Preliminary Findings from the Second Texas Air Quality Study (TexAQS II)

A Report to the
Texas Commission on Environmental Quality

by the
TexAQS II Rapid Science Synthesis Team

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These contributions include:

- Defining the objectives of TexAQS II,
- Instrumenting the various air-quality measurement platforms,
- Implementing and quality assuring the myriad field measurements during the course of the study,
- Completing the analysis, interpretation, and intercomparison of research results (including this report of Preliminary Findings from TexAQS II), and later
- Formulating carefully crafted consensus statements of research program findings to be used for policy purposes by TCEQ and other stakeholders.

Cooperating State Government Organizations

California Air Resources Board
Texas Commission on Environmental Quality
   Chief Engineer’s Office (CEO)
   Air Quality Division (AQD)
      Air Modeling and Data Analysis (AMDA)
      Industrial Emissions Assessment (IEA)
   Toxicology
Office of Compliance and Enforcement
Field Operations Division
   Region 4 – Dallas/Fort Worth
   Region 12 – Houston
Monitoring Operations (MonOps)
   Ambient Monitoring
   Air Laboratory and Mobile Monitoring
Data Management and Quality Assurance

Cooperating Texas Local Government Organizations

Alamo Area Council of Governments (AACOG)
Capital Area Council of Governments (CAPCOG)
City of Corpus Christi
City of Victoria

Cooperating Federal Government Agencies

Department of Defense (DOD)
   Navy Postgraduate School (NPS)
Department of Energy (DOE)
   Pacific Northwest Laboratory (PNL)
   Argonne National Laboratory (ANL)
   Los Alamos National Laboratory (LNL)
Department of Interior (DOI)
   Minerals Management Service (MMS)
Environment Canada (EC)
   Meteorological Service of Canada (MSC)
National Aeronautics and Space Administration
   Headquarters Science Mission Directorate and science teams for the
      Atmospheric Infrared Sounder (AIRS),
      Cloud-Aerosol Lidar Infrared Pathfinder Satellite Observations (CALIPSO),
      Moderate Resolution Imaging Spectroradiometer (MODIS),
      Multi-angle Imaging SpectroRadiometer (MISR)
      Ozone Monitoring Instrument (OMI), and
      Tropospheric Emission Spectrometer (TES)
Jet Propulsion Laboratory (JPL)
Langley Research Center (LRC)
National Oceanic and Atmospheric Administration (NOAA)
   Office of Oceans and Atmospheric Research (OAR)
      Earth System Research Laboratory (ESRL)
      Pacific Marine Environmental Laboratory (PMEL)
      Atlantic Oceanographic and Meteorological Laboratory (AOML)
      Air Resources Laboratory (ARL)
      National Weather Service (NWS)
      National Environmental Satellite Data and Information Service (NESDIS)
      Office of Marine and Aviation Operations (OMAO)
National Science Foundation (NSF)
   National Center for Atmospheric Research (NCAR)
Tennessee Valley Authority (TVA)
United States Environmental Protection Agency (USEPA)

Cooperating Research Universities
   Baylor University
   California Institute of Technology
   Chalmers University of Technology, Göteborg, Sweden
   Fort Hayes State University
   Georgia Institute of Technology
   Howard University
   Lamar University
      Texas Air Research Center (TARC)
   North Carolina State University
   Pennsylvania State University
Portland State University
Rice University
Scripps Institution of Oceanography
Texas A&M University
Texas Tech University
University of Alabama in Huntsville
University of California at Los Angeles
University of California at Santa Cruz
University of Colorado
  Cooperative Institute for Research in Environmental Science (CIRES)
University of Houston
University of Manchester, Manchester, UK
University of Maryland Baltimore County
University of Massachusetts
University of Miami
University of New Hampshire
University of Rhode Island
University of Texas in Austin
University of Washington
  Joint Institute for Study of Atmosphere Oceans (JISAO)
Valparaiso University
Washington State University

**Cooperating Private Sector Organizations**
Aerodyne Research Inc.
Baron Advanced Meteorological Systems
Exxon Mobil Corporation
Houston Regional Monitoring Network
Science Systems and Applications, Inc.
SensorSense, The Netherlands
Shell Oil Corporation
Sonoma Technology, Inc.
URS Corporation

**Other Cooperating Organizations**
Houston Advanced Research Center (HARC)
Texas Environmental Research Consortium (TERC)
Executive Summary

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 the Texas Commission on Environmental Quality (TCEQ). Answers to these important questions are needed by TCEQ and other stakeholders in Texas to help fulfill the Commission’s responsibility to develop scientifically sound State Implementation Plans (SIPs) by which to attain the recently implemented 8-hour National Ambient Air Quality Standards (NAAQS) for Ozone. SIPs for both the Houston-Galveston-Brazoria and the Dallas-Fort Worth Ozone Non-Attainment Areas are scheduled to be completed early in 2007.

The full report of Preliminary Findings from TexAQS II and this Executive Summary are designed to provide critical information as quickly as possible. The full report addresses: 1) significant sources of ozone and aerosol pollution in Texas, 2) the photochemical and meteorological processes that are responsible for the production and distribution of these pollutants, 3) a preliminary assessment of the skill of current air quality models and recommendations for improvement of these models, and 4) recommendations for further analysis and interpretation of the huge body of air quality data and information that has been accumulated during the 18-month-long TexAQS II study in 2005 and 2006, similar observations during the six-week-long TexAQS 2000 intensive study, and related but less comprehensive field measurements in 2002 and 2004.

This Executive Summary is designed to provide a short introduction to these Preliminary Findings for use by TCEQ managers and other air-quality decision makers and stakeholders in Texas. The Summary contains a complete list of the 12 important questions that are presently being faced by air quality managers in the state and a series of Preliminary Findings that have been developed in response to each of these questions.

The institutional affiliations of the scientists responsible for the analyses leading to these findings are given in the Acknowledgments. The full report also provides a brief discussion of the analyses that support each of these preliminary findings. The concerned reader should carefully consider the caveats contained in these discussions.

