Urban and Rural Point sources:
      TexAQS 2006 will include powerful tools for quantifying the emissions from point sources through ambient measurements. In principle, and in practice under favorable conditions, the absolute flux of a species emitted from a point source can be directly determined from measurements of its concentration in the downwind plume. The flux is equal to the wind speed

at the time of emission multiplied by the integral of the species concentration over the cross section of the plume perpendicular to that wind direction. The NOAA WP-3D aircraft, the NOAA RHB Research Vessel and the Solar Occulation Flux (SOF) instrument can collect these concentration data during transects of the plume. However, failure to collect data of adequate spatial resolution, variable winds and other confounding factors can prevent the determination of the absolute emissions. However, it is generally still possible to determine at least the ratio of the fluxes of two emitted species, even from only a partial transect of the emission plume. The slope of the correlation between the concentrations of two species is equal to the ratio of their fluxes. The measured emission fluxes or ratios can be directly compared with the continuous emission monitoring systems (CEMS) data collected by the plant at the time of emission of the sampled plume.

The two aircraft flight tracks shown in Figure 1 exemplify the emission flux determination. During each flight, the aircraft flew from Ellington Field in Houston to northeast Texas and conducted transects upwind of major industrial and electrical generation point sources. The aircraft then proceeded to cross the plumes from the sources as they were carried downwind (to the south on the eastern track, and to the north on the western track). Similar flights will be conducted in 2006.

Figure 2 shows the results of nearly 50 aircraft plume studies on over 30 CEMS-equipped power plants during field studies in 1995, 1997, 1999, 2000, and 2002 (Ryerson et al., 1998; Neuman et al., 2004; Fortin et al., 2005 and references therein.) Figure 2(a) compares the flux ratios of NO_x to CO_2 and SO_2 to CO_2 derived from CEMS to those derived from aircraft transects. On average these flux ratios agree within the estimated uncertainty of the ambient determination (plus or minus 20 percent), although there are occasional significant discrepancies. Figure 2(b) compares the absolute fluxes measured for NO_x, SO_2 and CO_2, with those derived from the CEMS data. Agreement on average is again within plus or minus 20 percent, again with occasional significant discrepancies. These comparisons indicate that emission fluxes of NO_x, SO_2 and CO_2 from point sources derived from CEMS measurements are highly accurate.

During TexAQS 2006 measurements will be made of the emitted NO_x, SO_2, CO_2, CO and primary aerosols (as well as the secondary chemical products and intermediates) in the plumes by the NOAA WP-3D aircraft the RHB Research Vessel. The SOF instrument will
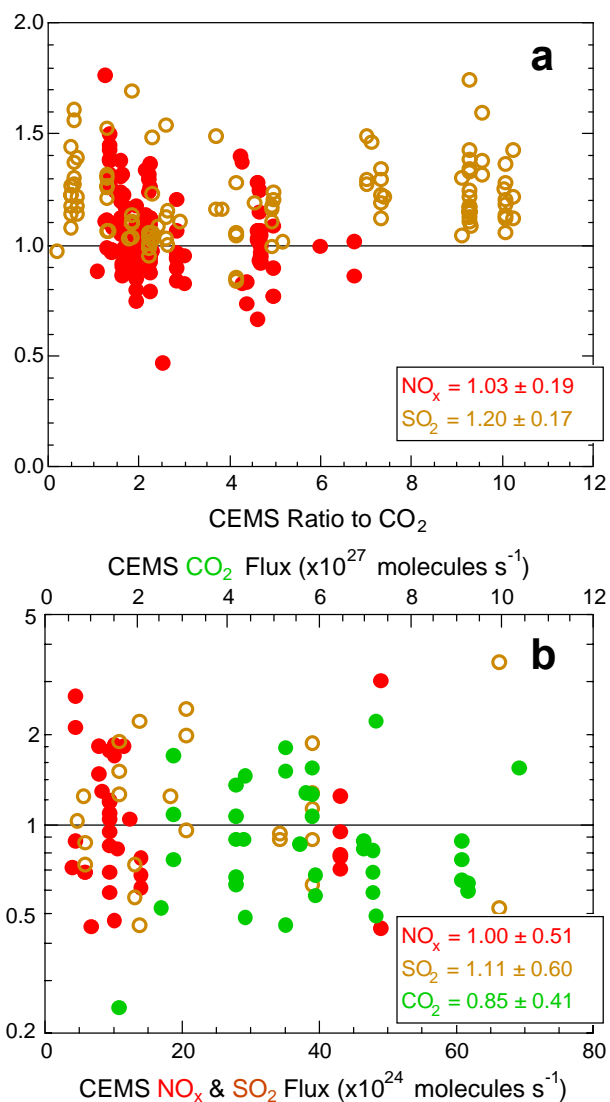
Figure 2. Power-plant emission fluxes from CEMS data compared to those determined from aircraft plume transect measurements. (a) Emissions of NO_x and SO_2 ratioed to those of CO_2. (b) Absolute fluxes of all three species. The annotations give the geometric average and standard deviations for the color-coded ratios.

potentially provide measurements of SO_2 and NO_2 in plumes, in addition to its primary goal of HRVOC flux determinations. The results will be compared with three other sets of emissions estimates. First, ambient determinations will be compared with the simultaneous CEMS data, much as was done in Figure 2. Second, the ambient measurements and the CEMS data will both be compared to emissions inventories. Third, the 2006 ambient determinations, CEMS data and emissions inventories will be compared to those for 2000. These comparisons will give a comprehensive picture of point source emission fluxes and their temporal variations.

We further intend to utilize the Research Vessel RHB to evaluate the emissions of NO_x SO_2, VOCs and CO_2 from off-shore oil platforms. These sources may contribute significantly to background levels in air over the Gulf of Mexico, which is a potential emissions source region for the HGB area.

On-road Vehicle Emissions:

Highway vehicles provide important, often dominant, contributions to the ambient concentrations of ozone precursors within all regions of Texas; thus, the accuracy of the estimated emissions is a major concern for SIP modeling. The recent NARSTO Emission Inventory Assessment (NARSTO, 2005) found significant concerns regarding the MOBILE6 model estimates of highway vehicle emissions:

> *"There are significant uncertainties in mobile source inventories particularly regarding the speciation of volatile organic compounds, the magnitude of carbon monoxide emissions, and the temporal trend of nitrogen oxide emissions."*

Therefore, a major goal of TexAQS 2006 is to provide an accurate picture of the volatile organic compound (VOC) speciation and an accurate estimate of the carbon monoxide (CO), and nitrogen oxide (NO_x) emissions from on-road vehicles. Measurement data collected at various times of day from a variety of surface sites, including the Moody tower TRAMP site, the NOAA RHB research Vessel and the NOAA WP-3D aircraft will provide spatial and temporal details of the on-road vehicle emissions sources to help define this picture.
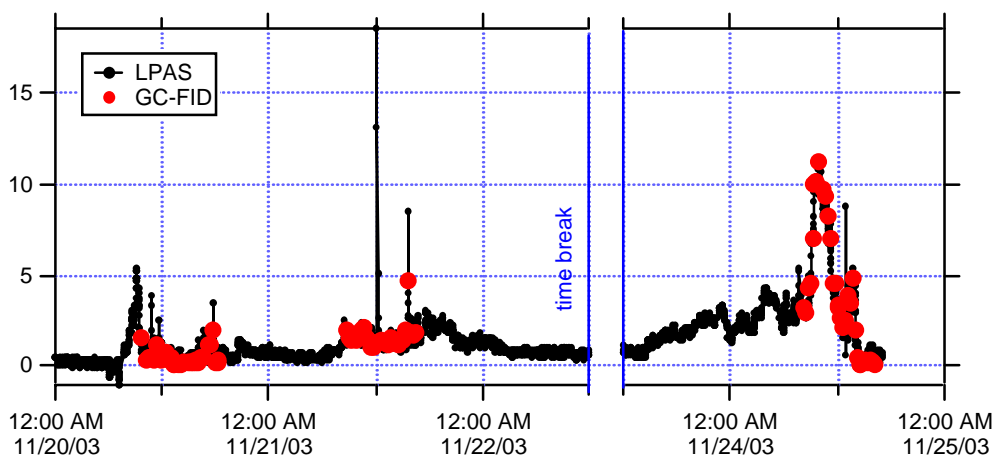
Figure 3. Time series of ambient air measurements of ethylene by laser photo-acoustic spectroscopy and gas chromatography techniques

An exciting new capability of the NOAA WP-3D is the continuous, selective and sensitive measurement of ethylene (ethene) with 0.1 ppbv precision for a 5 to 10 second averaging time. This measurement is based upon laser photoacoustic spectroscopy [*Kuster et al.*, 2005]. Figure 3 shows example data from a ground deployment of that instrument compared to a traditional gas chromatography measurement. The continuous ethylene and NO_x measurements will be combined with the traditional canister VOC measurements to provide stringent tests of VOC and NO_x emissions inventories. Ethylene and NO_x have very similar lifetimes during the photochemically active period of the day; thus, the measured ethylene to NO_x ratio provides a good direct measure of the ratio of ethylene to NO_x emitted into the sampled air parcel, even if
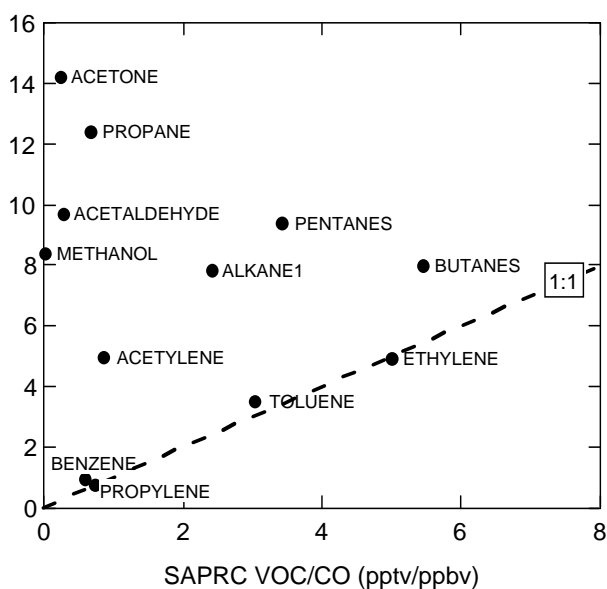
Figure 4. Emission ratios of various VOCs to CO measured in the Los Angeles Basin by the NOAA WP-3D aircraft in May, 2002 compared to the ratios calculated from SAPRC (C. Warneke, manuscript in

significant photochemical processing of those emissions has occurred before sampling. The measured ethylene to NO_x ratio can be combined with much less frequent canister-based VOC measurements to evaluate the species that make up the total VOC emissions, and to provide a direct experimental measure of the various VOC species to NO_x ratio emitted by mobile sources. Figure 4 provides an example of the type of results we expect to develop during TexAQS 2006. These data were collected by the WP-3D over Los Angeles in 2002. In accord with the conclusion of the NARSTO Emission Inventory Assessment cited in above we find some very large errors in the VOC speciation in the emission inventory. For example, the pentanes were under-estimated by a factor of nearly 3. Such errors in VOC composition certainly compromise the accuracy of air quality modeling. These results will provide a basis for testing current models and improving future calculations.

Aircraft measurements of CO and NO_y can provide a direct measure of the total CO and NO_x emitted from a given urban area. CO is an approximately conserved species emitted by mobile sources. A good estimate of the total CO emissions is given by the total CO flux from the urban area, which can be
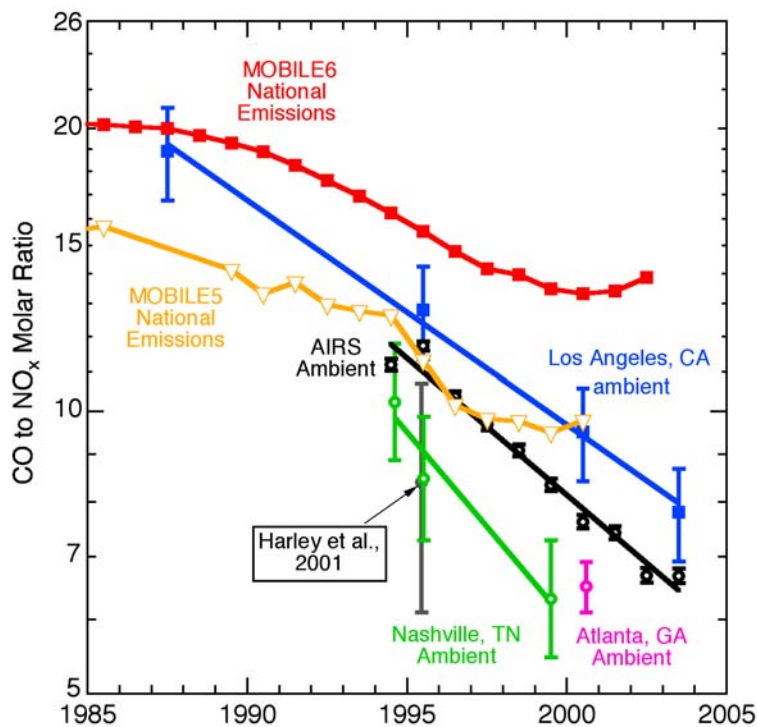
Figure 5. Semi-log plot of temporal trends of observed urban ambient CO to NO_x ratios compared to ratios from on-road vehicle emission estimates.

estimated by combining the aircraft in situ measurements across a downwind transect of the urban plume with meteorological fields available in the TexAQS 2006 Study (see e.g. [*Trainer, et al.*, 1995]). Cross-city transects will quantify the CO to NO_y ratio in the urban core before a significant fraction of NO_y is lost, which will then allow the total NO_x emissions to be estimated from the total CO flux. Both the Dallas-Fort Worth (DFW) and the Houston areas will be investigated in this manner.

Surface sites and the NOAA Research Vessel RHB also will have the capability to characterize on-road vehicle emissions during the morning rush hour when the boundary layer is shallow. The ship can evaluate these emissions from
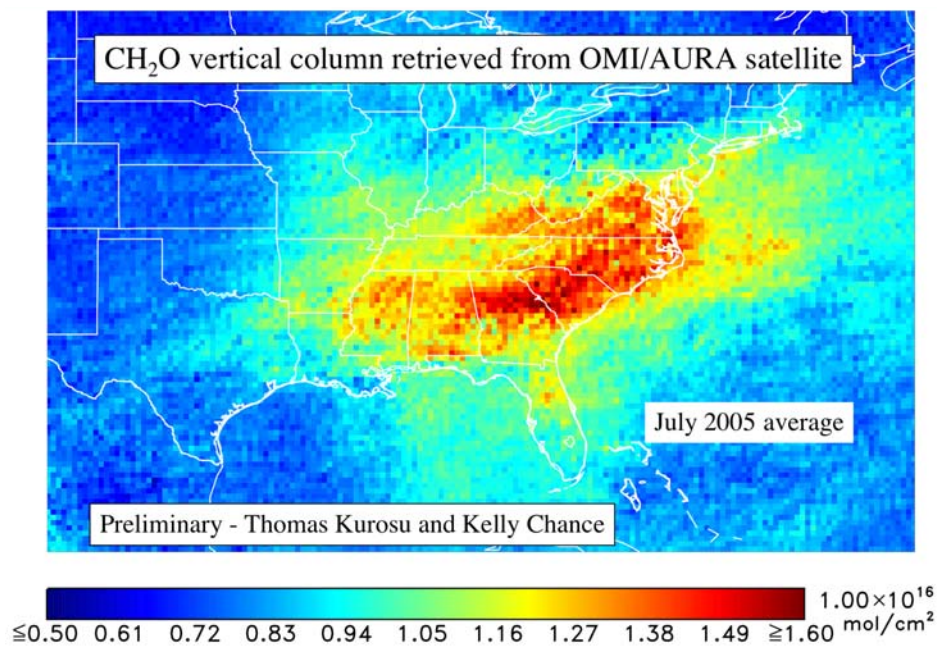
31 July 2006

the western end of the Houston Ship Channel when the surface wind is predominantly westerly. Measurements of CO and NO_y during this time can ascertain the CO/NO_x emission ratio and by comparison with data from TexAQS 2000 and other earlier studies, determine whether this emission ratio exhibits the same downward trend in the CO/NOx ratio that has been observed in other cities (Figure 5). It will be particularly useful to compare the measured emission ratios with those predicted by the MOBILE6 model, as Figure 5 indicates an overestimate by MOBILE6 of about a factor of two. Similar analyses can be performed for the emission ratios of specific VOC species to NO_x. CO, VOC, and NO_y data collected by the aircraft, ship and surface sites also can be parsed temporally to illuminate diurnal cycles and weekday/weekend contrasts.

Off-road Vehicle Emissions:

There is a special interest in characterizing emissions from commercial marine shipping because this is an important source of NO_x, SO_2, and particles in many ports and waterways. The Research Vessel RHB positioned in proximity to sea lanes near Galveston in the Gulf of Mexico can determine the composition of marine vessel exhaust plumes against the relatively clean Gulf of Mexico background air as these vessels transit in and out of the entrance to Galveston Bay. Under the appropriate meteorological conditions in the Houston Ship Channel, such studies also can be conducted to evaluate vessel emissions under idle conditions, which can vary significantly from underway emissions.

Biogenic VOC Emissions:

Figure 1 shows that several of the large power plants in east Texas are located in the forested, rural areas of northeastern Texas. Regional ozone formation in plumes from these plants depends upon the biogenic VOC emissions, which dominate the emission inventory for reactive hydrocarbons. These reactive biogenic VOCs coupled with the embedded anthropogenic sources of NO_x and SO_2 are expected to play an important role in the formation of ozone and aerosols over East Texas. However, these emissions depend strongly on meteorological conditions and land use, and thus can vary greatly from year to year. Figure 1 shows two example flights flown in 2000 that can be used to investigate the biogenic VOC emissions. Similar flights are planned for 2006. During these flights the measurement of isoprene and its principal reaction products - methacrolein, methylvinylketone, formaldehyde, and MPAN (a PAN-type compound that is formed in the oxidation of methacrolein) - will reflect the biogenic emission pattern along the flight tracks as well as the chemical processing that occurs over eastern

Figure 6. Satellite measurements of tropospheric column of formaldehyde. Satellite passes over at about 13:00 local time

Texas. The observed spatial and temporal patterns of these species will be compared with

emissions inventories. Particular attention will be paid to indication of emission dependence upon drought stress of the forest (2000 was a particularly intense drought) and changing land-use patterns.

The observed spatial and temporal patterns of the species emitted by biogenic sources and produced from those emissions will be compared with mesoscale model predictions. Sensitivity analyses will be performed utilizing current land use/land cover data as input to the most recently updated biogenic emissions model (MEGAN). Updated land use/land cover data from several sources will be incorporated into a revised LU/LC database for eastern Texas. The improved database will be used as input into the updated biogenic emissions model. Photochemical model results will be compared with aircraft measurements of biogenic VOC and their secondary oxidation products.

Satellite column measurements of formaldehyde will provide comparisons for the spatial distribution of isoprene emissions included in inventories. On regional scales it has been shown that spatial variability in ambient formaldehyde concentrations is determined by the distribution in isoprene emissions. For example, Figure 6 shows a monthly average of satellite retrievals of formaldehyde concentrations. Such retrievals are available daily.

Biogenic NO_x and NH_3 Emissions:

Biogenic emissions of NO_x from soils and NH_3 from agricultural and livestock operations may also make significant contributions to the mix of ozone and aerosol precursors in the eastern Texas region. Aircraft measurements in Texas rural areas of ambient NO_x and NH_3 concentrations will be made on the NOAA WP-3D during flights such as those in Figure 1. The patterns of measured concentrations will be compared with the available emission inventories.

Key TexAQS II or Other Study Data Needed:

1) Observational data from NOAA WP-3D and RHB Research Vessel transects of point source plumes.
2) SOF NO_2 and SO_2 data from transects of point source plumes if available.
3) Continuous emission monitoring system (CEMS) data for sources of sampled plumes.
4) Emissions inventories for point sources of sampled plumes for 2000 and 2006.
5) Laser photoacoustic spectroscopy measurements of ethylene and canister measurements of VOC from NOAA WP-3D
6) CO, NO_x, NO_y, and VOC measurements of on-road vehicle emissions from NOAA WP-3D, RHB Research Vessel and surface sites.
7) MOBILE6 emissions estimates for DFW and HGB areas as function of time of day and day of week.
8) Measurements of ship and off-shore oil platform emissions from NOAA RHB Research Vessel.
9) Aircraft measurements of biogenic VOC and their secondary oxidation products, NO_x, NH_3, CO, and CO_2 for comparison with biogenic emission inventoried.
10) Biogenic VOC, NO_x, NO_y, CO, and CO_2 emission inventories; improved database of updated land use/land cover data.
11) Photochemical model results of VOC and their secondary oxidation products.
12) Observations of formaldehyde columns from OMI instrument on AURA satellite.

Suggested Deliverable Products, Timelines and Lead Contacts:

1) Summary comparison of fluxes from ambient determinations, CEMS data, and emissions inventories for urban and rural point sources.
    Preliminary Report - October 31, 2006; Final Report – August 31, 2007;

Tom Ryerson, David Parrish

2) Observation-based analysis of the emissions of NO_x, SO_2, VOC, and CO_2 from off-shore oil platforms.
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>Eric Williams, David Parrish

3) Observation-based analysis of VOC speciation in on-road vehicle emissions, and comparison to MOBILE6 emissions estimates.
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>Joost deGouw, David Parrish

4) Observation-based analysis of CO/NO_x emission ratio in on-road vehicle emissions, emphasizing long-term, day of week and diurnal temporal trends, with comparison to MOBILE6 emissions estimates.
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>David Parrish

5) Observation-based estimates of total CO and NO_x emissions from mobile sources in the DFW and Houston urban areas and comparison to emission inventories.
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>David Parrish

6) Observation-based analysis of the emissions of NO_x, SO_2, and CO_2 from ships
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>Eric Williams, David Parrish

7) Updated land use/land cover data for eastern Texas incorporated into an improved database for development of next-generation biogenics inventory.
>February 2006
>David Allen

8) Updated biogenic emissions model for VOC, NO_x, NH_3, and CO emission inventories.
>July 31, 2006
>David Allen

9) Aircraft observation-based comparison of biogenic VOC and their secondary reaction products - methacrolein, methylvinylketone, formaldehyde and MPAN – with emission inventories.
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>Joost deGouw, David Parrish

10) Satellite observation-based comparison of formaldehyde with biogenic VOC emission inventories.
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>Joost deGouw, David Parrish

11) Model-based comparison of VOC and their secondary reaction products - methacrolein, methylvinylketone, formaldehyde and MPAN – with aircraft measurements
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>Joost deGouw, David Parrish

12) Observation-based comparison of NO_x and NH_3 measured by aircraft in rural areas with emission inventories.
>Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
>Chuck Brock, Tom Ryerson, David Parrish

Question E Approach

Question E:
Are there sources of ozone and aerosol precursors that are not represented in the reported
emissions inventories?
(**Note**: Questions C and D address all emissions that are known and therefore included in
reported emission inventories. Here Question E will focus on any ambient measurements
that indicate additional, unrecognized sources of precursor emissions. **To address this
question, TCEQ must define the inventory to which the observational analysis is to be
compared.**)

Question E Working Group:
Leader:
     David Parrish
Participants:
     David Allen
     Chuck Brock
     Joost deGouw
     John Jolly
     Tom Ryerson
     David Sullivan
     Eric Williams
     Barry Lefer

Analysis Approach:
It is difficult to define an analysis
approach for determining this unknown.
However, it is useful to note that the
NOAA WP-3D and Research Vessel
RHB are highly instrumented mobile
platforms that will sample over extensive
regions of Texas and along the adjacent
coastal areas. Figure 1 shows some
example WP-3D flight tracks and Figure
2 shows RHB operation area.
Measurements of primary emission
species will be made throughout the

**Figure 1. Location of major point sources of NO$_x$(red)
and the distribution of biogenic emissions from
forested regions of East Texas color coded in shades
of green according to the emission intensity.
Superimposed are two tracks flown by the Electra
aircraft during TexAQS 2000.**

aircraft flights and ship transects. The spatial and temporal patterns of these measurements will
be compared to emission inventories.
One obvious but critical need for this study is the identification of a complete emission
inventory as a comparison reference. Appendix E1 discusses this requirement in more detail.
Particular species and possible sources deserving examination in this study include:
- Alkane emissions from oil fields in northeast Texas and Oklahoma.
- VOC and NO$_x$ emissions from natural gas fields in northeast Texas and Oklahoma.
- VOC and NO$_x$ emissions from recreational marine vehicles.
- VOC, NO$_x$ and SO$_2$ emissions from facilities in port areas visited by the RHB (Figure 2).

Ambient concentrations measured by the aircraft and ship will be compared with those predicted
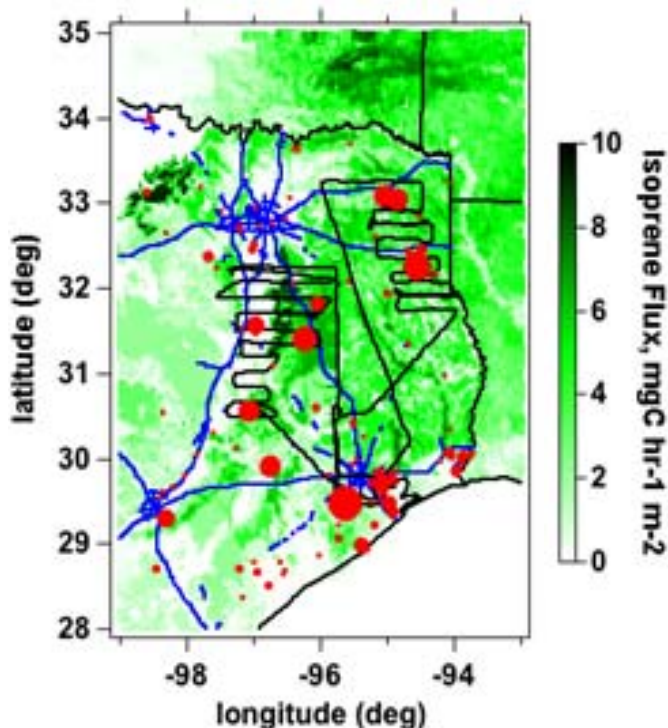by photochemical models. Much higher concentrations indicated by the observational data will

constitute evidence of sources that are uninventoried or under-inventoried. The locations of these high concentrations will indicate the approximate location of such sources.

Key TexAQS II or Other Study Data Needed:

1) Aircraft and ship measurements of VOC, NO_x, NO_y, SO_2, CO, NH_3 and CO_2 concentrations.
2) Daily/hourly emission inventories for all source types.
3) Meteorological data for photochemical models.
4) Photochemical model output.
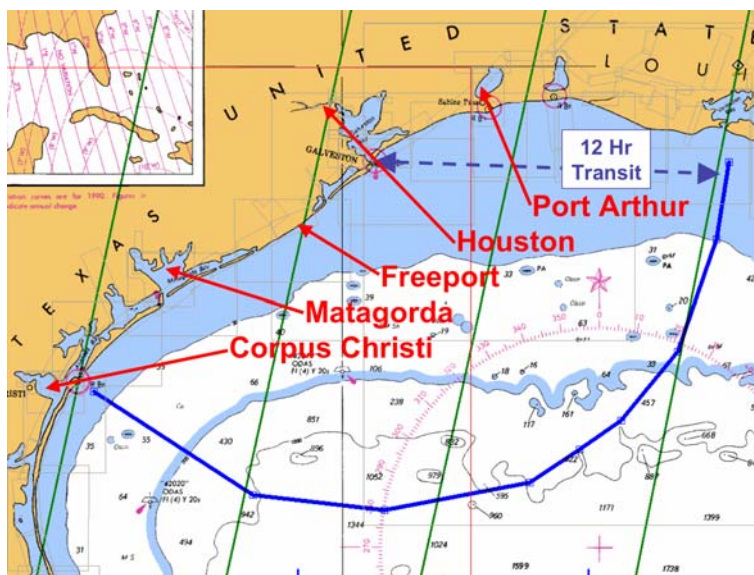
Figure 2. Approximate operations area of NOAA Research Vessel RHB with ports that are planned sampling objectives

Suggested Deliverable Products, Timelines and Lead Contacts:

1) In-field, qualitative comparison of observed concentrations with inventories.
   Preliminary Report - October 31, 2006;
   David Parrish and all interested group members
2) Quantitative comparison of observed concentrations with modeled concentrations.
   Final Report – August 31, 2007;
   David Parrish and all interested group members

Appendix E1: Need for Pre-Deployment Emissions Inventory Information:

Some data are critical to have available before the intensive study begins, as is the case with anthropogenic emission inventories. The State Implementation Plans rely heavily on regional Eulerian model results of specific O_3 episodes, so it is important that the modeling group at TCEQ incorporate the best, up-to-date information within the model runs. The measurements collected by the airborne and ship-based platforms during TexAQS II potentially could play a critical role as a point of validation for SIP model design. Because of the breadth, resolution, and quality of the measurements from these mobile platforms, they are particularly well suited for determining and verifying emission ratios from the various sources affecting O_3 and $PM_{2.5}$ in the Houston region. Information from these platforms also are essential for validating other important components of the SIP model, including: the determination of upwind or background conditions necessary for delta-O_3 calculations, the various transport processes and PBL dynamics, and the photochemical processing associated with O_3 and $PM_{2.5}$ formation. But given their fundamental importance to the SIP process, and the short turn-around time required for useful assimilation, the first-order priority should be in quantifying or verifying the emission estimates on which the SIP models rely.

Planning and preparation of the TexAQS II field study will rely on the knowledge gained from airborne observations collected during the TexAQS 2000 field experiment. In that study high O_3 levels and production efficiencies were found to correlate with highly reactive VOC such as ethylene and propylene originating from petrochemical facilities throughout the

Houston/Galveston region. Moreover, the emission estimates of propylene and ethylene relative to NO_x for most large petrochemical facilities were found to be higher by factors of 10 to 100 than emission inventory estimates available at that time, underscoring the need for accurate emissions estimates from these sources in O_3 assessment calculations for Eastern Texas. Since 2000, emission changes such as NO_x reductions at several power generation facilities due to Clean Air Act enforcement, changes in vehicle fleet emissions from improvements in catalytic converter technology, and changes in the apportionment of diesel versus gasoline fuel use are all expected to impact emissions in 2005/2006 compared to 2000. Additionally, more emissions data are available from continuous emissions monitors (CEMS) placed in service at many facilities since 2000. Proper planning for emission verification activities obviously requires the emissions expected for 2006 that are contained within the most recent emissions inventories be available for the Houston/Galveston region. As an integral part of its operations and expertise, TCEQ possesses the most recent and reliable emissions estimates available to TexAQS II planners and managers. It should be emphasized that many of the science questions put forth by TCEQ relate directly to how emissions have changed spatially and temporally since 2000. Without an updated emissions inventory, planning or preparation to address these questions is seriously compromised. Having emissions estimates in hand well before the summer of 2006 activities also enables the Rapid Synthesis Team to have necessary information readily available to make emissions inventory assessments.

Additional Benefits of Updated TCEQ Emissions Inventories to TexAQS II

As part of the TexAQS II field study, at least seven air quality forecast models will be predicting O_3 in real-time over East Texas, and have agreed to participate in a model evaluation project. Important details related to the individual models, the justification, and the integration of the model evaluation component within the TexAQS II study can be found in the ESRL/CSD TexAQS II planning document at http://www.esrl.noaa.gov/csd/2006/. The two main science questions the evaluation component addresses are: *How well can air quality models forecast air quality in Texas?* and *How accurately do the forecast models represent the individual processes controlling air pollution formation and transport?* These two questions are also part of TCEQ's SIP-Relevant Science Questions. The model evaluation project provides highly relevant information that can be leveraged by TCEQ within their SIP model development. Having verification statistics available for air quality and meteorological variables from several models as well as their own would make it possible for TCEQ to gauge the veracity of their simulations relative to other research-grade and operational forecast models.

The air quality forecast model evaluation component of TexAQS II builds upon the success of a similar project undertaken during the ICARTT/NEAQS-2004 study. In that project, eight models with significant differences in terms of basic structure, physical parameterizations, photochemical mechanisms, and emissions processing were evaluated. The model forecasts were collected at a central facility, and compared in near real-time with O_3 measurements at several AIRNow sites, with O_3 and its precursors taken at several ground sites and aboard *Ronald H. Brown* research vessel, and with upper-air measurements from wind profilers and RASS temperature sounders at several locations. These real-time comparisons were accessible to the planners, participants, and forecasters involved with the field program, allowing a qualitative glimpse of forecast reliability relative to observations. One of the lessons from the ICARTT/NEAQS-2004 study is that a large uncertainty in explaining model differences would be eliminated if the emissions inventories were consistent between the models involved in the evaluation. It was highly recommended that future evaluations use a common emissions inventory for seven ozone and particulate precursors (NO_x, CO, VOC, SO_2, PM_{10}, $PM_{2.5}$, and NH_3), and that the inventory be made available to those forecast and modeling groups well ahead of the study

period to ensure compatibility between different model photochemical mechanisms and different model resolutions. Close coordination with TCEQ, and the timely availability of a reference emissions inventory, would be necessary in order to ensure the model evaluation project satisfies the common emissions inventory recommendation, and is relevant to TCEQ objectives. The U.S. National Weather Service/NCEP CMAQ-ETA air quality model team in particular is requesting that any emissions data to be considered in the 2006 ozone forecast season be available for inclusion in their national inventories before January 1, 2006.

Question F Approach

Question F:
How do the mesoscale chemical environments (NO_x-sensitive ozone formation vs radical-sensitive ozone formation) vary spatially and temporally in Houston, Dallas and eastern Texas?

Which mesoscale chemical environments are most closely associated with high ozone and aerosol?

(**Notes:** Questions F and K are closely related. Question F will focus generally on contrasts between the Houston area, the Dallas area and the greater eastern Texas region. Question K will specifically address the Houston area and its unique source mixture in detail.)