We emphasize that these findings are tentative and based on initial analysis of preliminary data gathered during the several field studies described above. More through and comprehensive analyses are already underway and will yield a great deal of additional important information in the future.

* Note that questions in **blue** have been designated by TCEQ for special emphasis.
Preliminary Findings

Question 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., $\geq 84$ ppbv)?

Preliminary Finding A1: The highest (i.e. $> 125$ ppbv) ozone concentrations in Houston result from rapid and efficient ozone formation in relatively narrow, intense plumes, which originate from HRVOC and NOx, co-emitted from petrochemical facilities. Winds carry these plumes throughout the urban area; shifts in wind direction lead to the transient high ozone events observed at monitoring sites. Neither petrochemical facilities, nor transient high ozone events, are present in Dallas and eastern Texas, which accounts for the absence of the highest ozone in those regions. This general picture did not change between 2000 and 2006, although the maximum observed ozone levels were lower in 2006.

Preliminary Finding A2: A characteristic meteorology leads to the highest 8-hour average ozone concentrations (and ozone design values) observed in west Houston; the ozone formation during these episodes is controlled by high morning HRVOC concentrations in the Ship Channel, followed by further ozone production as the air parcels advect to west Houston.

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

Preliminary Finding B1: Boundary-layer structure and mixing near and over Galveston Bay and the eastern Houston ship channel area are spatially complex and variable from day to day. Vertical mixing profiles often do not fit simple models or conceptual profiles. High concentrations of ozone and aerosols are sometimes found above the planetary boundary layer in parts of the HGB ozone non-attainment area.

Preliminary Finding B2: Complex coastal winds are not necessary for accumulation of high concentrations of ozone in Houston.

Preliminary Finding B3: After sea breeze days, the Houston plume often is broadly dispersed at night through the formation of a low-level jet.

Preliminary Finding B4: The Dallas ozone plume can extend well beyond the existing ground-based ozone monitoring network.

Question C
Are highly reactive VOC and NOx 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 NOx?
Preliminary Finding C1: There are indications that HRVOC emissions from industrial sources in the Houston area have decreased by a factor of two since 2000.

Preliminary Finding C2: The latest available emission inventories still underestimate ethene emissions by approximately an order of magnitude.

Question D
What distribution of anthropogenic and biogenic emissions of ozone and aerosol precursors can be inferred from observations?

Preliminary Finding D1: Several rural electric utility power plants in the Houston area and in east Texas have substantially decreased their NOx emissions per unit power generated since the TexAQS 2000 study. With one exception, preliminary analysis suggests that SO2 emissions have not changed appreciably since 2000 for the plants sampled in 2006. Several power plants continue to emit substantially more CO than expected.

Preliminary Finding D2: On-road mobile emission inventories developed from MOBILE6 have significant shortcomings. MOBILE6 consistently overestimates CO emissions by about a factor of 2. It accurately estimated NOx emissions in the years near 2000, but it indicates decreases in NOx emissions since then, while ambient data suggests NOx emissions have actually increased. Consequently in 2006, NOx to VOC emission ratios in urban areas are likely underestimated by current inventories.

Preliminary Finding D3: NOx emissions from ships are a strong function of vessel speed, and inventories based on AP-42 emission factors will significantly overestimate ship NOx emissions in Galveston Bay and the Houston Ship Channel.

Preliminary Finding D4: Work is in progress to correlate measured mixing ratios of biogenic VOC over NE Texas with emission inventories. Preliminary findings indicate that: (i) there may be an area south of Dallas-Fort Worth in which isoprene emissions were lower than indicated by the inventories, and (ii) monoterpene mixing ratios in general were relatively low.

Question E
Are there sources of ozone and aerosol precursors that are not represented in the reported emissions inventories?

Preliminary Finding E1: The observed concentrations and distribution of ambient formaldehyde are broadly consistent with daytime photochemical production associated with olefin emissions. Primary formaldehyde emissions appear to be significantly less important, with more precise quantification awaiting additional analysis.

Preliminary Finding E2: Concentrated plumes of ammonia were observed occasionally in the Houston Ship Channel area.

Preliminary Finding E3: Concentrated plumes of gaseous mercury from at least one point source were observed in the Houston Ship Channel area.
Question F
How do the mesoscale chemical environments (NOx-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?

Preliminary Finding F1: At the highest ozone concentrations, the observed relationship between ozone and the products of NOx oxidation indicates less efficient ozone production in the Dallas area than in the Houston area. In the observation-based indicator species approach, this behavior corresponds to less NOx-sensitive and more VOC- or radical-sensitive ozone formation in Dallas compared to Houston.

Question 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?

Preliminary Finding G1: The maximum background ozone concentrations encountered in 2006 exceeded the 8-hour NAAQS. On average, air of continental origin had higher background concentrations than marine air. The average background O3 concentrations measured in 2006 in eastern Texas complement a previously developed climatology.

Preliminary Finding G2: The net ozone flux transported out of Houston averages about a factor of three larger than the corresponding flux from Dallas. The fluxes from these urban areas are significant contributors to the background ozone in the eastern Texas region.

Preliminary Finding G3: Elevated background ozone concentrations for urban areas include the recirculation of local emissions.

Preliminary Finding G4: Plumes from Texas urban areas make substantial contributions to the ozone, aerosol, and precursor concentrations in the rural regions of eastern Texas.

Preliminary Finding G5: Dust of African origin and sulfate aerosol advected into the region, even under southerly flow conditions from the Gulf of Mexico, make significant contributions to the background aerosol in the eastern Texas region.

Preliminary Finding G6: Nighttime chemistry influences the availability of oxides of nitrogen (NOx) and O3 the next morning.

Preliminary Finding G7: Low rural nighttime ozone concentrations have been observed at some, but not all, rural locations in northeast Texas; these low nighttime ozone concentrations are not replicated in the regulatory modeling.
Question H
Which areas within Texas adversely affect the air quality of non-attainment areas in Texas?
Which areas outside of Texas adversely affect the air quality of non-attainment areas in Texas?