Question F Working Group:
Co-Leaders:
      Basil Dimitriades
      David Parrish
Participants:
      David Allen
      Daewon Byun
      Harvey Jeffries
      Mark Estes
      Ken Schere
      Will Vizuete
      Barry Lefer
Observers:
      Carl Berkowitz
      Yulong Xie

Analysis Approach:
      This question is based upon the observation that the amount of ozone that can be produced from a given mix of emissions depends strongly on the ratio of VOC (an important radical source) to NO_x in that mix. Therefore, development of ozone control strategies should consider this ratio since the balance of control of VOC versus NO_x emissions will affect the efficacy of the control strategy. The goal of this analysis is to develop a broad picture, including spatial and temporal variability, of the sensitivity of ozone formation to NO_x and VOC in the east Texas region. A particular focus will be placed on the contrast between Houston, Dallas, and other regions in east Texas. Approaches based both on modeling and observations will be pursued.

      The modeling approach will entail regional modeling of eastern Texas. A PAQM equipped with an appropriate sensitivity analysis method (derived from the decoupled direct method (DDM) or other methods) will be utilized. The model output will include the sensitivity of both the daily maximum 1-hour and 8-hour average ozone to total VOC, HRVOC, BVOC (biogenic VOC), OVOC (other VOC), and NO_x emissions at each point of the modeling domain. Daily ozone sensitivity maps of the modeling domain will reflect the spatial variability of the ozone sensitivities, and the temporal variation of these maps will reflect the temporal variability. The modeling will cover as long a period as practical (for an entire ozone season if possible) to capture as many meteorological and emission situations as possible. Correlation analyses of

modeled ozone and aerosol levels with the various sensitivities will reveal the mesoscale chemical environments that are most closely associated with high ozone and aerosol.

The observation-based approach will rely on various "indicator" species and ratios (see Kleinman et al., 2000 and references therein) to determine sensitivity. As these methods have been applied, at least so far, they give an indication of NO_x versus VOC sensitivity of the chemistry that has produced the ozone in a sampled air parcel. Key measurements available in TexAQS 2006 include O_3, aerosol, NO_x, HNO_3, PAN, and formaldehyde. The observation-based approach will be applied to aircraft data sets as well as to any suitable ground-based measurements. Several different "indicator" analyses have been described in the literature. The predictions of these different analyses will be compared and contrasted. Assuming that a consistent picture emerges, the spatial and temporal variations of these predictions will be analyzed to determine how the mesoscale chemical environments vary spatially and temporally in Houston, Dallas, and eastern Texas, and to determine which mesoscale chemical environments are most closely associated with high ozone and aerosol.

The approach described in the preceding paragraphs is general and lacks crucial details in many respects. The **initial tasks** of this analysis will be to identify clearly the modeling and observation-based approaches to be implemented. These tasks include:
- Identification and clear definition of the modeling program, the desired output, and the means by which that output is to be obtained;
- Identification of the personnel to implement the modeling;
- Securing the resources to support that modeling;
- Selection of the observation-based approaches to be implemented, and application of the approaches to presently existing data sets.

At the end of the process an **assessment of the reliability** of the findings will be crucial. This assessment should include:
- Comparisons of model-predicted concentrations of species to observations. This should include concentrations of ozone, aerosols, their precursors, and other secondary pollutants.
- Comparisons of results from several observation-based approaches.
- Evaluation of the consistency between the model-derived and observation-derived conclusions regarding the sensitivity.

Finally it must be recognized that this is a very ambitious proposed approach to addressing this question, and completion of the total proposal is far from certain, especially since resources to support the needed work have not been identified. The primary deliverables will be expected to be state-of-the-analysis progress reports.

Key TexAQS II or Other Study Data Needed:
1) Spatially and temporally resolved inventories for total VOC, BVOC, HRVOC, and NO_x emissions for the east Texas region for the modeling period.
2) Appropriate model output on maximum 1-hour and 8-hour average ozone sensitivities to VOC emissions and NO_x emissions.
3) Appropriate model output on maximum aerosol sensitivity to various aerosol precursors.
4) Aircraft measurements of O_3, aerosols, other secondary pollutants, speciated VOC, NO_x, HNO_3, PAN, formaldehyde SO_2, NH_3, and sunlight intensity.
5) Available measurements at surface sites similar to 4) for aircraft measurements.

Suggested Deliverable Products, Timelines and Lead Contacts:

1)   Analysis of model-computed ozone sensitivities to VOC and NOx emissions, comparing Houston, Dallas and other regions in east Texas.
        Final Report – August 31, 2007
        Basil Dimitriades , David Parrish

2)   Analysis of observation-based approaches applied to TexAQS 2000 data
        Preliminary Report - October 31, 2006
        David Parrish, Basil Dimitriades

3)   Analysis of observation-based approaches applied to TexAQS 2006 data
        Preliminary Report - October 31, 2006
        David Parrish, Basil Dimitriades

4)   Synthesis of model-computed and observation-based approaches
        Final Report – August 31, 2007
        David Parrish, Basil Dimitriades

Question G Approach

Question G (three parts)**:**
How do emissions from local and distant sources interact to determine the air quality in Texas?
What meteorological and chemical conditions exist when elevated background ozone and aerosol
    from distant regions affect Texas?
How high are background concentrations of ozone and aerosol, and how do they vary spatially
    and temporally?
(**Note**: Question G is closely related to Question H. Thus, Question G will focus on:
   1) characterizing the background ozone and aerosol distributions, and
   2) the chemical and physical processes that affect the background concentrations of ozone
       and aerosol in Texas.
   Question H will focus on the transport processes and source-receptor relationships of those
   background concentrations.)

Question G Working Group:
Co-Leaders:
    David Allen
    David Parrish
Participants:
    Chuck Brock
    Steve Brown
    Joost de Gouw
    Basil Dimitriades
    Michael Hardesty
    John Jolly
    Bryan Lambeth
    David Sullivan

Analysis Approach:
    Throughout rural regions of the US, background concentrations of ozone and aerosols are
significantly elevated above those found in remote regions. A wide variety of plumes from the
manifold of emission sources in the country are transported within that background. During that
transport, those plumes disperse into the background and strongly influence the evolution of that
background. The regional background and the embedded plumes were investigated in TexAQS
2000 and will be more intensively investigated in TexAQS 2006 by measurements from ground
stations, the Ronald H. Brown Research Vessel, several aircraft, and satellites. The analyses to
be undertaken here will use those measurements to:
   1) Characterize the spatial and temporal variability of the concentration and composition of
       the regional ozone and aerosol backgrounds and of the embedded plumes;
   2) Characterize the levels of anthropogenic and biogenic precursors of ozone and aerosols in
       the rural regions; and
   3) Characterize, as fully as possible, the daytime and nighttime processes that drive the
   evolution of ozone and aerosol concentrations and composition within this system.

1. Variability of Regional Background and Embedded Plumes:

   The TexAQS 2006 study will bring together a wide suite of in situ and remote sensing measurements to characterize the regional distributions of gas-phase and aerosol species throughout Texas as well as upwind and downwind areas. The NOAA WP-3D aircraft has the range and the in situ instrumentation to characterize the gas-phase and aerosol species throughout this region. The NOAA Twin Otter and NASA King Air lidar aircraft will characterize the distributions of ozone and aerosols throughout the boundary layer of the east Texas region. The CIRPAS Twin Otter aircraft and the NOAA research vessel Ronald Brown will make in situ measurements of aerosol properties in a

Figure 1. In situ O$_3$ measurements (see color code) within the boundary layer made from the Electra aircraft during 3 flights in TexAQS 2000.

variety of air masses, and the ship will also make in situ gas phase measurements as well as lidar measurements of ozone and aerosols. Size-resolved aerosol composition and aerosol properties will be measured under a variety of conditions, such as downwind of point and regional sources; at different altitudes and distances from shore; under different meteorological conditions; and at different times of the day.

   An important aspect of the investigation of the regional background is the study of plumes transported from urban areas and from power plants and other point sources located within the background areas. Figure 1 shows ozone measurements from 3 tracks flown in northeast Texas. Elevated background levels, the Dallas-Ft. Worth (DFW) urban plume and plumes from power plants in east Texas are readily apparent. The August 23 data are particularly interesting in this regard. The wind was from the southeast, and the air entering the DFW area had a strong gradient from about 60 ppbv to the southwest and 80 ppbv to the northwest. In the air exiting the urban area, the DFW urban plume added about 40 ppbv to that gradient.

   Satellite measurements potentially add another comprehensive tool for both aerosol and ozone background characterization. Aerosol data from over-passing satellite sensors will be collected and coordinated with measurements taken from the ship and aircraft over the Gulf of Mexico and Texas, in order to validate satellite aerosol measurements. The satellite instruments will in turn provide regional information on the aerosol distribution. Figure 2 presents an example of the aerosol information potentially available from satellite imagery. Two features should be noted: first, the pollution episode illustrated is a particularly concentrated aerosol event, with maximum surface concentrations above 150 ug/m^3; and second, although the spatial patterns in the satellite and surface data qualitatively agree, the quantitative correspondence between aerosol optical depth retrieved from the satellite and the in situ PM$_{2.5}$ concentration is a very complicated and spatially varying function of boundary layer depth, humidity, and several other factors.

   Retrievals of concentrations of gas-phase species from over-passing satellite sensors will also be compared with measurements taken from aircraft for validation purposes, and the satellite instruments also will provide information on regional distributions. Figure 3 shows an example
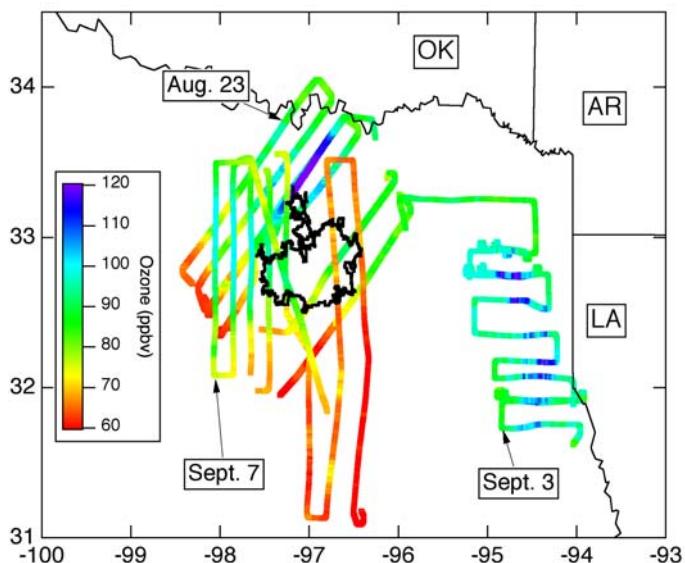
of the ozone and NO_2 distributions potentially available. Similarly to Figure 2, although the
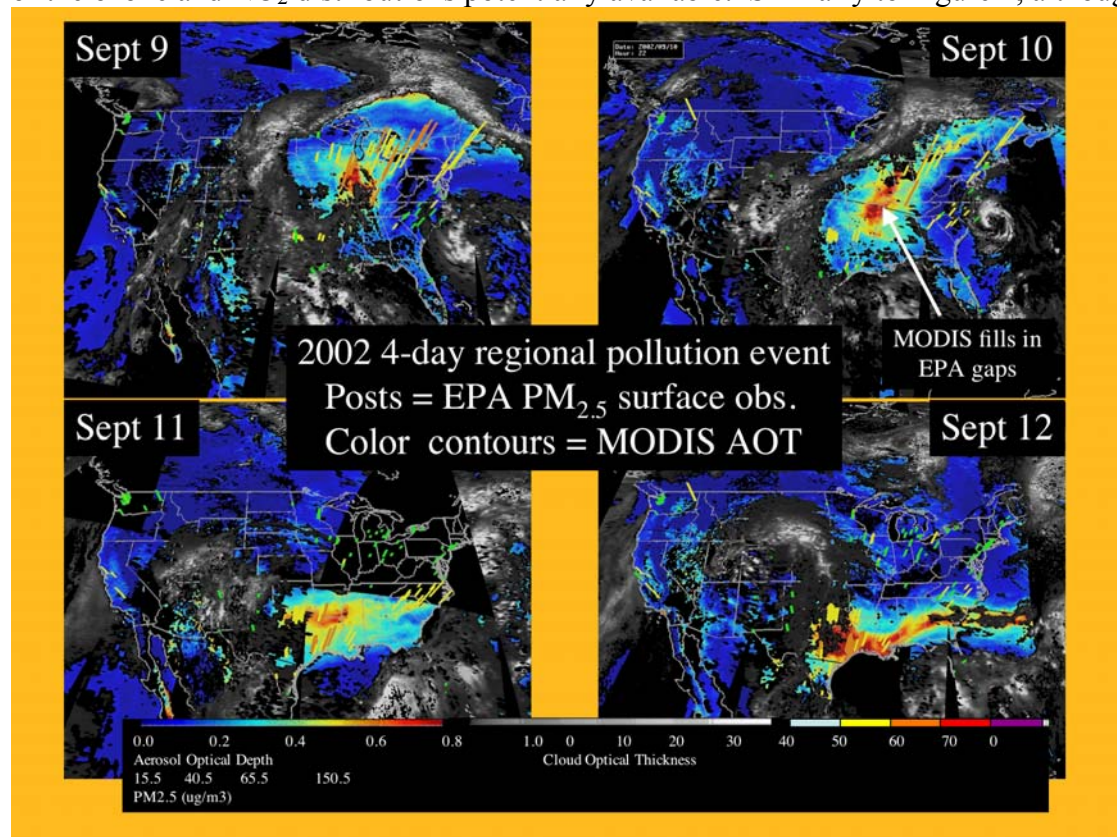

Figure 2. MODIS satellite retrievals of aerosol optical depth compared with surface PM$_{2.5}$ measurements given by the colored bars.
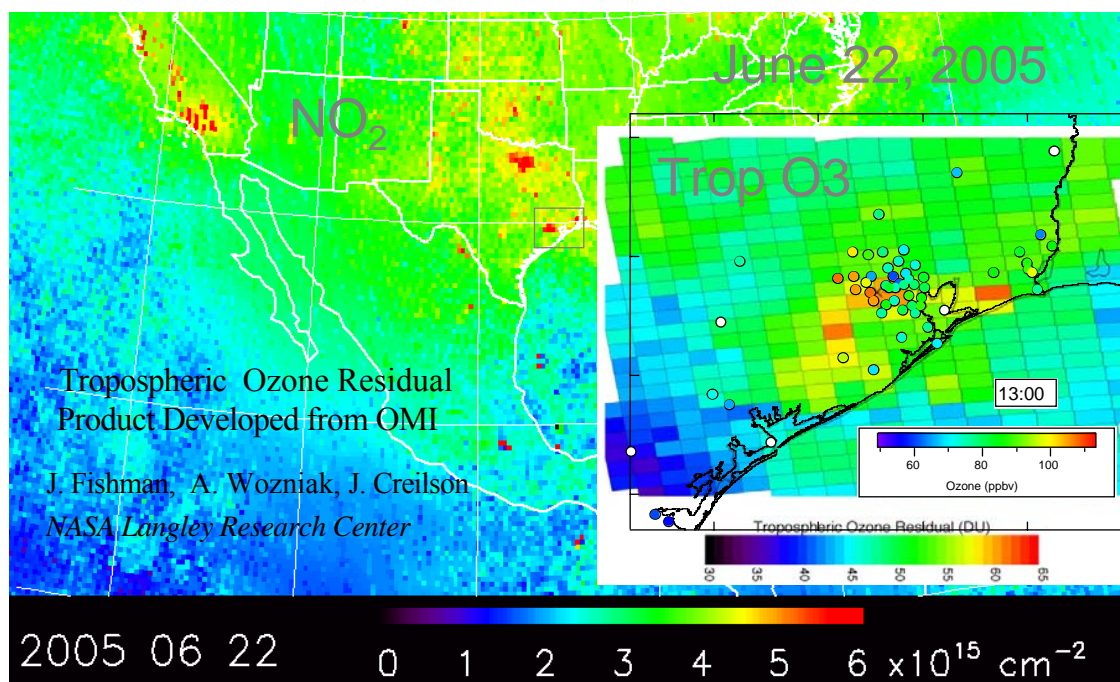

Figure 3. OMI satellite retrievals of tropospheric O$_3$ (inset) and NO$_2$ columns (background). The O$_3$ columns are compared with surface O$_3$ measurements (circles in inset). Different color scales are given for O$_3$ (Dobson Units), NO$_2$ columns (molec/cm^2) and surface O$_3$ measurements (ppbv).

spatial patterns in the satellite and surface data qualitatively agree, the quantitative correspondence between tropospheric O_3 and NO_2 columns retrieved from the satellite and the in situ surface concentrations is a very complicated and spatially varying function of boundary layer depth, altitude sensitivity of satellite instrument, and several other factors.

In summary, the suite of specially deployed platforms with in situ and remote measurements and the satellite-based measurements along with the extensive surface network of ozone, aerosol and precursor measurements will be unprecedented in scope and potential to characterize the regional distributions of ozone and aerosols. There are, however, considerable challenges to reaching a coherent and comprehensive picture from this suite of measurements. In particular the limitations of the in situ and satellite data must be kept in mind. The in situ methods provide data limited to a single point, but do provide information of temporal variability. Aircraft-borne instruments convolve the temporal variability with spatial variability, since they make measurements at a point whose location is changing with time. The satellite measurements are generally made during a single overpass each day that occurs at the same local time each day.

2. Magnitude of anthropogenic and biogenic precursors in eastern Texas

Top-down tests of inventoried emissions through comparison with ambient data have been an integral part of tropospheric field programs, including TexAQS 2000. In 2006 the NOAA WP-3D will acquire data that are suitable to evaluate regional emission inventories in unprecedented detail. The distributions of these sources, their relation to each other, and the changes that may have occurred between 2000 and 2006 will play important roles in assessing the contribution of these local sources to the regional distributions of ozone and aerosol precursors.

Figure 4 shows an example of two flights flown in 2000 that can be used to quantify the emission levels of ozone and aerosol precursors. These flights were designed to quantify the emissions and resulting ambient concentrations of precursors from large coal-fired power plants in eastern Texas and to investigate the spatial distribution of biogenic VOC emissions. The biogenic emission distribution is reflected in the distribution of isoprene itself as well as the distributions of its oxidation products including methacrolein, methylvinylketone, formaldehyde and MPAN (a PAN type compound that is formed in the oxidation of methacrolein). Similar
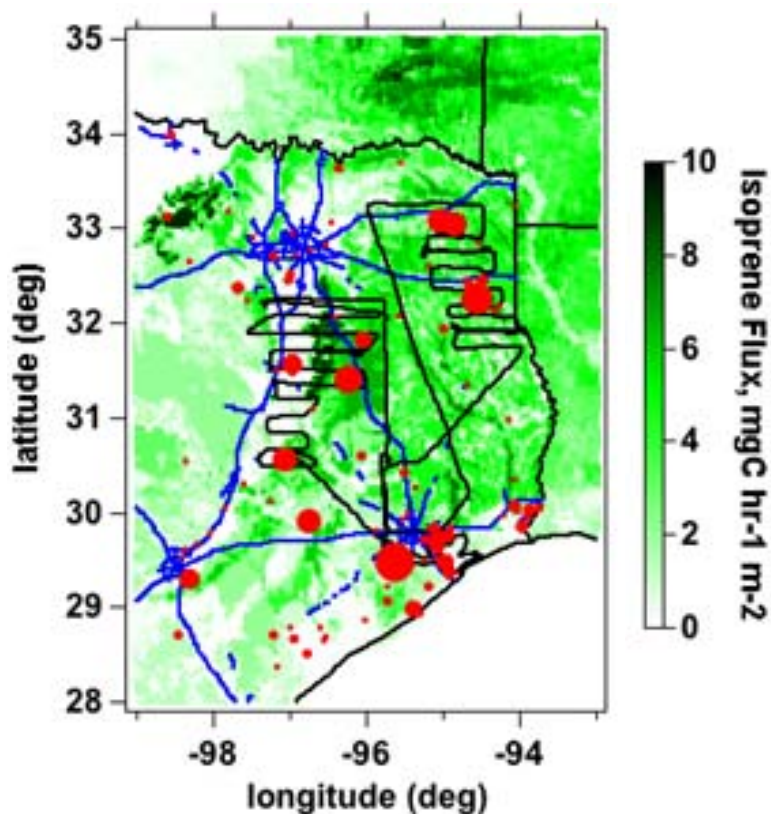
Figure 4. Location of point sources of NO$_x$ in red (sized proportional to emissions), highways in blue, and the distribution of biogenic VOC emissions from the forested regions of East Texas, color coded in shades of green according to the intensity of the emissions. Superimposed are two flight tracks made by the Electra during TexAQS 2000.

flights are planned for 2006 with analysis extended to 1) the biogenic emissions of ammonia, 2) black carbon emissions, and 3) improved instrumentation for measurement of isoprene and its secondary oxidation products. The aircraft data potentially will be complemented by satellite measurements of NO_2 as exemplified in Figure 3.

3. Photochemical Processes Driving Evolution of Regional Ozone and Aerosols:

The photochemistry that produces ozone in rural areas as well as in more concentrated plumes is now reasonably well understood, but questions do remain regarding photochemical processing of ozone and aerosol precursors that reduce the confidence that can be placed on chemical modeling results. The instrumentation on the WP-3D and the R/V Ronald Brown will provide rigorous tests of the models of this photochemistry throughout eastern Texas and the offshore region. The WP-3D will conduct flights similar to those illustrated in Figures 1 and 4. Of particular note are the measurements of the temporal and regional distributions of:

- Primary radicals involved in the photochemistry (OH and peroxy radicals),
- Critical intermediates and secondary carbonyl products of anthropogenic VOC (such as formaldehyde and acetaldehyde),
- Critical intermediates and secondary carbonyl products of biogenic VOC, including methacrolein, methylvinylketone, formaldehyde and MPAN,
- Organic nitrates including a wide suite of PAN-type compounds,
- Nitric and sulfuric acids.

These measurements will test and constrain models used for forecasting, SIP development, and general investigation of photochemical processes. In addition, flight transects conducted sequentially further downwind from specific sources will allow the determination of ozone and aerosol formation rates and efficiencies in the emission plumes from those sources.

4. Nighttime Processes Driving Evolution of Regional Ozone and Aerosols:

Nighttime processes that remove or transform emitted precursors, and thus affect the resulting ozone and aerosol levels, must be well characterized to provide a complete picture of atmospheric processing of ozone and aerosol precursors. Ozone reacts with NO_2 to produce the NO_3 radical. During the day, photolysis of NO_3 and reaction with NO combine to keep NO_3 levels very small. At night NO_3 can accumulate and react with NO_2 to produce N_2O_5. Depending on the conditions, NO_3 or N_2O_5 can irreversibly react at surfaces, including aerosols, in which case the net effect is removal of both O_3 and NO_x from the atmosphere. In other cases NO_3 can react with VOCs, including aldehydes and sulfur-containing compounds. Characterization of the nighttime processes is of particular importance, as regional sources release NO_x throughout the night, which can be transported over long distances. If the NO_x is still present, or if it can be released from accumulated NO_3 and N_2O_5 at sunrise, it can interact with fresh emissions during the following day's photochemistry. However, nighttime processes will convert some fraction of the NO_x to aerosol species that are unavailable for further photochemical processing.

During the daytime, pollutants can accumulate at low wind speeds and are generally well mixed through the boundary layer. By contrast, at night when the residual boundary layer becomes decoupled from the surface by the relative shallow nocturnal boundary layer, horizontal transport can be greatly enhanced while vertical mixing is greatly reduced. The vertical wind profile is usually characterized by strong directional shear. This means that horizontal layers can remain relatively concentrated while the ozone and ozone precursors in these layers can be distributed over a large regional area. These conditions not only produce local pollution near major source regions during daytime, but also contribute to regional pollution as a result of nocturnal transport (Banta et al., 1998, 2005). Such days often cluster together into multi-day

episodes, during which rural background concentrations of pollutants increase as a result of the nocturnal transport from the source regions and the overall relatively weak synoptic winds.

As is the case with transport, the chemical processing that occurs during the nighttime hours is much less well understood. In situ measurements of NO_2, NO_3, N_2O_5 and VOCs, such as isoprene that react rapidly with these nitrogen compounds, along with the end products such as HNO_3, particulate NO_3^-, and organic nitrogen in aerosols will allow this chemistry to be characterized. The WP-3D and R/V Brown measurements during the 2006 study will address the importance of the nighttime oxidation as a loss process for NO_x and investigate its influence on ozone production.

WP-3D flight patterns similar to those shown in Figures 1 and 4 can be used to determine the influence of nocturnal transport and chemistry on the regional distribution of ozone and aerosols. However, understanding the chemistry over the continent during the night will present a significant challenge due to the vertical layering of the atmosphere. This nighttime vertical layering makes finding and tracking plumes at the surface or from an aircraft extremely difficult. For 2006, profiler data will be available in near real time, and a trajectory-calculating tool will be available for analysis, also in near real time. This resource will be used to guide aircraft during nighttime and early-morning flights to find the pollution layers and to characterize the regional transport and the fate of pollutants from the previous day. These aircraft measurements will be used to confirm the origin and characterize the photochemical age of the air mass. These measurements over East Texas will provide important new information concerning loss mechanisms for NO_x at night. Analyses of these data sets can be used to assess the ability of coupled chemical/transport forecast models to properly and accurately represent the regional ozone and aerosol distribution.

Key TexAQS II or Other Study Data Needed:
1) Data sets of in situ measurements of gas phase and aerosol species from the NOAA WP-3D and the CIRPAS Twin Otter aircraft during daytime and nighttime regional flights.
2) Data sets of in situ and remote measurements from the NOAA R/V Ronald Brown during regional cruise legs.
3) Lidar data sets from the NOAA Twin Otter and NASA King Air aircraft.
4) Aerosol optical depth data sets from MODIS and MISR satellites.
5) O_3 and NO_2 column data sets from SCIAMACHY and OMI satellites.

Suggested Deliverable Products, Timelines and Lead Contacts:
1) Characterization of regional levels of ozone, aerosols and known anthropogenic precursors in the continental boundary layer from in situ surface and aircraft measurements;
    Preliminary Report - October 31, 2006; Final Report – August 31, 2007
    Chuck Brock, John Jolly, David Sullivan David Parrish, David Allen
2) Characterization of regional levels of ozone, aerosols and anthropogenic precursors in the marine boundary layer from in situ aircraft and ship measurements;
    Preliminary Report - October 31, 2006; Final Report – August 31, 2007
    David Parrish
3) Characterization of regional levels of ozone and aerosols in the marine and continental boundary layers from lidar aircraft measurements;
    Preliminary Report - October 31, 2006; Final Report – August 31, 2007
    Mike Hardesty, Chuck Brock, David Parrish
4) Characterization of regional levels of ozone, aerosols and NO_2 in the marine and continental boundary layers from satellite measurements;

Preliminary Report - October 31, 2006; Final Report – August 31, 2007
David Parrish

5) Characterization of regional levels of isoprene and ammonia from WP-3D measurements;
Preliminary Report - October 31, 2006; Final Report – August 31, 2007
Chuck Brock, Joost de Gouw, David Parrish

6) Synthesis characterization of regional levels of ozone, aerosols and precursors;
Final Report – August 31, 2007;
David Parrish and all group members.

7) Description of significant advances in our understanding of photochemical processes driving evolution of regional ozone and aerosol concentrations and composition.
Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
Chuck Brock, David Parrish

8) Description of significant advances in our understanding of nighttime processes driving evolution of regional ozone and aerosol concentrations and composition.
Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
Chuck Brock, Steve Brown, David Parrish

Question H Approach

Question H (two parts):
Which areas within Texas adversely affect the air quality of non-attainment areas within Texas?
Which areas outside of Texas adversely affect the air quality of non-attainment areas within
   Texas?
(**Note**: Question H is closely related to Question G. Thus, Question H will focus on
   1) the source-receptor relationships that determine the background concentrations of ozone
      and aerosol in Texas and
   2) the meteorologically driven transport processes.
   Question G will focus on characterizing the background concentrations and the chemical and
   physical processes that affect those background concentrations.)

Question H Working Group:
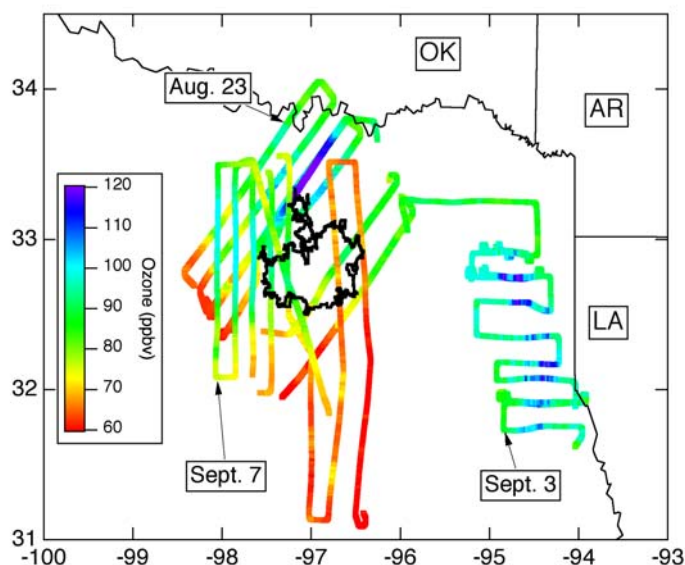Co-Leaders:
        David Allen
        David Parrish
Participants:
        Chuck Brock
        Basil Dimitriades
        Mark Estes
        Michael Hardesty
        John Jolly
        David Sullivan
        Greg Yarwood
        Bryan Lambeth

Data Analysis Approach:
        Throughout rural regions of the
US, the background concentrations of
ozone and aerosols are significantly elevated
above those found in remote regions. For
example, Figure 1 shows that ozone can
approach and exceed 80 ppbv throughout

Figure 1. In situ O$_3$ (see color code) within the boundary layer measured from the Electra aircraft during 3 flights in TexAQS 2000.   The Dallas-Fort Worth area is outlined in black.

large regions of East Texas. The elevated background results from the dispersion of plumes of
emissions as they are transported away from source regions to more rural areas. The regional
background and the embedded plumes were investigated in TexAQS 2000 and will be more
intensively investigated in TexAQS 2006 by measurements from ground stations, several aircraft
with in situ and remote instrumentation, and satellites. The analyses to be undertaken here will
use those measurements combined with model calculations to determine the source regions, both
within and outside Texas, responsible for the elevated background within Texas. Particular
focus will be placed upon the background advected into non-attainment areas. A four-pronged
approach will be used to determine the source regions responsible for the elevated background
within Texas:
   1. A systematic analysis of ground monitoring sites to characterize ozone and aerosol fluxes
      through critical boundaries. This analysis will be complemented by similar analysis of
      aircraft lidar data.

2. Intensive investigation of specific transport events through aircraft measurements and transport modeling.
3. Three source apportionment studies based upon photochemical air quality modeling.

To complement the source attribution studies:

4. Investigation of the meteorological processes that drive the dispersion of the emission plumes and advect the resulting background, with particular focus on vertical transport and mixing.

1. Characterization of Ozone and Aerosol Fluxes:

The extensive ground-based monitoring network established for TexAQS II, in conjunction with the TCEQ monitoring network, will be used to develop ozone and fine particulate matter isopleths that cover the entire eastern half of Texas with one-hour time resolution. The ozone and PM isopleths can be combined with wind field information, developed using meteorological models and measurements of wind fields and mixing heights from the TexAQS II profiler network. The coupled wind field and pollutant isopleths can be used to calculate pollutant fluxes across state lines, upwind of urban areas and downwind of urban areas. These flux estimates, with hourly time resolution, will be generated for each day that the ground network operates in 2005 and 2006. The results are expected to be robust during midday when the boundary layer is well developed. Estimates of pollutant fluxes based on ground data assume a boundary layer that is homogeneous. Aircraft flying during the intensive sampling period will test this assumption.

An important complement to the ground-based flux determination will be a similar analysis performed on the ozone and aerosol lidar data from several flights of the NOAA Twin Otter and perhaps the NASA King Air. The curtain data from the lidar characterizes the ozone and aerosol concentrations through the depth of the boundary layer and above. Combining this information with wind data will allow flux calculations through the measurement curtain. The lidar aircraft will fly along critical boundaries for which the ground-based approach calculates fluxes to provide comparisons to the ground-based results. This approach will, of course, be limited to the time periods of the aircraft flights. An advantage of the lidar approach is that it can provide flux estimates during periods that the boundary layer is not well developed (e.g. during early morning and at night), and determine the representativeness of the ground-based flux determinations.
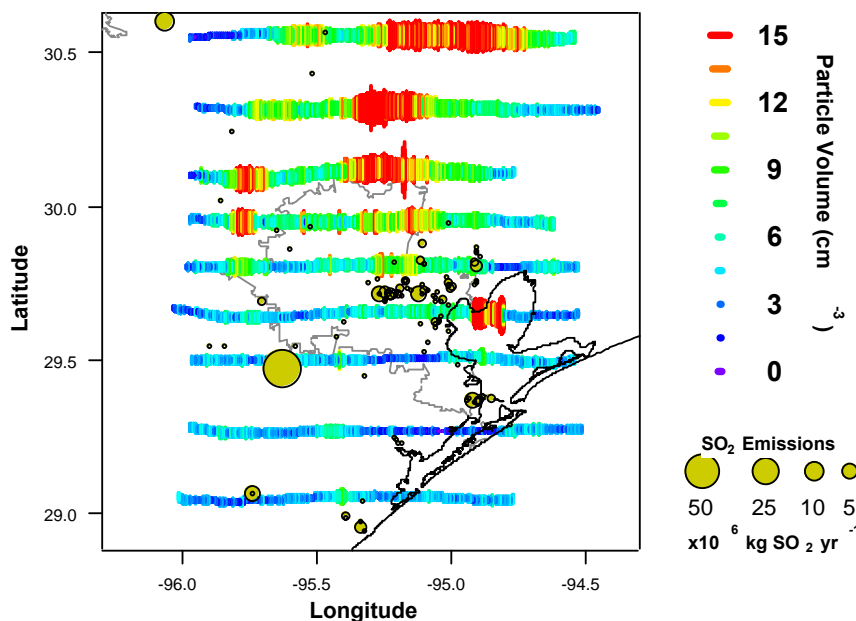
2. Intensive Investigation of Transport Events:

The overall quantification of net ozone and PM fluxes derived from the ground-based monitoring network and the lidar aircraft data will be complemented by aircraft studies of the transport patterns that take place above the surface, particularly at night, and studies of the transported precursors and chemical processes that determine these net ozone and PM fluxes. Transport events can be predicted reasonably well by regional-scale tracer transport models such as FLEXPART, which allows targeted flights to determine the import of pollutants from upwind source regions into a region of interest. Under favorable conditions, intra- and inter-regional transport of the plumes can be tracked with satellite imagery and transport models can be run in forecast mode during the experiment to identify where and when the plumes originated. The aircraft can then be deployed to intercept these plumes. The studies will not be limited to following plumes during single flights. Forecast forward trajectories can be run from a flight track as soon as the flight is completed to indicate the location of the sampled air masses over the next several days. The aircraft can then target these trajectory locations on subsequent days to create a regional-scale, semi-Lagrangian study of the chemical and dispersive evolution of polluted air masses. These studies will provide key tests and diagnoses of model results for both chemical and meteorological parameters. Some example studies from TexAQS 2000 are discussed below.