Preliminary Finding H1: Ozone can be transported into the Dallas area from the Houston area.

Preliminary Finding H2: High ozone concentrations in eastern Texas result from both in-state sources and transport of continental air from the east and northeast.

Preliminary Finding H3: A synthesis of satellite and in situ measurements with photochemical modeling and Lagrangian trajectory analyses provides a quantification of regional influences and distant sources on Houston and Dallas air quality during TexAQS 2006.

Preliminary Finding H4: Ozone transport modeling for the Dallas area shows that local emissions and transport each contributed about equally to the average 8-hr ozone exceedance in 2002.

Question I
Why does the SAPRC chemical mechanism give different results than the carbon bond (CB-IV) mechanism?
Which replicates the actual chemistry better?

Preliminary Finding I1: Air quality modeling for both 2000 and 2006 shows substantial differences in the ozone concentrations predicted by the SAPRC and CB-IV chemical mechanisms.

Preliminary Finding I2: Comparison of environmental chamber experiments with mechanism predictions indicates that both SAPRC and CB-IV under-predict ozone concentrations under conditions with high NOx availability.

Preliminary Finding I3: In regions with very high hydrocarbon reactivity, near high NOx emission density, differences in ozone formation and accumulation predictions between the SAPRC and CB-IV mechanisms are due to differences in: (1) the chemistry of mono-substituted aromatics (e.g., toluene), (2) nitric acid formation rates, and (3) the rates of free radical source terms in the SAPRC and CB-IV mechanisms.

Preliminary Finding I4: Ozone productivities predicted by the SAPRC mechanism are generally higher than those predicted by CB-IV.

Question J
How well do air quality forecast models predict the observed ozone and aerosol formation?
What are the implications for improvement of ozone forecasts?

Preliminary Finding J1: Photochemical model ensembles, particularly when they are combined in an optimal manner, outperform any individual forecast model overall.

Preliminary Finding J2: Sophisticated data assimilation of meteorological and even chemical observations is essential for improving photochemical model forecasts.

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?

Preliminary Finding K1: Both Eulerian and Lagrangian plume modeling approaches indicate that in 2000 the high ozone in the HGB area was sensitive to both VOC and NOx emission reductions (Wert et al., 2003; TCEQ, 2004, 2006).

Preliminary Finding K2: An observation-based approach to determine the sensitivities of high ozone in the HGB non-attainment area to the precursor VOC and NOx emissions has been investigated; it has yielded ambiguous results.

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

The final report for Question L can be found in Appendix 2 of this Report.
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). Responses to these important questions, listed 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 by which to address TCEQ’s SIP-Relevant Science Questions were 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). These approaches are described in a Progress Report from the RSST dated July 31, 2006. 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 Working Group consists of 8-15 individuals (listed on pages 3 and 4; contact information is given in Appendix 1) drawn from various university-, state-, federal-, and private-sector organizations. All of these individuals have specialized knowledge in realms of science that are essential to provide insight into one or more of TCEQ’s High Priority SIP-Relevant Science Questions.

TCEQ has delineated these Science Questions to provide information for their development of SIPs for two very different and very large ozone non-attainment areas within Texas:

1) The HGB ozone non-attainment area is a COASTAL urban region of about 4 million people. It 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 (especially the Houston Ship Channel and other nearby industrial sites).

2) The DFW ozone non-attainment area is an INLAND urban region of about 5 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 nearby locations within northeastern Texas.

Technical Liaison within TCEQ for the science assessment functions of the RSST is provided mainly by Mark Estes and Jim Smith 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.
TCEQ’s High Priority SIP-Relevant Science Questions and Leaders (L), Participants (P) and Observers (O) in Working Groups of 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 de Gouw, Basil Dimitriades, David Allen, Mark Estes, Bernhard Rappenglück, 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?

C Are highly-reactive VOC and NOx 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 NOx?
L – David Parrish, P – David Allen, Joost de Gouw, 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?

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 de Gouw, David Sullivan, John Jolly, David Allen, Eric Williams, Barry Lefer, Bernhard Rappenglück

Sensitivity to VOC and NOx emission reductions

F How do the mesoscale chemical environments (NOx-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?
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?

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?

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 de Gouw, Barry Lefer, Bernhard Rappenglück, 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?

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?

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

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

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, tall tower-based, and ground-based field measurements was organized under the scientific leadership of Peter Daum of Brookhaven National Laboratory, Jim Meagher and Fred Fehsenfeld of NOAA (in what was then called the Aeronomy Laboratory of NOAA), the SOS Office of the Director at NC State University, Jim Thomas, Jim Price, and others of the Texas Commission on Environmental Quality, 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 NOx 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 Houston Ship Channel and Galveston Bay.

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 including aircraft-based, research-vessel-based, tower-based, balloon-based, ground-based, and satellite-based measurements, as well as 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 2005 and extended through October 15, 2006. Like the First Texas Air Quality Study (TexAQS 2000), the field-measurements part of TexAQS II was one of the most comprehensive air quality field research studies ever undertaken in the United States. Also, as in the case of TexAQS 2000, the analysis and interpretation phases of TexAQS II will extend for many months (and most likely several years) after completion of the field measurements part of this program.

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 did occur, both
together with and separately from, occasional episodes of high concentrations of airborne particulate matter.

The TexAQS II study culminated during the months of August, September, and October 2006 with a very intensive series of coordinated chemical and meteorological measurements and modeling studies. In order to distinguish this relatively short-term but very intensive 2-and-a-half-month-long intensive study from the earlier parts 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 air-quality measurement platforms used during TexAQS 2006 included:

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, a mobile solar occultation flux research laboratory, 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 was positioned at locations within the Houston Ship Channel and Galveston Bay 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-foot-tall Moody Tower at the University of Houston.
5) Extensive observations of ozone, aerosols, and carbon monoxide by an array of instruments based on NASA’s Aura, Aqua, Terra and NOAA GOES satellite platforms.

The multimillion-dollar 18-month-long TexAQS II field research study and its embedded short-term intensive study, TexAQS 2006, was conducted jointly by staff of TCEQ and by scientists and engineers working under contracts issued by TCEQ, the Texas Environmental Research Consortium (TERC) through the Houston Advanced Research Center (HARC), and through formal and/or informal agreements for cooperation with the many other research organizations listed in the *Acknowledgments* of this Report.

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 already have been invested in completing the field measurements and preliminary analyses of the measurement and modeling studies that are summarized in this Preliminary Report to TCEQ. But much more time and even more creative intellectual energy will have to be applied in thorough analysis, interpretation, synthesis, and eventual translation of 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.

The very limited time available between completion of many of the TexAQS II field measurements and the deadline for preparation and final submission of the SIPs required for eastern Texas is extraordinarily short. Thus, careful plans have been made by the RSST and other TexAQS II scientists and engineers in order to use with efficiency the very limited time that is available – 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 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.

**Formulation of “Preliminary Findings” from TexAQS 2000 and TexAQS II Results**

During the entire 18-month period of TexAQS II, the measurement data obtained from all of the several field observation platforms described above were subjected to very preliminary screening for obvious errors and then stored in centralized data files that are accessible for more detailed quality assurance and quality control checks before more rigorous analysis and interpretation by the RSST and other investigators within the several TexAQS II Science Teams. These databases are maintained by several of the institutions whose scientists and engineers are involved in TexAQS II. The Chemical Sciences Division of NOAA’s Earth System Research Laboratory also provides a valuable website for large parts of the TexAQS II data archives and essentially all of the deliverable products developed by members of the RSST ([http://esrl.noaa.gov/csd/2006/](http://esrl.noaa.gov/csd/2006/)).

As shown on this website, during August and September 2006, various members of the RSST provided very preliminary reports of measurements made and some of the results that were relevant to one or more of TCEQ’s SIP-Relevant Science Questions (see the list of presentations dated August 18 and 25 and September 1, 8, 15, 22 and 29). These presentations were shared with other RSST and TCEQ scientists and engineers through the interactive Webinar system maintained by TCEQ.

On October 12 and 13, 2006, even more detailed initial analyses of TexAQS II results were presented at a day-and-a-half long face-to-face RSST Workshop by members of the RSST. Each of these presentations will be available on the TCEQ website ([http://www.tceq.state.tx.us/implementation/air/airmod/texaqs-files/TexAQS_II.html](http://www.tceq.state.tx.us/implementation/air/airmod/texaqs-files/TexAQS_II.html)).

All of these 41 presentations were developed on the basis of air quality measurements that were carefully made. But these data have not yet been subjected to the rigorous quality assurance and quality control checks, and, even more importantly, to the data and information intercomparisons that are essential in the development of firm and well supported scientific conclusions.

As President Theodore Roosevelt once said: “Scientists are intellectuals who view each others’ work with quarrelsome interest.” This is why the research results described in these earlier RSS Webinar presentations, the presentations at the RSST Workshop, and even the results described in this RSS report of Preliminary Findings are indeed called “Preliminary Findings” – they are still at the stage of “quarrelsome interest” among our RSST colleagues. Thus, the Preliminary Findings presented in this report will still undergo more rigorous discussion and debate, not only among TexAQS II scientists and engineers, but also together with other scientists and engineers in the wider scientific community.
A carefully developed set of “Guidelines for Formulation of Scientific Findings to be used for Policy Decision Purpose” developed some year ago by the Oversight Review Board for NAPAP – the National Acid Precipitation Assessment Program – were provided to all scientists and engineers in the TexAQS II field research program.

Bearing in mind these ideas and guidelines about “preliminary,” “rigorous,” and “policy-relevant” scientific findings, let us now examine some of the data and information developed in TexAQS II research that is relevant to each of TCEQ’s 12 SIP-Relevant Scientific Questions.
Preliminary Response to Question A

Question 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)?

Question A Working Group
Leader: David Parrish; Participants: Tom Ryerson, Joost de Gouw, Basil Dimitriades, David Allen, Mark Estes, Bernhard Rappenglück; Observer: Noor Gillani.

Preliminary Findings

Preliminary Finding A1: The highest (i.e. > 125 ppbv) ozone concentrations in Houston result from rapid and efficient ozone formation in relatively narrow, intense plumes, which originate from HRVOC and NOx co-emitted from petrochemical facilities. Winds carry these plumes throughout the urban area; shifts in wind direction lead to the transient high ozone events observed at monitoring sites. Neither petrochemical facilities, nor transient high ozone events, are present in Dallas and eastern Texas, which accounts for the absence of the highest ozone in those regions. This general picture did not change between 2000 and 2006, although the maximum observed ozone levels were lower in 2006.

Overview of ozone exceedances in Houston and Dallas
Figure A1 shows that maximum ozone concentrations throughout Houston and Dallas have decreased from 1978 to 2005. (The 8-hour O3 design value for each monitor is the 3-year average of the fourth-highest daily maximum 8-hour-averaged ozone concentrations measured at that monitor; these values are representative of the maximum ozone observed and the levels of specific concern in developing control strategies.) The decrease is greater in Houston, from over 150 ppbv to near 100 ppbv, than in Dallas, from about 120 ppbv to near 95 ppbv. However, most of the decrease in Houston occurred before 1990. The fluctuations in both urban areas since 1990 make it difficult to determine whether the apparent decreases since 1999 are due to emission changes or to meteorological variations.

The design values in Houston are now approximately the same as in Dallas, but acute ozone episodes are much more frequent in Houston than Dallas. In the 2000-2005 period Houston has had 219 8-hour ozone exceedance days, while Dallas has had 203. In contrast, in the same period Houston has had 147 one-hour ozone exceedance days, but Dallas has had only 24. Over 60% of Houston’s eight-hour ozone exceedances were accompanied by one-hour exceedances.