The DFW region has local, regional, and extra-regional contributions to air quality degradation that make photochemical modeling of this area a challenge; it is a non-attainment region that will be a particular focus of transport studies during TexAQS 2006. In turn, ozone and aerosols from this urban area can be transported to other regions, with potential adverse impacts on air quality in those regions. In Figure 1, the DFW urban plume is clearly discernable in the flights over that urban area (outlined in black). Winds were generally southeasterly on August 23, northerly on September 3, and easterly on September 7.

Figure 1 illustrates some of the transport issues for the DFW area. The maximum ozone observed on August 23 (128 ppbv) and September 7 (102 ppbv) differed substantially, but this difference is similar to the difference in the upwind ozone levels entering the urban area, August 23 (84 ppbv) and September 7 (66 ppbv). Although other factors were likely important, these two days emphasize the impact that upwind ozone levels can have on levels measured within an urban area. Given that the air entering the DFW area on August 23 was near the 8-hour air quality standard, SIP planning for DFW cannot be considered solely from a local perspective. The September 3 flight illustrates one source of upwind ozone, i.e. formation in power plant plumes in east Texas. The August 23 flight illustrates an additional concern; the maximum ozone was observed well downwind from the center of Dallas. Transport of ozone from this urban area affects air quality in downwind areas. Similar flights will be conducted in 2006 under different meteorological scenarios to help constrain the relative importance of local and upwind pollution sources.
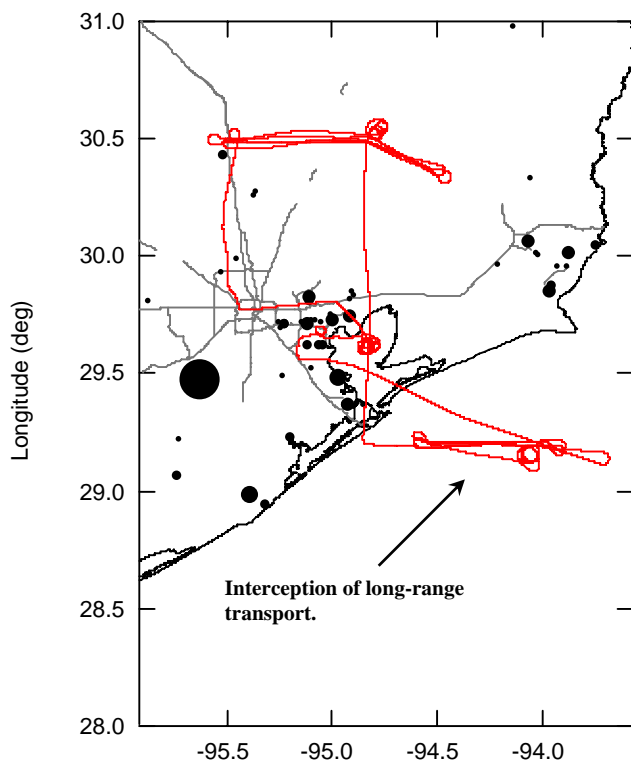
Other urban areas also contribute significantly to regional pollution in East Texas. Along with the formation of ozone, particle formation and growth in urban plumes can be measured and its contribution to regional haze assessed. For example, during TexAQS 2000 plumes originating from the Parish gas and coal-fired power plant, petrochemical industries along the Houston ship channel, the petrochemical facilities near the Gulf coast, and the urban center of Houston were studied (Figure 2). Most of the particle mass flux advected downwind of the Houston area came from the industries and the electrical generating unit at the periphery of the city rather than from sources in the urban core. In fact, clearly detectable gas-to-particle conversion was found only in plumes from large SO_2 sources. In SO_2-rich plumes that did not contain elevated concentrations of VOC, the gas-to-particle conversion was consistent with the expected oxidation of SO_2. However, in plumes that were rich in *both* SO_2 and VOC, the observed particle growth greatly exceeded that expected from SO_2 oxidation

Figure 2. Illustration of the evolution of aerosols downwind of power plant, urban area and urban/industrial emissions observed during the 28 August 2000 flight conducted under southerly winds. The yellow circles show SO_2 point sources sized according to their emission strength

Figure 3. Flight track of 18 August 2000

alone, indicating the formation of organic particulate mass (Brock et al., 2003). Finally, in plumes that were enhanced in VOC but had little SO_2, as in the plume of the Houston urban center, no particle volume growth with increasing plume oxidation was detected. Since substantial particle volume growth was associated only with SO_2-rich plumes, these results suggest that photochemical oxidation of SO_2 is the key process regulating particle growth in all the studied plumes in the Houston-Galveston air shed. Clearly, however, organic matter must contribute substantially to particle mass in petrochemical plumes rich in both SO_2 and VOC. Quantitative studies of particle formation and growth in photochemical systems containing NO_x, VOC, and SO_2, with improved real-time capability to measure particle composition, with the attendant ability to establish the identity of particular urban areas or point sources within urban areas, will be an important addition to the 2006 study.
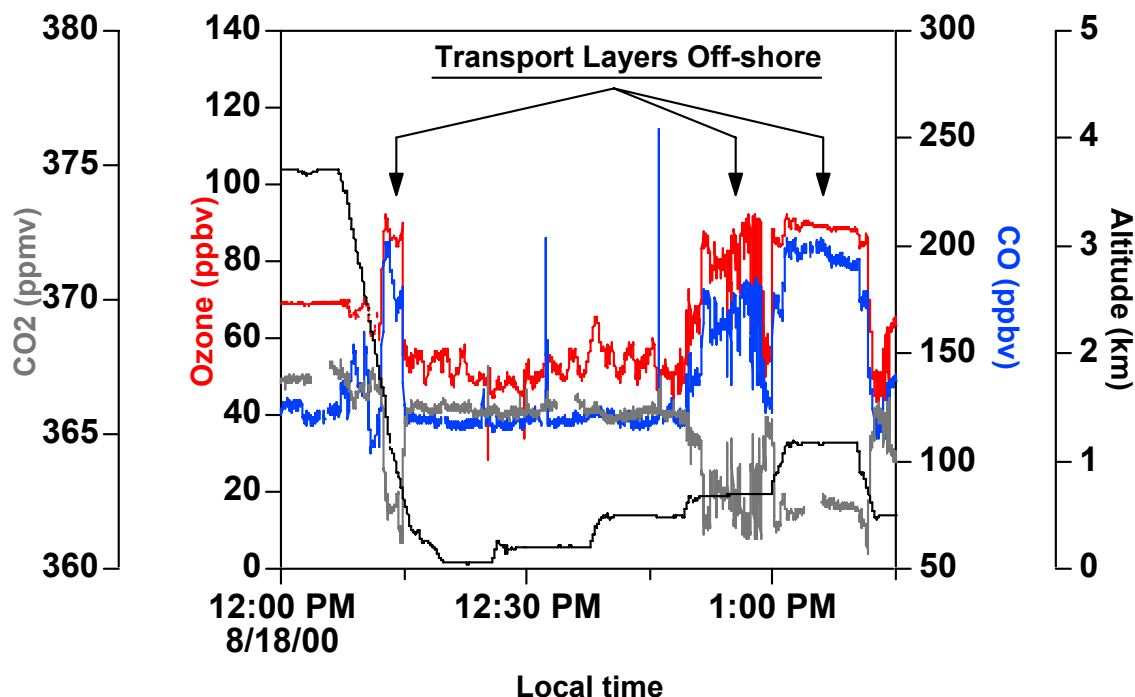
The influence of long-range transport from sources outside of Texas into the state was observed in 2000. A flight on 18 August 2000 studied the import of pollutants from distant sources into East Texas. In Figure 3, several of the large NO_x point sources around the Houston area are shown by the black symbols. During several offshore, east-west transects of about 70 km length, a transport layer with elevated concentrations of carbon monoxide and ozone (Figure 4) was observed between 0.6 and 1.7 km above a much cleaner maritime boundary layer. Back trajectory calculations indicated that this pollution layer had been transported from the southeastern United States to the coast of Texas. The CO_2 measurements supported this interpretation. While the vegetation over eastern Texas was drought stressed during the summer of 2000 and took up little CO_2, uptake of CO_2 by vegetation over Florida and Georgia resulted in the reduced CO_2 concentrations observed in the transport layer.

Regional transport events such as the one observed during the August 18 flight can be predicted reasonably well by the FLEXPART tracer transport model, which will allow targeted flights of the NOAA WP-3D to determine the import of pollutants from upwind source regions into eastern Texas. Under favorable conditions, the interregional transport of the plumes can be tracked with satellite imagery and the FLEXPART model can be run in forecast mode during the experiment to identify where and when the plumes originated. The aircraft can then be deployed to intercept these plumes. Furthermore, forecast forward trajectories can be run from a flight track as soon as the flight is completed to indicate the location of the sampled air masses over the next several days. The aircraft can then target these trajectory locations on subsequent days to create a regional-scale semi-Lagrangian study of the chemical and dispersive evolution of polluted air masses.

Figure 4.   Elevated levels of ozone (red trace), CO$_2$ (gray trace), and CO (blue trace) were encountered aloft over the Gulf of Mexico on the flight of August 18, 2000, showing transport to Texas from sources in the southeastern United States.

3. Source Apportionment Studies:

Source apportionment studies based upon photochemical air quality models (PAQM) provide methods to determine spatially and temporally resolved contributions to local ozone and aerosol concentrations. Various techniques allow the modeled local concentrations to be approximately apportioned among local, upwind regional, and more distant upwind sources, as well as to boundary conditions. At least three techniques are potentially available for application to TexAQS 2006.

The aircraft studies described in the preceding section will address: (1) The ozone and aerosols formed from the anthropogenic point sources and the distributed anthropogenic and biogenic sources of ozone and aerosol precursors within the region; (2) The dispersed region-wide residual of ozone, aerosols and their precursors transported from urban areas in the region; (3) Anthropogenic sources of ozone, aerosols and their precursors that are located outside of the region; and (4) The influence of nocturnal transport and chemistry on regional distributions of ozone and aerosols. These data will be taken under well-defined conditions that are needed to best analyze these sources. The will allow us to evaluate the ability of a model to simulate the concentrations of ozone and aerosols, their precursors from these sources, and other intermediates and secondary products produced by the atmospheric chemical processes. One model that will be used in this regard is the Weather Research and Forecasting with Online Chemistry (WRF-Chem) model. Several other models also will be involved in forecasting and retrospective analysis of the aircraft data sets. In these model calculations the influence of emissions from various sources will be evaluated.

$$y = 1.19x + 41.49$$
$$R^2 = 0.88$$
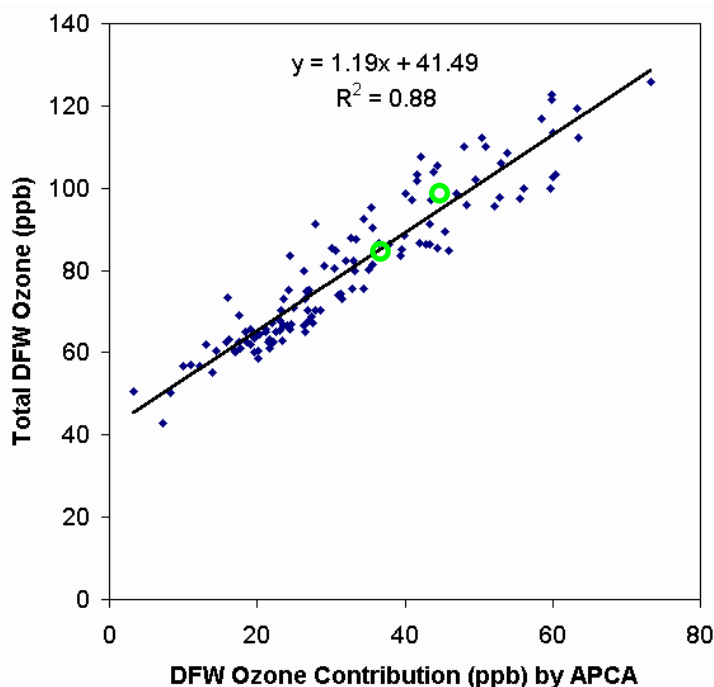
Figure 5. Modeled (by the APCA method) peak 8-hour average O$_3$ in the DFW area compared to the DFW contribution to that peak for all days June 1 to September 30, 2002.

The APCA ozone source apportionment scheme in the CAMx PAQM is a more systematic source apportionment technique that will also be used to investigate source apportionment of O$_3$ specifically in the DFW urban area. Figure 5 presents some results (blue symbols) from this method for the 2002 ozone season. In general, it suggests that the peak 8-hour average O$_3$ in the DFW area has an imported contribution of 41.5 ppbv + 19% of the O$_3$ increase above 41.5 ppbv.

The green circles in Figure 5 show the results from the August 23 and September 7 flights illustrated in Figure 1. The peak 8-hour O$_3$ for these two flights are from the APCA model and the DFW contribution is estimated from the difference between the downwind and upwind legs of the flights. At least for these two days the estimates of the O$_3$ imported into the DFW area from the aircraft data are in excellent agreement with the general trend from the APCA model.

The APCA model also apportions the ozone to production from precursors emitted in regions throughout the U.S.; Table 1 gives an example of the results. As expected, the major contribution comes from the DFW area itself. However, perhaps surprisingly, the surrounding areas of Texas make relatively small contributions, while more distant regions make similar contributions, and the boundary conditions have a very large contribution. This feature may well be an artifact of the APCA model, which apportions the ozone according to net ozone production and loss in each model grid cell. This method should be compared with a source apportionment method that apportions ozone according to gross ozone production and loss in each cell, such as the decoupled direct method (DDM) (Dunker et al., 2002). Such a method is expected to apportion a much larger contribution to nearby regions, and to de-emphasize the boundary conditions.

Table 1. Average contribution to peak 8-hr ozone (ppbv) for days in 2002 with DFW ozone ≥ 85 ppb and maximum ozone observed to the west of central DFW.

Source Region	Contribution	Source Region	Contribution
DFW NAA	45.9	Florida	0.3
North Texas	1.0	Kansas	0.4
NE Texas	3.4	Missouri	0.8
Central Texas	2.2	Tennessee	1.6
Houston	1.0	Mid Atlantic States	2.3
South Texas	0.3	Nebraska	0.1
West/Southwest Texas	0.1	Iowa	0.2
Mexico + Gulf	0.1	Illinois	0.7
Oklahoma	1.4	Indiana	0.7
North Louisiana	3.5	Kentucky	1.0
South Louisiana	0.8	Ohio	0.6
Arkansas	4.5	Northeast US	0.8
Mississippi	2.6	Northern Plains	0.5
Alabama	2.2	Initial Conditions	0.0
Georgia	1.6	Boundary Conditions	20.3

4. Investigation of Meteorological Processes that Drive Dispersion and Advection:

An important aspect of atmospheric transport is the diurnal evolution of the convective boundary layer (CBL). In the late afternoon the CBL collapses and large vertical wind shear develops in the absence of strong surface heating. As a consequence, during nighttime the residual CBL as well as plumes from elevated stacks can be "sheared apart" and dispersed widely at varying speeds depending upon the details of the wind fields. Nighttime flights will capture the general features and the specific details of this transport. During the morning and early afternoon the CBL increases in depth, and grows through elevated layers of the atmosphere that may contain emissions transported overnight. These transported emissions are then mixed into the fresh emissions injected into the CBL. It is not unusual in Texas to find a layer of cleaner background air below about 2,000 to 3,000 feet with a more southerly wind flow with a more polluted layer aloft with easterly winds from about 3,000 to 6,000 feet or more. In these situations, background levels measured at surface stations can appear to increase in the afternoon as more of the higher layer mixes to the ground. Land breeze/sea breeze circulations near the coast further complicate this picture. Early morning flights are planned that will characterize these transported emission layers. This nighttime and early morning characterization will provide valuable tests of the ability of models to accurately describe such transport processes.

With all of the complexities involved, having an extensive data set of wind fields, temperature, humidity, ozone, ozone precursor, and fine particulate measurements in 4-dimensional space-time is very desirable – the more the better. Our challenge here is to integrate the information from surface measurements, remote sensing, and mobile monitoring platforms (ship, aircraft, and balloon) into a practical model(s) that can simulate accurately what has been measured. That requires accurate emissions information as well.

Key TexAQS II or Other Study Data Needed:
1) Ozone and fine particulate matter data from the TexAQS II and TCEQ monitoring networks.
2) Meteorological fields from the wind profiler, surface stations and sonde networks.
3) Lidar data sets from the NOAA Twin Otter and NASA King Air aircraft.
4) Data sets of in situ measurements of gas phase and aerosol species from the NOAA WP-3D aircraft during daytime and nighttime regional flights.
5) Source apportionment analysis from WRF-Chem and CAMx with APCA and DDM modules.