In Houston the local design value maxima have not changed locations during that period, and have persisted in the vicinity of Deer Park, Bayland Park, and Aldine. There is a local minimum in ozone design value at sites located in the urban core of Houston, presumably because of the abundant fresh NO emissions there, which can suppress ozone formation, or titrate ozone transported into the area.
Observation-based analyses of ambient ozone production in Houston area

Ryerson et al. (2006) examined the four Electra flights during TexAQS 2000 that encountered ozone concentrations above 150 ppbv. Figure A2 shows the flight track segments where the highest ozone was observed. In each case these plumes were traced back to industrial emission sources in the Houston Ship Channel area by trajectory analysis. Measured chemical characteristics of the plumes (simultaneous high NOx, SO2, CO2, and oxidation products of HVROC) confirm this source attribution. The relationship between the transport times derived from the trajectory analysis and the observed enhancements in ozone provided a measure of the net average ozone production rates in the plumes. Figure A2 also shows the observed relationship between ozone and the products of NOx oxidation for those four flights; the slopes of these relationships provide an estimate of the net ozone production efficiencies in these plumes.
Figure A2. 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 [Ryerson et al., 2006].

Figure A3. Highest ozone observed by the WP-3D aircraft and RHB research vessel during TexAQS 2006. The figure is in the same format as Figure A2, but with different ranges on axes (data from Ryerson, Neuman, Williams, et al.–NOAA; Flocke et al.–NCAR).

Figure A3 presents a similar analysis for the three NOAA WP-3D daytime flights and the RHB cruise segment during TexAQS 2006 that encountered ozone concentrations near or above 120 ppbv. A simple wind direction analysis, coupled with the chemical plume signatures, indicate that in each case these plumes also trace back to industrial emission sources in the Houston Ship
Channel area. Figure A3 also shows the relationship between ozone and the products of NOx oxidation in these plumes.

Comparison of Figures A2 and A3 show that the ozone production environment in the Houston area was similar in 2000 and 2006. Very similar ozone production efficiencies are seen in each year, although the maximum observed ozone in 2006 was associated with a somewhat lower efficiency (5.4) than in 2000 (7.3). Lower maximum ozone concentrations were observed in 2006, but this difference may be partially due to meteorological factors; the background ozone, as indicated by the y-intercepts in the two left-hand plots in Figures A2 and A3, is lower in 2006 and the lower background leads to lower maximum concentrations. The lower 2006 background may indicate lesser effects of stagnation that year. Finally, the maximum ozone concentrations are seen at greater distances from the ship channel in 2006 than in 2000. This difference may be attributable to slower ozone production or greater transport speeds in 2006; the relative contribution of these two factors will be a focus of continuing analysis.

**Preliminary Finding A2:** A characteristic meteorology leads to the highest 8-hour average ozone concentrations (and ozone design values) observed in west Houston; the ozone formation during these episodes is controlled by high morning HRVOC concentrations in the Ship Channel, followed by further ozone production as the air parcels advect to west Houston.

**Overview of meteorological conditions during ozone exceedances in Houston**

Ozone events can occur in Houston under a number of distinctly different meteorological conditions, which can be described as interactions between the local diurnal wind forcings and the larger-scale synoptic forcings (see TCEQ conceptual model, 2002, 2006 for detailed discussion.). A typical “veering” pattern, in which winds slowly change direction in a clockwise fashion, is most common. Under these conditions the emissions from the industrial and urban areas of Houston are slowly carried to the east, southeast, or south during the early morning hours. The August 25, 2000 episode in Figure A2 occurred under “veering” conditions. A “flow reversal” is a second common pattern. Under this pattern, the early morning emission plumes are pushed back over the high-emission industrial and urban areas, where they can receive a second dose of fresh emissions. The winds that cause a flow reversal can be a rapid veering pattern, a rapid backing pattern (i.e., counterclockwise wind shift), or simply an abrupt ~180° wind shift. Near stagnation often accompanies this pattern. The August 30, 2000 episode in Figure A2 occurred under this pattern.

A third common pattern of ozone event is the “steady wind” pattern, when the winds often blow from virtually the same direction most of the day, with only minor fluctuations. Two episodes in Figure A2 occurred under this pattern. On September 6, 2000, steady northeasterly winds produced a long plume of high ozone from SE Harris County, across the southern suburbs of Houston and into the rural areas SW of Houston. On September 1, 2000, steady westerly winds stretched a plume of ozone from Houston, across Galveston Bay, and into the rural areas between Houston and Beaumont.
The highest ozone concentrations now observed in the Houston area occur under the “veering” or “flow reversal” patterns. The highest 8-hour-averaged ozone values are observed on the west side of Houston on a path between the Ship Channel and west Houston. Figure A4 shows the development of a typical exceedance that occurred on September 7, 2006, under classical “veering” winds. A similar pattern is responsible for virtually every day with ozone concentrations greater than 100 ppbv at Bayland Park, the Houston monitor with the highest ozone design value. Such days yield outliers in the ozone probability distribution, but these outliers determine the ozone design value, and therefore must be addressed by the SIP planning.

**Required Additional Analyses**
A more comprehensive observational approach will need to account for the effects of any meteorological differences between 2000 and 2006, which may be confounding the initial comparison presented here.
Providing reliable answers to Question A will require a comprehensive modeling effort. This modeling will require both inventory assembly and photochemical modeling:

1. Develop the most nearly realistic emission inventory possible, for the Houston, Dallas and east Texas area for both 2000 and 2006. The inventory must include AVOC, BVOC, HRVOC, OVOC, and NOx; must pay particular attention to appropriate magnitude and spatial distributions (i.e. co-emission with NOx) of HRVOC emissions; and be compared to the fullest extent possible with available observations (e.g. NOAA WP-3D and Solar Occultation Flux measurements in 2006.) An available, open inventory is critical so that the results of different models can be directly compared.