Suggested Deliverable Products, Timelines and Lead Contacts:
1) Development of software to estimate daily pollutant fluxes, based on ground data; selection of the specific areas in which fluxes will be calculated in consultation with the TCEQ;
   March 31, 2006
   David Allen
2) Calculation of daily flux estimates from ground-based approach;
   March 31, 2006 to September 30, 2006
   David Allen
3) Weight-of-evidence document on ozone transport into Texas, including a section describing aircraft-based testing of the assumption of a homogeneous mixed layer;
   Preliminary Draft - October 31, 2006
   David Allen, Mark Estes, John Jolly

4) Calculation of aerosol and ozone fluxes from lidar aircraft measurements;
    Preliminary Report - October 31, 2006
    Michael Hardesty, David Parrish
5) Synthesis characterization of aerosol and ozone fluxes from ground-based and lidar aircraft measurements;
    Final Report – August 31, 2007
    David Allen, Michael Hardesty, Mark Estes, John Jolly
6) Synthesis report of the intensive investigation of transport events observed in TexAQS 2000 and 2006;
    Preliminary Report - October 31, 2006
    Final Report – August 31, 2007;
    Chuck Brock, David Parrish.
7) APCA-based ozone transport analysis for DFW 8-hour ozone exceedance days in 2002.
    Preliminary Report – May 3, 2006
    Greg Yarwood
8) Comparison of DDM- and APCA-based ozone transport analysis for DFW 8-hour ozone exceedance days in 2006.
    Final Report – August 31, 2007;
    Greg Yarwood, Basil Dimitriades, David Parrish.
9) Synthesis characterization of nighttime transport and CBL evolution;
    Preliminary Report - October 31, 2006; Final Report – August 31, 2007;
    Bryan Lambeth, Mark Estes, John Jolly, David Parrish.

Question I Approach

Question I (two parts):

Why does the SAPRC chemical mechanism give different results than the Carbon Bond (CB-IV) mechanism?

Which replicates the actual chemistry better?

Question I Working Group:
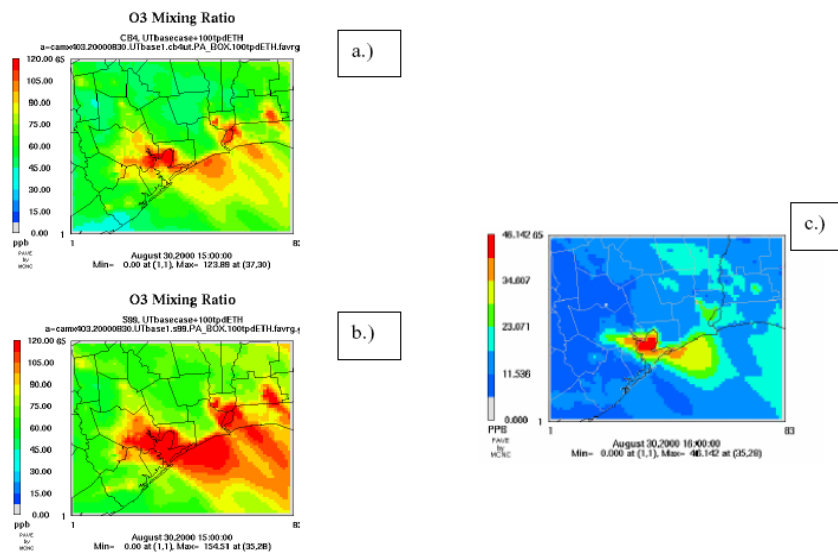Co-Leaders:
        David Allen
        Greg Yarwood
Participants:
        Harvey Jeffries
        Will Vizuete
        Bill Carter
        David Parrish
        Stu McKeen
        Joost deGouw
        Barry Lefer
Observers:
        Mark Estes
        Noor Gillani

Figure 1. Predictions of ozone concentrations using (a) CB-IV96, and (b) SAPRC99 in CAMx on August 30, 2000. Differences (c) can exceed 45 ppb.

Analysis Approach:

Gridded, regional photochemical models, used in developing State Implementation Plans (SIPs), use simplified photochemical reaction mechanisms. The two mechanisms that are most commonly used are the [California] Statewide Air Pollution Research Center (SAPRC) mechanism and the Carbon Bond (CB) mechanism. Both mechanisms are approved for use by the USEPA and are updated periodically to incorporate new experimental findings. Versions of the mechanisms currently in use include SAPRC99, the CB-IV version from 1996, and several updated CB-IV mechanisms. For most urban areas, the CB-IV and SAPRC mechanisms yield similar results, but for the modeling done of the summer of 2000 in southeast Texas, which is being used by the State of Texas to develop SIPs for southeast Texas, the SAPRC mechanism leads to concentrations of ozone that are 30-50 ppb higher than in CB-IV.

Although the two mechanisms lead to very different predictions of ozone formation under the conditions modeled for the summer of 2000, once significant NO_x reductions are imposed, the ozone concentrations predicted by the two mechanisms converge. In Houston, significant NO_x emission reductions have been proposed. After application of the proposed controls, both SAPRC and CB-IV predict similar absolute ozone concentrations. Therefore, SAPRC predicts consistently larger relative reductions in ozone due to NO_x controls, than CB-IV. These differences in photochemical mechanisms could have significant consequences for determining the levels of emission reductions that will be required to demonstrate attainment with the NAAQS for ozone, with concentrations averaged over 8 hours.

31 July 2006

The goals of this portion of the TexAQS II science synthesis will be to characterize why the two mechanisms are leading to different predictions and to assess which mechanism more accurately represents atmospheric chemistry under Houston conditions.

Modeling analyses:

A variety of modeling analyses, including box model simulations and gridded photochemical model simulations, have been conducted to assess the reasons for the differences in predictions between SAPRC and CB-IV. These simulations suggest that the free radical source terms, particularly aldehyde formation pathways, differ significantly between the two mechanisms. The SAPRC mechanism has several additional source reactions for higher aldehydes that are not present in CB-IV. The higher aldehyde concentrations lead to higher free radical production rates in SAPRC. Ongoing modeling analyses will compare and contrast the rates of key chemical processes under simulation conditions that lead the mechanisms to diverge and simulation conditions when the mechanisms lead to similar predictions.

Comparisons with chamber studies

Both the SAPRC and CB-IV chemical mechanisms have been evaluated by comparing model predictions to data collected in environmental chambers. The environmental chamber data, primarily from the University of California-Riverside, and the University of North Carolina-Chapel Hill, include a wide range of conditions representative of a variety of urban areas. The mechanisms have been tuned to represent as broad a set of scenarios as possible. Subsets of the environmental chamber data, which are particularly relevant to the conditions under which the mechanism predictions diverge, can be used to evaluate the performance of the two mechanisms.

Comparisons with TexAQS II observations

Current analyses of the differences between the two mechanisms suggest that additional production pathways for higher aldehydes in SAPRC are among the primary reasons for the differences in predictions between the two mechanisms. This suggests that detailed analyses of higher aldehyde production rates at a few key locations (such as the Moody Tower) could provide the data necessary for a performance evaluation of the two mechanisms. These measurements of higher aldehydes should be coordinated with other measurements of free radical sources and sinks, so that the overall performance of the mechanisms in modeling free radical sources and sinks can be evaluated. The evaluations should be performed under both NO_x-rich and NO_x-lean conditions.

Key TexAQS II or Other Study Data Needed:
1) Observational data from Moody Tower site on free radical sources, free radical sinks, and free radical concentrations.
2) Observational data for speciated hydrocarbons and oxides of nitrogen at the site where free radical measurements are collected.
3) Photochemical box model predictions of free radical source and sink rates at conditions measured at the observational sites.

Suggested Deliverable Products, Timelines and Lead Contacts:
1) Summary comparison of model predictions and observations at the Moody Tower
    Preliminary Report – October 31, 2006; Final Report – August 31, 2007;
    David Allen, Bill Carter, Harvey Jeffries, Barry Lefer (and other members of the
    Moody Tower Team with TexAQS II.)

Question J Approach

Question J (two parts):
How well do air quality forecast models predict the observed ozone and aerosol formation? What are the implications for improvement in air quality forecasts?

Question J Working Group:
Leader:
     Stu McKeen
Participants:
     Greg Carmichael
     Bryan Lambeth
     Ken Schere
     James Wilczak
     Greg Yarwood
     Daewon Byun
     John Nielsen-Gammon
     Michael Hardesty

Analysis Approach:
     Several research and forecast centers will be providing real-time forecasts O_3 and $PM_{2.5}$ aerosol during the TexAQS 2006 field study. Table 1 lists the modeling groups that have tentatively agreed to provide either the real-time forecasts or post-experiment results to a central facility, along with pertinent model details. Note that three of the models will provide two separate forecasts with different model resolutions. The full set of model forecasts will be part of a broader informal model comparison/evaluation that will statistically evaluate each model relative to the suite of photochemical, aerosol, and meteorological data collected from the various surface networks and mobile platforms operating in the vicinity of Houston. The primary short-term focus will be on evaluating their ability to forecast surface O_3 and $PM_{2.5}$ levels in comparison surface network data (CAMS and AIRNOW) that is typically available in near real-time. This comparison work will consist of two components, one of them in near real-time, where observations and model results are displayed on a web site for a few select surface sites (and the Ronald H. Brown ship data) during the experiment. The other component involves a detailed analysis of results for the entire study period, where standardized operational statistics will be used to identify biases and other deficiencies in each model, as well as for the ensemble determined from all the model forecasts. This component will provide a base set of statistics to directly address the first science question of this section, and provide initial guidance for addressing the second science question. A secondary, longer-term effort is necessary in order to identify sources of model bias and relative performance as more relevant, detailed, and quality-assured data become available from the various mobile platforms and intensive field sites typically not available until after the experiment.

O_3 and $PM_{2.5}$ surface networks: real-time model comparisons:
     NOAA's ESRL/CSD laboratory will host the central repository for air quality forecast model (AQFM) data collected in real-time during the TexAQS 2006 study period, as well as those forecasts made available after the field study willing to participate in the informal evaluation. NOAA ESRL/CSD will also collect near real-time AIRNOW network O_3 and $PM_{2.5}$ observations for a large fraction of the southern and midwestern US, TCEQ CAMS network O_3, $PM_{2.5}$, CO and NO_x observations available throughout Texas and western Louisiana, and O_3,

$PM_{2.5}$, CO, SO_2 and odd-nitrogen species from the NOAA Ronald H Brown research vessel. Web-based comparisons between time series of model forecasts and observations will be generated by NOAA's ESRL/PSD and CSD laboratories in near real-time for several of the network sites in eastern Texas as well as the ship data. The land-based sites will be chosen according to location relative to Houston and Dallas (upwind or downwind) and coincidence to other measurements available during the experiment (e.g. wind profilers, Moody Tower, Williams Tower, etc.). This near real-time analysis serves a two-fold purpose: the unambiguous and transparent collection of the real-time forecasts, and immediate guidance to each of the forecast groups as to relative model performance and veracity. The intention is to have the real-time comparison of the land-based sites up and running at least two weeks before the start of the intensive study that begins August 1, 2006. O_3 and $PM_{2.5}$ ensemble forecasts, based on techniques developed during the ICARTT/NEAQS-2004 model evaluation study, also will be provided at the selected network sites.

There is also the possibility of near real-time comparisons of forecast O_3 with data collected from the NOAA Twin-Otter ozone lidar that will be operational between August 1 and September 15, 2006. The infrastructure is in place to display comparisons with this platform on the same web site as the surface network comparisons. The limiting factors are the turn-around time, and the quality of the ozone retrievals that would be available in real-time.

O_3 and $PM_{2.5}$ surface networks: post-experiment statistical analysis

With all of the observations from the surface networks and model forecasts during the August-September 2006 time period in hand, NOAA's ESRL/CSD and PSD labs will provide summary statistics for O_3 and $PM_{2.5}$ according to previously developed statistical metrics. These include "bulk" statistical metrics such as correlation, bias, and root mean square error for the daily maximum 8 -and 1-hour averages for the case of O_3, and the 24-hour average for the case of $PM_{2.5}$. "Discrete" statistical measures relative to the maximum 8-hour O_3 average limit of 80 ppbv, and the daily $PM_{2.5}$ average of either 65 (current limit) or 35 $\mu g/m^3$ (proposed limit) will also be evaluated. The bulk statistics provide a basis for answering the primary question of how well do air quality forecast models predict observed ozone and aerosol formation for mean or median conditions. The discrete statistics address this same question for the extreme events of interest to those involved with regulation and compliance of O_3 and $PM_{2.5}$. Experience from the ICARTT/NEAQS model evaluation study has shown that no single forecast model simultaneously yields the best bulk and discrete statistics, that all models have high O_3 biases and nearly all have low $PM_{2.5}$ biases, and that corrected ensemble forecasts display the best "skill" in terms of both the bulk and discrete statistics. These results had direct implications for the improvement of air quality forecasts in the northeastern US, so one can logically expect the TexAQS 2006 model evaluations to contribute to similar implications for the region of eastern Texas.

Detailed post-experiment photochemistry/aerosol/meteorological analysis

Though this work is beyond the time frame of the Rapid Science Synthesis Team mandate, it is important to follow up the characterization of model biases and deficiencies determined from the surface network comparisons with explanations for their sources. The distributions of O_3 and $PM_{2.5}$ are determined by precursor levels, local and regional meteorology, as well as other factors that can only be examined through the integrated set of measurements within the TexAQS 2006 study. Relating deficiencies in emissions, transport and transformations within Eulerian models to the wealth of compositional and meteorological data collected from disparate observational platforms requires time, patience, and hard work from the detectives knowledgeable of the inner workings of each model.

Key TexAQS II or Other Study Data Needed:
1) Network connections, scheduling and deliveries of air quality forecast model results to the central repository.
2) Network connections, scheduling and deliveries of TCEQ CAMS data to the central repository (AIRNOW and NOAA Ronald H Brown data transfers already secured).
3) Determination of network sites to display for real-time comparisons.
4) Determination of real-time model display products that may be useful in addition to those outlined here.
5) Characterization of differences within emission inventories used by each forecast model.
6) All available data collected during TexAQS 2006 (for the detailed post-experiment analysis).

Suggested Deliverable Products, Timelines and Lead Contacts:
1) Securing data connections between forecast groups and central repository; July 1 to July 15, 2006;
Stu McKeen (NOAA ESRL/CSD), Jeff McQueen (NOAA NWS/NCEP), Richard Moffet (CMC), Wanmin Gong (CMC), Georg Grell (NOAA ESRL/GSD), Greg Carmichael (U of Iowa), Daewon Byun (U of Houston)
2) Real-time display of forecasts and observations at select network sites; Begin July 15, 2006;
Jim Wilczak (NOAA ESRL/PSD)
3) Statistical evaluation of O_3 and $PM_{2.5}$ forecasts for the entire study period; Preliminary Report - November 15, 2006; Final Report – August 31, 2007; Stu McKeen and Jim Wilczak

Table 1. Air quality forecast models available during TEXAQS-2006

Model Name	WRF-CMAQ	CHRONOS	AURAMS	WRF-Chem	BaronAMS MAQSIP-RT	U of Iowa STEM-2K3	U of Houston MM5/CB-IV
Met model	WRF-NMM	GEM	GEM	WRF-ARW	MM5	WRF-ARW	MM5
Horizontal res.	12km	21km	42km	12km	12km 4km	12km 4km	12km 4km
Vertical levels (in lowest 2km)	12	14	14	16	13	9	12(?)
Met IC's / BC's	GFS-GSI/ GFS	GEM/GEM	GEM/GEM	RUC/RUC	Eta/Eta GFS/GFS	GFS/GFS	GFS/GFS
Chemical mechanism	CBM-IV	ADOM-II	ADOM-II	RADM2	CBM-IV	SAPRC-99	CBM-IV
Anthro emissions	2001 NEI MOBILE6	CEPS	CEPS	NEI-99	NEI-2001 MOBILE5b	NEI-99	TCEQ-2001
Biogenic emissions	BEIS3.12 BELD3	BEIS2 BELD3	BEIS2 BELD3	BEIS3.11 BELD3	BEIS v3.9 BELD3	IGAC-GEIA	BEIS3.12 BELD3(?)
Chemical IC's and BC's	CMAQ default profiles	zero inflow open outflow	zero inflow open outflow	McKeen et al., 2002		nest within 60km res. / MOZART-2	CMAQ default profiles(?)
Aerosol Module	CMAQ modal	Bulk	Sectional-8	MADE/SORGAM modal	CMAQ modal	Sectional-6	CMAQ modal
Real-time availability	Surface O_3 only	Yes	Yes	Yes	No	Yes	Yes

Question K Approach

Question K:
How can observation and modeling approaches be used for determining:
    (i) the sensitivities of high ozone in the HGB non-attainment area to the precursor VOC and
        NOx emissions, and
    (ii) the spatial/temporal variation of these sensitivities?
(**Notes:** Questions F and K are closely related. Question K will specifically address the Houston
    area and its unique source mixture in detail. Question F will focus more generally on
    contrasts between the Houston area, the Dallas area and the greater eastern Texas region.)