2. Analysis through traditional Eulerian AQ modeling with a focus on 8-hour average ozone and its sensitivities to variation in AVOC, BVOC, HRVOC, OVOC, and NOx emissions.

**Key Citations and Information and Data Sources**


TCEQ, Ozone Animation for September 7, 2006, [http://www.tceq.state.tx.us/compliance/monitoring/air/monops/sigevents06.html](http://www.tceq.state.tx.us/compliance/monitoring/air/monops/sigevents06.html)
Preliminary Response to Question B

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

Question B Working Group

Background
Meteorology generally affects ozone concentrations through modulation of source concentrations (wind speed, mixing height), background ozone and precursor concentrations (transport winds), photochemistry (solar radiation, temperature), and air parcel history (local winds).

Preliminary Findings

Preliminary Finding B1: Boundary-layer structure and mixing near and over Galveston Bay and the eastern Houston ship channel area are spatially complex and variable from day to day. Vertical mixing profiles often do not fit simple models or conceptual profiles. High concentrations of ozone and aerosols are sometimes found above the planetary boundary layer in parts of the HGB ozone non-attainment area. In the HGB area, the depth of the daytime mixed layer is subject to many influences including coastal effects and the effects of Galveston Bay. The coastal zone is a transition region between the maritime boundary layer, where shipboard measurements showed mixed-layer depths of ~200 m (± ~100 m) over the Gulf of Mexico, and inland, where peak afternoon mixing heights are generally between 1.5 and 2.5 km, but sometimes reach altitudes of 4 km or more. Inland, the mixed-layer grows through mid-afternoon, eventually exceeding 2 km on most days, whereas the mean mixing height near the coast reaches a peak altitude less than 2 km around midday and then decreases, owing to inland penetration of the sea breeze.

Midday mixed-layer heights as measured near Waco (Moody) were relatively consistent from day to day, with a mean depth of ~1.5 km. At LaPorte, however, much greater variability in mixed-layer depth was observed, including high frequencies below 1 km; this indicates much more complex influences on mixing depth due to interactions among large-scale wind flows, coastal wind circulations, and instances of westward advection of the shallow Galveston Bay mixed layer. Sounding observations from the University of Houston (UH) campus and from the R/V Ronald Brown (when stationed in Galveston Bay) often showed a very complex vertical structure, with no easily identified transition between the local boundary layer and the air above. This complexity is likely to be underrepresented in numerical models.

Spatial variability of mixing depth was also evident in airborne lidar flights, with more shallow mixing layers over Galveston Bay and higher altitude mixing depths over the Houston urban area as a result of urban heat-island effects. Other variations in mixing depth may result from
differences in land-use or soil-moisture conditions, or may reflect advection of higher or lower altitude mixed-layer depths downwind of the urban area or Galveston Bay, for example.

Nighttime boundary layer structure is difficult to characterize reliably. UH tethersonde and ozonesonde data suggest nighttime ozone depletion can occur at altitudes up to ~ 200 m; this implies that the nighttime mixed-layer depth in this urban area is normally ~200 m or less. Nighttime mixing and transport effects are a challenging area for longer-term research.

**Figure B1.** Airborne lidar time-height cross sections of aerosol backscatter (top, in units of $10^{-8} \text{ m}^{-1} \text{ sr}^{-1}$) and ozone concentrations (bottom, in ppb) for a), b) 30 August 2006, when high ozone and aerosol concentrations were confined to the mixed layer, and c), d) 4 September 2006, when the mixed layer was indicated by higher aerosol concentrations, but the high ozone was above the boundary layer (data from Senff et al.–NOAA).

O$_3$ and aerosol pollutants usually are confined to the mixed layer (Fig. B1a,b). Occasionally, however, significant concentrations of pollutants were observed above the mixed-layer height (Fig. B1c,d). Pollutants, especially aerosols, sometimes exhibit a complex layered structure, in which the original sources of pollution in the individual layers are difficult to determine (Fig. B2). In analyses of measurements made during TexAQS 2006, high pollutant concentrations observed in deep layers (more than a few hundred meters thick) above the mixed layer (Fig. B1d) were determined to originate in regions to the northeast or east of Texas. Airborne ozone lidar flights sampling air masses entering Texas from the east on three different days found concentrations of 50, 80, and 90 ppb in the inflow air.

**Figure B2.** Ozonesonde profiles of ozone (left, 0-100 ppb) and temperature (right, 270-300 K) from the surface to 6,000 m above ground level, for a 6:00 AM LST ozonesonde launch on 31 August 2006 from the University of Houston campus. The minimum concentration of ozone observed in the ozone profile near 1,000 m above ground level was associated with a layer of high relative humidity and visible clouds (data from Rappenglück–U. Houston; Morris–Valparaiso U.).
Preliminary Finding B2: *Complex coastal winds are not necessary for accumulation of high concentrations of ozone in Houston.*

In the Houston area, a strong negative correlation was found between wind speed and the maximum increase (enhancement) in ozone concentration above the background ozone concentration (see red data and line on Fig. B3). Stronger winds apparently caused greater dilution of precursor emissions, and thus lower concentrations of ozone. For the strongest wind speeds, however, some of the decrease in ozone concentrations was due to the pollution plume being blown out of the network before the photochemical reactions were complete, and also, an ozone plume becomes narrower with increasing wind speed, making it harder to detect with a monitoring network.

![Figure B3](image_url)

**Figure B3.** Houston ozone enhancement (peak ozone values in urban plume minus background values) plotted vs. displacement of 10-hr trajectories, representing the vector-mean wind for the period, starting at Houston at 8:00 am CST. Red symbols indicate data from surface measurement network, and blue symbols indicate data from airborne ozone lidar. Peak lidar ozone concentrations for weakest winds (smallest displacements) were probably underestimated due to calibration issues that are currently being resolved, so many of the blue points for weak winds may be adjusted upward. Lines are linear best-fit lines (data from Banta et al.–NOAA).

The blue points on Figure B3 show the airborne-lidar-determined peak ozone concentrations vs. 10-hr trajectory displacements, a surrogate for mean wind speed. The observed ozone concentrations decreased with increasing wind speed, but not as quickly as indicated by the surface network (red dots). This suggests that, under strong wind conditions, the highest ozone concentrations are very likely occurring at non-monitored locations. For example, on 12 August 2006 the airborne lidar measurements showed peak O$_3$ concentrations of 115 ppb, but the highest concentration measured within the existing monitoring network was 51 ppb.

The Houston-Galveston Bay area produces large amounts of ozone. Even under relatively strong wind conditions, the result is high ozone and aerosol concentrations, although the very highest concentrations are produced on days with weak-wind or sea-breeze reversal conditions.
**Preliminary Finding B3:** *After sea breeze days, the Houston plume often is broadly dispersed at night through the formation of a low-level jet.*

Trajectory analysis of nighttime transport of the Houston plume, based on the wind profiler network, indicates that the Houston plume sometimes remains a coherent entity, subject to little wind shear (see Fig. B4a, b), but at other times is dispersed over a broad portion of Texas by strongly shearing winds (Fig. B4c,d). Broad dispersal is favored after sea breeze days, when nighttime decoupling allows a strong low-level jet to form from the remains of the sea-breeze circulation. The wind speed is strongest at 300-500 m, decreasing above and below.

![Figure B4](a)(b)(c)(d)

**Figure B4.** Overnight trajectories for winds detected at four different altitudes near Houston, based on hourly radar wind profiler measurements, on the nights of a) 16-17 August, b) 14-15 August, c) 31 August-1 September, and d) 1-2 September 2006. Red trajectories were averaged over the vertical interval from 200 to 500 m; black, from 500-800 m; green, from 800-1200 m; and blue, from 1200-1800 m. Lower altitude trajectories or those ending up to the north of their origin are not likely to be contaminated by a signal from migrating birds. (The trajectory map was created using the NOAA Physical Science Division (PSD) upper air back-trajectory tool [http://www.etl.noaa.gov/programs/2006/texaqs/traj/]).

**Preliminary Finding B4:** *The Dallas ozone plume can extend well beyond the existing ground-based ozone monitoring network.*

An airborne O₃ lidar flight, sampling the DFW ozone plume on 13 September 2006 under northerly wind-flow conditions with wind speeds of ~ 5 m s⁻¹, observed peak ozone concentrations of 90-95 ppb with a background ozone concentration of ~ 65 ppb (Figure B5). These measurements indicate an enhancement of 25-30 ppb in ozone concentration, in agreement with previous estimates. These high O₃ concentrations were observed in a distinct urban plume extending past the southernmost cross-wind flight leg at a distance of 85 km downwind of DFW, indicating that the ozone plume extended even farther downwind. It seems very likely that the highest ozone concentrations occur beyond the margin of the ground-based ozone monitoring network on such occasions. Under southerly large-scale wind-flow conditions, recently installed ozone sensors in southern Oklahoma also indicated high ozone concentrations resulting from the DFW plume, at a distance of at least 240 km (near Lawton, Oklahoma).
Figure B5. a) Flight track of the Twin Otter airborne ozone lidar, showing color-coded ozone concentrations averaged between 500 and 1000 m above mean sea level (ozone scale from 50 to 100 ppb), for 13 September 2006, a day with stiff north-northeasterly flow. b) Vertical time-height cross section of ozone [ppb, same scale as in a), vertical scale from 0 to 1800 m MSL, horizontal scale from 2145 to 2230 UTC] for southernmost cross-wind leg, showing plume of higher ozone from Dallas-Ft. Worth (data from Senff et al.–NOAA).

Required Additional Analyses
The results reported here are preliminary. Most of the data discussed in this summary have yet to be subjected to comprehensive quality control procedures. In addition to quality control, it will be useful to compare results from different platforms and observing systems in order to develop a comprehensive picture of the PBL during TexAQS-II. Observations from several valuable or unique instruments, such as the Doppler lidar on board the R/V Ronald Brown, have yet to be analyzed in any detail. Numerical model simulations, with data assimilation, will provide a useful framework for integrating the various bits of observational information. Finally, it will be useful to investigate the extent to which the meteorology of the 2006 field intensive differed from that of the 2000 intensive and from typical conditions.
Preliminary Response to Question C

Question C
Are highly reactive VOC and NOx 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 NOx?

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

Preliminary Findings

Preliminary Finding C1: There are indications that HRVOC emissions from industrial sources in the Houston area have decreased by a factor of two since 2000.

TexAQS 2006, TexAQS 2000, and other aircraft measurements
Among the highly reactive volatile organic compounds (HRVOC), ethene received the most attention during the TexAQS 2006 study. Both onboard the NOAA R/V Ronald H. Brown (RHB) and the NOAA WP-3D aircraft, ethene was measured by two different techniques and at high time resolution. Onboard the RHB, ethene was measured by an on-line GC instrument and a quantum cascade laser (QCL) absorption method. Onboard the WP-3D, ethene was measured by laser photo-acoustic spectroscopy (LPAS) and from whole air samples (WAS) collected during the flights.

Numerous point sources were individually characterized using the aircraft measurements. Determination of emission ratios was most straightforward for the isolated petrochemical plants to the south of Houston. These facilities were extensively investigated in 2000 and 2006, and an additional research flight was made in 2002, when the NOAA WP-3D was on its way to a study in California. Figure C1 shows the flight track in 2002 (Ryerson et al., 2003) and an example of a flight made in 2006, along with results of the NOx and ethene measurements. Apart from Texas City, there appear to be changes in the ethene/NOx emission ratios. The results are further summarized in Table C1, and show decreases in the ratio by a factor of 3-7 for Sweeny, Freeport and Chocolate Bayou. Further research is necessary to determine if the lower emission ratios were systematic, or only happened to be lower on the September 29 flight; preliminary analyses have shown that emission ratios are variable within factors of 2-3 between different flights. In addition, the high-time-resolution ethene data from the NOAA WP-3D have indicated that ethene and NOx enhancements are not always well correlated. Evidently the sources of these species are not always co-located, making it difficult even to define emission ratios in these cases.
Figure C1. Measurements of NO<sub>x</sub> and ethene downwind from 4 isolated petrochemical plants to the south of Houston. The top panels show the flight tracks of the NOAA WP-3D on April 22, 2002, (Ryerson et al., 2003) and on September 29, 2006 (data from Ryerson, de Gouw, et al.–NOAA; Atlas et al.–U. Miami). The lower panels show the measurement results plotted as a function of longitude.