Question K Working Group:
Co-Leaders:
        Basil Dimitriades
        David Parrish
Participants:
        Mark Estes
        Harvey Jeffries
        Ted Russell
        Tom Ryerson
        David Sullivan
        Will Vizuete
        Greg Yarwood
        Barry Lefer
Observers:
        Noor Gillani

Analysis Approach:
        This question is based upon the observation that the amount of ozone that can be
produced from a given mix of emissions depends strongly on the ratio of VOC (an important
radical source) to NO_x in that mix. Therefore, development of ozone control strategies should
consider this ratio since the balance of control of VOC versus NO_x emissions will affect the
efficacy of the control strategy. The goal of this analysis is to develop as detailed a picture as
possible, including spatial and temporal variability, of the sensitivity of ozone formation to NO_x
and various VOC emission categories in the Houston area. The unique mixture of sources in the
Houston-Galveston-Brazoria (HGB) area presents an exciting challenge for this study.
Approaches based both on modeling and observations will be pursued.
        The modeling approach will require high resolution modeling of the HGB area. A
PAQM equipped with an appropriate sensitivity analysis method (derived from the decoupled
direct method (DDM) or other methods) will be utilized. The model output will include the
sensitivity of both the daily maximum 1-hour and 8-hour average ozone to total VOC, HRVOC,
BVOC (biogenic VOC), OVOC (other VOC), and NO_x emissions at each point of the modeling
domain. Daily ozone sensitivity maps of the modeling domain will reflect the spatial variability
of the ozone sensitivities, and the temporal variation of these maps will reflect the temporal
variability. The modeling will cover as long a time period as practical, but will focus on the 5-
week period of the TexAQS-2006 field campaign. Correlation analyses of modeled ozone and
aerosol levels with the various sensitivities will reveal the mesoscale chemical environments that
are most closely associated with high ozone and aerosol.

The observation-based approach will rely on various "indicator" species and ratios (see Kleinman et al., 2000 and references therein) to determine sensitivity. As these methods have been applied, at least so far, they give an indication of NO_x versus VOC sensitivity of the chemistry that has produced the ozone in a sampled air parcel. Key measurements available in TexAQS 2006 include O_3, aerosol, NO_x, HNO_3, PAN and formaldehyde. The observation-based approach will be applied to aircraft data sets as well as to any suitable ground based measurements. Particular attention will be focused on the TRAMP data set to be collected at the Moody Tower of the University of Houston during TexAQS-2006. Several different "indicator" analyses have been described in the literature. The predictions of these different analyses will be compared and contrasted. Assuming that a consistent picture emerges, the spatial and temporal variations of these predictions will be analyzed to determine how the mesoscale chemical environments vary spatially and temporally across the HGB area, and how these variations correlate with dominant source region and meteorological conditions.

The approach described in the preceding paragraphs is general and lacks crucial details in many respects. The **initial tasks** of this analysis will be to clearly identify the modeling and observation-based approaches to be implemented. These tasks include:

- Identification and clear definition of the modeling program, the desired output, and the means by which that output is to be obtained.
- Identification of the personnel to implement the modeling.
- Securing the resources to support that modeling.
- Selection of the observation-based approaches to be implemented, and application of the approaches to presently existing data sets.

At the end of the process an **assessment of the reliability** of the findings will be crucial. This assessment should include:

- Comparisons of model predicted concentrations of species to observations. This should include concentrations of ozone, aerosols, their precursors, and other secondary pollutants.
- Comparisons of results from several observation- based approaches.
- Evaluation of the consistency between the model derived and observation derived conclusions regarding the sensitivity.

Finally it must be recognized that this is a very ambitious proposed approach to addressing this question, and completion of the total proposal is far from certain, especially since resources to support the needed work have not been identified. The primary deliverables will be expected to be state-of-the-analysis progress reports.

Key TexAQS II or Other Study Data Needed:
1) Spatially and temporally resolved inventories for total VOC, BVOC, HRVOC, and NOx, emissions for the HGB region for the modeling period.
2) Appropriate model output on maximum 1-hour and 8-hour average ozone sensitivities to VOC emissions and NOx emissions.
3) Aircraft measurements of O_3, other secondary pollutants, speciated VOC, NO_x, HNO_3, PAN, formaldehyde, and sunlight intensity.
4) Available measurements at surface sites similar to 3) for aircraft measurements.

Suggested Deliverable Products, Timelines and Lead Contacts:
1) Analysis of model-computed ozone sensitivities to VOC and NO_x emissions, throughout the HGB area.
   Final Report – August 31, 2007

Basil Dimitriades , David Parrish
2) Analysis of observation-based approaches applied to TexAQS 2000 data
Preliminary Report - October 31, 2006
David Parrish, Basil Dimitriades
3) Analysis of observation-based approaches applied to TexAQS 2006 data
Preliminary Report - October 31, 2006
David Parrish, Basil Dimitriades
4) Synthesis of model computed and observation-based approaches
Final Report – August 31, 2007
David Parrish, Basil Dimitriades

Question L Approach

Question L:

What existing observational databases are suitable for evaluating and further developing meteorological models for application in the HGB area?

Question L Working Group:

Co-leaders:

> Robert Banta
> Lisa Darby

Participants:

> John Nielsen-Gammon
> Daewon Byun
> Wayne Angevine
> Mark Estes
> Bryan Lambeth
> Stuart McKeen

Analysis Approach:

1) Compile a list of databases useful for model evaluation.
    a) Permanent measurements
    b) Enhanced measurements due to TexAQS II deployments

2) Determine which databases are most useful to modelers (quality control, accessibility, regional coverage, time resolution, etc.)

Key TexAQS II and other data sources:

1) Catalog of experiment measurements, including background, coverage, PIs, links to data, notes.
2) Use TexAQS II measurements to determine how the permanent measurements could be expanded to provide more useful data for modelers.

Listed below are databases that are potentially useful to those performing air quality modeling for Texas. A brief description follows many of the links to these databases.

SURFACE METEOROLOGY AND CHEMISTRY DATA

COOP observations

Wayne Angevine

http://www7.ncdc.noaa.gov/IPS/CDPubs?action=getstate

Consists of monthly printed pages (available as PDFs online) containing station observations. No description of QA is provided on the web site.

Because these data are not in machine-readable format, they are unlikely to be useful for any systematic study. They are redundant, in the sense that the same observations should be in the normal NWS data streams.

Crop Weather Program, Texas A&M University
Bryan Lambeth
http://cwp.tamu.edu/cgi-bin/htmlos.cgi/6742.2.1749378041063346623

    The Crop Weather Program for South Texas (CWP) was developed to help farmers and consultants make management decisions conducive to profitable crop production. It replaces an earlier cotton monitoring system known as the Weather Station Network Program. The CWP is the gateway for access to weather data measured by a network of 21 automated weather stations spread across 10 South Texas counties and provides hourly measurements of air temperature, relative humidity, solar radiation, wind direction and speed, precipitation, and soil temperature at 1", 3", and 8" depths. The wind direction is reported based on a 16-point compass and the wind speed appears to be arithmetic (no vector average direction or speed). The wind also appears to be measured about 10 feet above ground level based on an example site photo provided (this could exacerbate exposure problems where buildings and/or trees are nearby).

Harris County Office of Homeland Security and Emergency Management
Lisa Darby
http://www.hcoem.org/

    The Harris county rainfall map site allows you to enter an amount of time (in days, hours, or minutes) before the current time, and it produces a map of accumulated rainfall amounts from each site, over the time requested. The data come from 163 automatic remote sensors (part of the flood alert system) across the metropolitan area, and they are "unofficial" (probably means not QC'd). The density of the network allows for detailed information regarding the horizontal distribution of the rainfall. Their locations can be found on a map link and a text link, which includes latitudes and longitudes. There is a link to an archive site where you can indicate a given amount of time before your date of interest to obtain a map of accumulated rainfall, but I could not get this part to work. If this does eventually work, this could be a useful site for modelers, although it looks like the only output would be a map (i.e., no text dump). I suggest a following up on this site to determine if there a way to order the archived data.

    Also on the main page for Harris County Office of Homeland Security and Emergency Management is a link to a real time Houston speed map. Along the outlines of the major highways the current speed of traffic is shown in color (indicating speeds <20, 20-29, 30-39, 40-49, and 50+ MPH, or no data). On this site is a link to the Houston speed map archives (http://traffic.houstontranstar.org/map_archive/map_archive.aspx). From this site you can select a date and time (down to 15-minute intervals) and you get a traffic speed map for that time. This could be useful to determine if gridlock was worse on some days compared to others.

Texas A&M data
Lisa Darby
http://dallas.tamu.edu/Weather/index.html

    This web site has data from two sites near Dallas. The sites are run by the Texas A&M Dallas Agricultural Research and Extension Center (phone: 972.231.5362), and details are sketchy. The locations are not specified, although one is on a research farm (Prosper) and the other is just called "Dallas." The "Dallas" site has, by date, max/min soil temperature, max/min air temperature, max/min RH, a single column labeled "wind" (no units indicated on any of the columns), max/min soil moisture, and total rain. Some years have a column labeled ET_o (evapotranspiration?). At the end of each month is a row for monthly medians for each column and another row with the max, min, or total for each column (depending on the variable). The

Prosper site has the same variables, plus "RAD" (radiation?), wind speed, wind direction and battery voltage. The Dallas site has data archived from 2000 and the Prosper site has data archived from 1997. Given how important soil moisture measurements are for modelers, it may be useful to investigate this database further to determine the location of the sites and the robustness of the soil moisture data.

Lower Colorado River Authority network
Lisa Darby
http://hydromet.lcra.org/index2.shtml

Lower Colorado River Authority network. This web page has a wealth of information regarding measurements throughout the Colorado River watershed (which extends from NW to SE of Austin, becoming quite narrow at Matagorda Bay). The network is most dense around Austin. They have: rainfall (24-hr accumulation, accumulation since midnight, and the most recent measurement); stage, flow, lake level, air temperature, relative humidity, and conductivity data, shown on maps. You can download historic data for a single site (precipitation, air temperature, relative humidity, wind speed and direction), but this is not very practical for obtaining data from many sites. It is stated that real-time data are provisional, but there is no indication about the quality of the archived data. It may be worth investigating if it is possible to obtain archived data directly from the agency.

Texas A&M agricultural weather site
Stu McKeen
http://texaset.tamu.edu/weatherstns.php

Soil Climate Analysis Network, US Agriculture Department
Stu McKeen
http://www.wcc.nrcs.usda.gov/scan/
http://www.wcc.nrcs.usda.gov/scan/site.pl?sitenum=2016&state=tx

Louisiana agricultural weather data network
Stu McKeen
http://www.agctr.lsu.edu/subjects/weather/

Louisiana Universities Marine Consortium weather network.
Mark Estes
http://weather.lumcon.edu/

CAMS (TCEQ organized surface met and chem. data)
Daewon Byun
http://www.tceq.state.tx.us/nav/eq/mon_sites.html
http://www.tceq.state.tx.us/compliance/monitoring/air/monops/historical_data.html
METARs (NWS surface data)
Daewon Byun
http://www.nndc.noaa.gov/cgi-bin/nndc/buyOL-001.cgi

UPPER AIR DATA

ESRL (formerly ETL) Profiler Network, South Central Texas
John Nielsen-Gammon
http://www.etl.noaa.gov/et7/data/

The ESRL (formerly ETL) network page allows access to real-time and archived plots of profiler winds and other profiler data. Real-time plots are provided through a clickable map interface. Archived plots and ASCII data can be downloaded for single profilers. A trajectory tool allows the calculation of forward and backward trajectories using profiler data. The site includes all regular wind profilers from the NOAA and TCEQ network as well as all those installed for the TexAQS-II field program. The data includes profiler winds and signal-to-noise ratio, RASS virtual temperature and virtual potential temperature, and surface meteorological observations from profiler sites. Data should remain available for several months after the experiment, as well as the profiler trajectory tool.

NOAA National Profiler Network graphical display
John Nielsen-Gammon
http://www.profiler.noaa.gov/npn/

The NOAA site used to include all permanent profilers, but now it appears to contain only the profilers in the NOAA demonstration network, including Ledbetter, Palestine, and Jayton in Texas. Users can request real-time plots or generate plots using archived data. There is considerable flexibility in the online data plotting interface. Archived data are available from the web site hosts.

Rapid Update Cycle (RUC) soundings
John Nielsen-Gammon
http://rucsoundings.noaa.gov/

This sounding page allows the user to generate plots or ASCII data dumps of soundings from rawinsondes, profilers, and RUC/MAPS forecasts. The output is Java-based, allowing mouse-over data information and animation/looping of soundings. The interface requires the user to know the name or site ID's of the stations to plot. Most of the data is available only in real-time or near-real-time, except that an online rawinsonde archive was begun early in 2006. Perhaps the most useful aspect of the web site is the ability to plot forecast soundings from the RUC model. These forecasts are available for any arbitrary location and extend up to 12 hours into the future, so they provide detailed guidance for mixing heights, vertical wind shear, and convection.

University of Wyoming sounding page
John Nielsen-Gammon
http://weather.uwyo.edu/upperair/sounding.html

This web site allows the user to select a station using a clickable map and generate graphical soundings or ASCII data output from real-time or archived rawinsonde observations. The output format includes all common sounding diagram types and ASCII data formats. Large amounts of data would be difficult to obtain, but this site is the best available on the web for individual archived soundings.

ACARS aircraft observations
John Nielsen-Gammon
http://amdar.noaa.gov/

ACARS observations are in situ meteorological observations made by commercial aircraft. The data include temperature, wind, and often dewpoint. The wind precision is not very good, but the temperature and dewpoint data are useful for estimating mixing heights and their diurnal variation. Most ACARS observations in Texas come from the Dallas-Fort Worth area, usually about two dozen per day. Much less frequent observations are available from Houston and other major airports. The data is not freely available in real time on the web, but it is available for research purposes upon approval by NOAA. Texas A&M presently receives ACARS data but is not funded by TCEQ to process or use the data for analysis or forecasting during 2006.

COASTAL AND BUOY DATA SETS

Texas Coastal Ocean Observation Network, Texas A&M Corpus Christi, Conrad Blucher Institute
Wayne Angevine
http://lighthouse.tamucc.edu/TCOON/HomePage

Large network of coastal stations. Some of the reported stations are regular NOAA or other agency stations, and these are not identified as such. The additional stations seem to primarily provide water level, water temperature, and air temperature. Machine-readable historical data are available. Some QA is apparently done, but specifications are not easily found on the web site. This data set is possibly useful for improving resolution of model validations for simple parameters.

NDBC (National buoy data)
TABS/NOAA buoys and c-man stations
Bob Banta
http://www.ndbc.noaa.gov/Maps/WestGulf.shtml

NOAA PORTS buoys and platforms
Bob Banta
http://www.srh.noaa.gov/hgx/marine/pro.htm

SATELLITE DATA SETS
Satellite images (cloud & skin temperature)
Bob Banta
http://www.ssec.wisc.edu/

Volunteer?
Satellite data (sea surface winds)

SOLAR RADIATION

Texas Solar Radiation data, from a solar energy research group at UT.
Mark Estes
http://www.me.utexas.edu/~solarlab/tsrdb/

National Renewable Energy Lab (solar radiation data)
Mark Estes
http://rredc.nrel.gov/solar/new_data/confrrm/

MADIS
Bryan Lambeth
http://madis.noaa.gov/

The Meteorological Assimilation Data Ingest System (MADIS) is dedicated toward making value-added data available from the National Oceanic and Atmospheric Administration's (NOAA) Earth System Research Laboratory (ESRL) Global Systems Division (GSD) (formerly the Forecast Systems Laboratory (FSL)) for the purpose of improving weather forecasting, by providing support for data assimilation, numerical weather prediction, and other hydro-meteorological applications.

MADIS subscribers have access to an integrated, reliable and easy-to-use database containing the real-time and archived observational datasets described below. Also available are real-time gridded surface analyses that assimilate all of the MADIS surface datasets (including the highly-dense integrated mesonet data). The grids are produced by the Rapid Update Cycle (RUC) Surface Assimilation System (RSAS) that runs at ESRL/GSD, which incorporates a 15-km grid stretching from Alaska in the north to Central America in the south, and also covers significant oceanic areas. The RSAS grids are valid at the top of each hour, and are updated every 15 minutes.

- Observations
    - Meteorological Surface
        - METAR
        - SAO
        - Maritime
        - Modernized NWS Cooperative Observer
        - Integrated Mesonet
            - Observations from local, state, and federal agencies and private mesonets (including GPSMET water vapor)
    - Radiosonde
    - NOAA Profiler Network
    - Hydrological Surface
    - Automated Aircraft
        - Automated Aircraft Reports
        - Profiles at Airports
    - Multi-Agency Profiler
    - Radiometer
    - Satellite Wind
        - GOES Operational 3-Hour
        - GOES Experimental 1-Hour
    - Satellite Sounding
        - NOAA POES
    - Satellite Radiance
        - NOAA POES
    - Snow
- Grids
    - RSAS Surface Analyses

TCEQ Air Pollution Events
Bryan Lambeth
http://www.tceq.state.tx.us/compliance/monitoring/air/monops/sigevents06.html

The TCEQ Air Pollution Events web pages provide preliminary analyses of large-scale high ozone and/or particulate events in Texas. The analyses include satellite imagery, webcam imagery, ozone contour animations, ozone plume animations, backward air trajectories, upper air data graphs, and pollution data time series graphs. The discussions describe the intensity and geographic coverage of each event. The discussions also report any transport related aspects to the pollution, if appropriate, and provide an estimate of background levels and local add-on for ozone cases.

EDAS (NCEP grid reanalysis)
Daewon Byun
http://www.cdc.noaa.gov/cdc/reanalysis/reanalysis.shtml
http://dss.ucar.edu/pub/reanalysis/

Suggested Deliverable Products, Timelines and Lead Contacts:
1)   List of databases for modelers' use, including background, evaluations, and links to web sites;

Compiled list of experiment databases – September 30, 2006; Final Report – October 31, 2006;

Question L Working Group participants.

APPENDIX A. **A Partial List of Potentially Useful Reports, Journal Articles, and Web Links for Use by the Rapid Science Synthesis Team**

1) **SOS Report of Texas Relevant Scientific Findings – 1988-2005**

Excerpts from SOS News You Can Use: Texas Related Scientific Findings – 1988-2005, http://www.ncsu.edu/sos/pubs/SOSNYCU_Texas.pdf

2) **State Implementation Plans for Ozone in Texas Ozone Non-Attainment Areas – 2000-2007**

General website for various SIP documents is: http://www.tceq.state.tx.us/implementation/air/sip/sipplans.html

HGB   – 2000 SIP based on modeling of 1993 ozone episodes
　　　　-- 2002 revision, based on 2000 ozone episodes
　　　　-- 2004 revision, based on 2000 ozone episodes
　　　　-- 2007 SIP based on modeling of extended 2000 episodes
　　　　The currently expected "attainment year" for the 2007 HGB SIP is 2010.
DFW   – 1999 based on modeling of 1995 and 1996 ozone episodes
　　　　-- 2000 revision, also based on modeling of 1995 and 1996 ozone episodes – cement kilns added to emission sources of concern
　　　　-- 2001 further revision, also based on modeling of 1995 and 1996 ozone episodes --
　　　　-- 2002 still further revision, also based on modeling of 1995 and 1996 ozone episodes --
　　　　-- 2007 based on modeling of 1999 and 2002 ozone episodes
　　　　The currently expected "attainment year" for the 2007 DFW SIP is 2012.

TCEQ SIP Technical Support Documents

For the technical work performed for the 2002 Houston SIP revision, here is the website: http://www.tceq.state.tx.us/implementation/air/airmod/docs/hgmcr_tsd.html .

For the technical work performed for the 2004 Houston SIP revision, here is the website: http://www.tceq.state.tx.us/implementation/air/sip/dec2004hgb_mcr.html . The relevant documents are found in Chapter 3, which encompasses the photochemical grid modeling, and Chapter 4, which includes data analysis.

3) **Accelerated Science Evaluation Reports – 2001-2003**

Overview, 9/13/01, http://www.utexas.edu/research/ceer/texaqsarchive/accel_science_eval.PDF

Emissions Inventories, 2/05/03, http://www.utexas.edu/research/ceer/texaqsarchive/pdfs/Emission%20Inventoryv3.pdf

Atmospheric Chemistry, 5/26/02, http://www.utexas.edu/research/ceer/texaqsarchive/pdfs/Chemistry05_02.PDF

Meteorology, 5/30/02, http://www.utexas.edu/research/ceer/texaqsarchive/pdfs/Meteorology-version2.0final.PDF

Photochemical Air Quality Modeling, 2/17/02, http://www.utexas.edu/research/ceer/texaqsarchive/pdfs/Modeling02_17_02.PDF

Executive Summary, 11/13/02, http://www.utexas.edu/research/ceer/texaqsarchive/pdfs/EXEC_SUMMARY_Nov_02.pdf

4) **HARC Reports -- 2004–2006**
   http://www.harc.edu/Projects/AirQuality/Projects/ReportList

H029.2003. Investigation of unusual hydrocarbon observations during TexAQS 2000, by Larry Kleinman and Peter Daum, BNL. Relevant question = A

H012.2004.8HRA. The conceptual models prepared by John Nielsen-Gammon of Texas A&M. Relevant question = B

H006E.2002. Direct decoupled modeling of Houston, testing model sensitivity to magnitude of VOC emissions, Greg Yarwood, Environ. Relevant question = C

H044A.2005. Flights of TVA aircraft in support of 2005 field studies. Relevant question = C

H006B.2002. Lagrangian plume modeling study of TexAQS 2000 aircraft observations--a "top-down" emissions inventory approach, by Noor Gillani of UAH. Relevant question = D

H006C.2003. Positive matrix factorization of auto-GC VOC data, to do an observation-based source apportionment, by Phil Hopke and Sonoma Tech. Relevant question = D

H005.2002. Infrared camera study of ethene leaks, by Environ. Relevant question = E

H012.2004.8HRA. The conceptual models prepared by John Nielsen-Gammon of Texas A&M. Relevant question = G

H060, Phase I. Transport study for DFW, by Environ. See also H027, H028, and H035, all of which were modeling studies of DFW and/or E Texas, and most of which looked at some transport issue. Relevant question = H

H044.T117.2004, Tasks 4, 5. North East Texas Plume Study 2005. Preliminary results, by Noor Gillani, UAH. Relevant question = H

H012.2004. UT/Environ and UH final reports on modeling sensitivities, which examined modeling sensitivities to CB4/SAPRC, vertical mixing schemes, and alternative biogenic emissions. Relevant question = I

H045.S.2004. Ozone forecast modeling for 2005, UH and TAMU. Relevant question = J

H012.2004. UT/Environ and UH final reports on modeling sensitivities, which examined modeling sensitivities to CB4/SAPRC, vertical mixing schemes, and alternative biogenic emissions. Relevant question = J

H056.2005. C-band radar deployment in Dallas and Houston during summer 2005, by Larry Carey of Texas A&M. Relevant question = L

H46.T28.2004. New land cover data for the Houston nonattainment area, by UT Center for Space Research. Relevant question = L

H030.2004. Science synthesis of TexAQS 2000 and other Texas air quality studies, by Dave Allen of UT.

5) **TCEQ internal reports**

VOC characterization

Detection limits for auto-GC target compounds: http://www.tceq.state.tx.us/cgi-bin/compliance/monops/agc_esls

Estes et al., 2002. Analysis of auto-GC data from 1996-2001 to determine VOCs with largest ozone formation potential. [This document is also part of the 2002 SIP revision]. http://www.tceq.state.tx.us/assets/public/implementation/air/am/docs/hgb/tsd1/attachment6-agc_voc.pdf . Relevant questions = A, C, D, F

Boyer et al., 2002. Analysis of TexAQS 2000 canisters, as a part of the 2002 Houston SIP revision. http://www.tceq.state.tx.us/assets/public/implementation/air/am/docs/hgb/tsd1/attachment5-airborne_canister.pdf . Relevant questions = A, D, F, K

Data Analysis, 2003. DA Reports and appendices:
- Fang and McDowell, 2003. Analysis of canister data for the Houston-Galveston and Beaumont-Port Arthur areas. Appendix CC of Chapter 4 of the 2004 Houston SIP revision. http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/04042sipapcc.pdf . Figures for Appendix CC: http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/04042sipapccfigs.zip . Relevant questions = A, C, D, E, F
- Jolly, 2003. Assessing the importance of carbonyl compounds in ozone formation in Houston-Galveston: Relative reactivities of carbonyl and hydrocarbon species. Appendix EE of Chapter 4 of 2004 Houston SIP revision. http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/04042sipapee_pro.pdf . See also the figures for Appendix EE. Relevant questions = A, C, D, E, F
- Mercado, 2003. Time of daily peak ozone in the Houston area. Appendix AA of Chapter 4 of 2004 Houston SIP revision. http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/04042sipapaa_pro.pdf . Relevant questions = A, F, G, K

Jolly et al., 2004. Comparing the emissions inventory and ambient measurements for Houston. http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/HGBAppB.5.pdf and http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/HGBAppB.6.pdf . Relevant questions = A, D, E

Jolly and Schroeder, 2004. Analysis of HGB Enhanced Industry Sponsored Monitoring (EISM) data. July 21, 2004. http://www.tceq.state.tx.us/assets/public/implementation/air/am/committees/pmt_set/20040721/Analysis_of_HG_EISM_Data-JohnJolly.pdf . Relevant questions = A, C, D, E, F

Jolly, 2004. EISM data: Update of analysis. December 7, 2004. http://www.tceq.state.tx.us/assets/public/implementation/air/am/committees/pmt_set/20041207/EISM-JohnJolly.pdf . See also Appendix DD of Chapter 4 of the 2004 Houston SIP revision. http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/04042sipapdd_pro.pdf . Relevant questions = A, C, D, E, F

Jolly et al., 2004. An analysis of VOC reactivity in Houston. Appendix to Chapter 4 of 2004 Houston SIP revision. http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/04042sipapgg_pro.pdf . Relevant questions = A, C, D, E, F

Jolly, 2005. Environmental Monitoring and Emergency Response System (EMRS). June 15, 2005.

http://www.tceq.state.tx.us/assets/public/implementation/air/am/committees/pmt_set/20050615/EMRS-JohnJolly.pdf . Relevant questions = A, C, D, E, F

Jolly, 2005. EMRS data analysis update. November 10, 2005. http://www.tceq.state.tx.us/assets/public/implementation/air/am/committees/pmt_set/20051110/jolly-emrs_update.pdf . Relevant questions = A, C, D, E, F

Ozone

URS, 2004. Case studies of 2003 ozone episodes, using EISM data. http://www.tceq.state.tx.us/assets/public/implementation/air/sip/sipdocs/2004-05-HGB/04042sipapic_pro.pdf . Relevant questions = A, C, D, F, K

TCEQ ozone forecast accuracy statistics: http://www.tceq.state.tx.us/compliance/monitoring/air/monops/ozonestats.html Relevant question = J

Air quality monitoring data from aircraft: http://www.tceq.state.tx.us/implementation/air/data/projects/aircraft/data.html Relevant questions = D, G, H, L

QA data for aircraft monitoring data: http://www.tceq.state.tx.us/implementation/air/data/projects/aircraft/qa.html Relevant questions = D, G, H, L

Air trajectories for Texas cities: http://www.tceq.state.tx.us/assets/public/compliance/monops/data/trajectories/houstontraj.html Relevant questions = G, H, J, L

Historical air pollution data in Texas: http://www.tceq.state.tx.us/compliance/monitoring/air/monops/historical_data.html

FTIR operated at Seabrook: http://raqis.radian.com/pls/raqis/friendshippark . These last two web links are for data, not for analyses.

6) **TCEQ external contractor reports, and the resulting peer-reviewed journal articles.**

Senff et al., 2002. Spatial and temporal variations in mixing height in Houston. TNRCC Project F-20, http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/mm/Mixing_Height_Variations_Houston.pdf . Relevant question = B

Xie and Berkowitz, 2005. Source attribution and emission adjustment study: Task 1. Back trajectory climatology and identification of key source regions. 10 January 2005. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/ei/Source_Attribution_and_Emission_Adjustment_Study_Task1.pdf   Additional figures available from TCEQ—contact Mark Estes at mestes@tceq.state.tx.us .

Xie and Berkowitz, 2006. The use of positive matrix factorization with conditional probability functions in air quality studies: An application to hydrocarbon emissions in Houston, Texas. *Atmos. Environ*., 40(17):3070-3091.

Buzcu and Fraser, 2005. Source identification and apportionment of volatile organic compounds in Houston, TX. *Atmos. Environ*., 40(13): 2385-2400. Relevant questions = A, C, D, E, F, K.

Darby et al. Evaluation of Houston sea breeze and circulation of pollutants. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/mm/Houston_Sea_Breeze_and_Pollutants_Circulation.pdf . See also Lisa S. Darby. 2005: Cluster Analysis of Surface Winds in Houston, Texas, and the Impact of Wind Patterns on Ozone. *Journal of Applied Meteorology*: Vol. 44, No. 12, pp. 1788–1806. Relevant questions = B, G, H

NOAA researchers, 2003. TexAQS 2000, analysis of NOAA data. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/da/TexAQS2000_NOAA_Data_Analysis.pdf

Ryerson et al., 2003. Effect of petrochemical industrial emissions of reactive alkenes and NOx on tropospheric ozone formation in Houston, Texas. *Journal of Geophysical Research*, VOL. 108, NO. D8, 4249, doi:10.1029/2002JD003070, 2003.

Wert et al., 2003. Signatures of terminal alkene oxidation in airborne formaldehyde measurements during TexAQS 2000. *Journal of Geophysical Research*, VOL. 108, NO. D3, 4104, doi:10.1029/2002JD002502, 2003.

Brock, C. A., et al., Particle growth in urban and industrial plumes in Texas, *J. Geophys. Res.*, 108(D3), 4111, doi:10.1029/2002JD002746, 2003. Relevant questions = A, C, D, F, I

White and White. TexAQS 2000 wind profiler and GPS sounding quality control. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/da/Profiler_Sounding_QC.pdf
Relevant question = B

Hafner Main et al., 2001. Characterization of auto-GC data in Houston http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/da/CharacterizationAutoGCdata.pdf

Brown and Hafner Main, 2002. Acquisition, review and analysis of 1998-2001 auto-GC VOC data in the Houston area. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/da/AutoGC_VOC_Data_Houston_Final_Report.pdf

Brown and Hafner Main, 2003. Exploratory source apportionment of Houston's Clinton Drive auto-GC 1998-2001 data. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/da/Source_Apportionment_of_AutoGC_Data.pdf

Kim et al., 2005. Characterization of non-methane volatile organic compounds in Houston during 2001 using positive matrix factorization. *Atmos. Environ*. 39:5934-5946.
Relevant questions = C, D, E, F, K

Kleinman L. I., P. H. Daum, D. Imre, Y.-N. Lee, L. J. Nunnermacker, S. R. Springston, J. Weinstein-Lloyd, and J. Rudolph, Ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston, *Geophys. Res. Lett.*, 29 (10), doi:10.1029/2001GL014569, 2002. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/oth/Ozone_Production_Rate_and_Hydrocarbon_Reactivity.pdf

Kleinman L. I., P. H. Daum, D. Imre, Y.-N. Lee, L. J. Nunnermacker, S. R. Springston, J. Weinstein-Lloyd, J. Rudolph, Correction to "Ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston", *Geophys. Res. Lett.*, 30 (12), 1639, doi:10.1029/2003GL017485, 2003. Relevant questions = A, D, F, I, K

COAST Study of 1993

7) **John Nielsen-Gammon Conceptual Models of 2005 and the TCEQ Conceptual Model – 2006**

John Nielsen-Gammon's Conceptual Meteorological Models are already available and selected parts of the more general TCEQ Conceptual Model will soon become available within 2006 – all three of these documents contain detailed bibliographies.
http://www.harc.edu/Projects/AirQuality/Projects/Projects/H012.2004.8HRA

8) **TCEQ Reports prepared by external contractors but not yet submitted to TCEQ -- 2006**

Ryerson, T.B., K.K. Perkins, M. Trainer, D.K. Nicks Jr., J.S. Holloway, J.A. Neuman, F. Flocke, A. Weinheimer, S.G. Donnelly, S. Schauffler, V. Stroud, E.L. Atlas, D.D. Parrish, R.W. Dissly, G.J. Frost, G. Hubler, R.O. Jakoubek, P.D. Goldan, W.C. Kuster, D.T. Sueper, A. Fried, B. P. Wert, R.J. Alvarez, R.M. Banta, L.S. Darby, C.J. Senff, and F.C. Fehsenfeld. Chemical and meteorological influences on extreme (>150 ppbv) ozone exceedances in the Houston metropolitan area. Draft report, TCEQ Contract No. 582-4-65613.

9) **David Allen's State of Science Reports – 2004-2006**

H030 – State of the Science of Air Quality in Eastern Texas: Major Scientific Findings and Recommendations, 7/31/2004,
    http://files.harc.edu/Projects/AirQuality/Projects/H030.2004/H30FinalReport.pdf

H004 – Particulate Matter Concentrations, Compositions, and Sources in Southeastern Texas: State of Science and Critical Research Needs,
    http://files.harc.edu/Projects/AirQuality/Projects/H004.2002/H4PMScienceReport.pdf

10) **Selected Peer-Reviewed Publications**

Murphy, C.F. and D.T. Allen. 2005. Hydrocarbon emissions from industrial release events in the Houston-Galveston area and their impact on ozone formation. Atmos. Environ. 39: 3785-3798. Relevant questions = A, C, F

Geyer, A., et al. 2003. Direct observations of daytime NO_3: Implications for urban boundary layer chemistry, J. Geophys. Res.-Atmos., 108, 4368, doi:4310.1029/2002JD002967. (Destruction of O_3 thru NO_3 in TexAQS 2000)

Lei, W., R. Zhang, X. Tie, and P. Hess. 2004. Chemical characterization of ozone formation in the Houston-Galveston area: A chemical transport model study, J. Geophys. Res., 109, D12301, doi:10.1029/2003JD004219.

Morris, G.M., et al., Alaskan and Canadian forest fires exacerbate ozone pollution over Houston, Texas, on 19 and 20 July 2004, J. Geophys. Res., in press, 2006.

Zhang, R., W. Lei, X. Tie, and P. Hess, Industrial emissions cause extreme urban ozone diurnal variability, PNAS, 101, 6346–6350, 2004. www.pnas.org doi: 10.1073pnas.0401484101

Also, see bibliographies in many of the resources listed above.