Table C1. Ethene/NO<sub>x</sub> emission ratios determined from measurements in 2000, 2002 and 2006, compared with emission inventories.

<table>
<thead>
<tr>
<th>Location</th>
<th>1999&lt;sup&gt;a&lt;/sup&gt;</th>
<th>2004&lt;sup&gt;b&lt;/sup&gt;</th>
<th>2000&lt;sup&gt;c&lt;/sup&gt;</th>
<th>2002&lt;sup&gt;c&lt;/sup&gt;</th>
<th>2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweeny</td>
<td>0.05</td>
<td>0.019</td>
<td>3.6</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Freeport</td>
<td>0.05</td>
<td>0.030</td>
<td>1.5</td>
<td>0.62</td>
<td>0.32</td>
</tr>
<tr>
<td>Choc. Bayou</td>
<td>0.08</td>
<td>0.048</td>
<td>2.0</td>
<td>1.2</td>
<td>0.62</td>
</tr>
</tbody>
</table>

<sup>a</sup> TNRCC emission inventory.<br>
<sup>b</sup> TCEQ point source emission inventory with 1999 VOC speciation.<br>
<sup>c</sup> Ryerson et al., 2003.

Another approach to investigating ethene emissions is to investigate if reduced emissions of ethene have caused generally lower mixing ratios of ethene and of its photoproducts, e.g. formaldehyde, throughout the Houston area. Cumulative probability distributions were calculated for ethene and formaldehyde in 2000 and 2006 from aircraft measurements taken in the boundary layer within a box around Houston as shown in Figure C2. We note that WAS canister ethene data from 2006, which are not yet available, will be critical to include in this plot, as the WAS sampling scheme may preferentially capture higher values in plumes, complicating
direct comparison to the LPAS in this manner. Further, some of the differences between the formaldehyde data may come from the use of different averaging times (10-second data from 2000 study, versus the 1-minute averaged data from 2006) in this preliminary report.

Figure C2 suggests that observed ethene and formaldehyde mixing ratios were significantly lower during TexAQS 2006 in comparison with TexAQS 2000. However, this difference can result from either changing emissions, or from different dilution rates due to changes in wind speeds or boundary layer heights, between the two study periods. Figure C3 shows that during the 2006 experiment wind speeds were higher than during 2000, especially at the lower speeds characteristic of high-ozone stagnation episodes sampled in 2000. Boundary layer heights will be obtained from wind profilers, and from the aircraft data and will be compared between the two years. Further careful analysis of the existing data is needed to quantify the magnitude of HRVOC emissions changes, if any, between 2000 and 2006.

Figure C2. Cumulative probability distributions for the ethene and formaldehyde observations in 2000 and 2006. The only data included were those collected in the box around Houston shown in the upper panel, and below 1000 m altitude. Also added are the cumulative probability functions for the wind speed in the same box during the 2000 and 2006 studies (data from de Gouw et al.–NOAA; Fried et al.–NCAR).
**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 C3 presents results from two sites near the Ship Channel. The median ambient ethene levels at both sites indicate decreasing trends of about a factor of two.

![Figure C3. Results of ethene measurements by auto-GCs at two sites near the Houston Ship Channel: 9 years of data from Clinton (on the western end) and 8 years of data from Deer Park (on the eastern end) (data and analysis from TCEQ).](image)

**Summary of evidence**
Emission ratios of ethene relative to NOX from several isolated petrochemical plants in 2006 were lower in comparison with results from 2000 and 2002. In addition, lower mixing ratios of ethene and formaldehyde were observed in 2006 in comparison with 2000; the extent to which observed differences in dilution rates affect this interpretation still needs to be determined.

Preliminary analyses based on four different measured parameters (ethene/NOx emission ratios in plumes, ambient distribution of ethene, ambient distribution of formaldehyde, and long-term auto-GC ethene measurements) have all found evidence for a significant decrease in ethene. Each analysis can be questioned, and each needs to be strengthened by further study, but their unanimity increases our confidence that a significant decrease in HRVOC emissions from Houston area petrochemical facilities has actually occurred in the period between 2000 and 2006.
**Preliminary Finding C2:** The latest available emission inventories still underestimate ethene emissions by approximately an order of magnitude.

In TexAQS 2000 it was established that emissions of HRVOC were underestimated by one to two orders of magnitude (Ryerson et al., 2003.) A remarkable feature of Table C1 is that appreciation of this finding has not entered into the inventory. For example, total HRVOC emissions included in the Harris County Point Source EI for 2000-2004 were fairly steady across those years, with the lowest year (2002, at 3300 tons) being about 83 percent of the highest year (2004, 4000 tons). Total VOCs in the county in the 2000-2005 period differed approximately 13 percent between the lowest year (2003, ~29,000 tons) and the highest year (2000, ~33,500 tons). Consequently, the latest available emission inventories still underestimate HRVOC emissions (as judged by the ethene comparisons summarized in Table C1) by approximately an order of magnitude.

**Required Additional Analyses**

All of the material presented here is based on preliminary analysis of a few example data. All findings are tentative at this point. Additional analysis will focus on a much more comprehensive evaluation of the complete data sets that will put the findings and ultimate conclusions on a more firm foundation.

Regarding the TexAQS 2006 intensive measurements, a great many additional analyses will be pursued including investigation of economic factors that may affect the level of activity at the petrochemical facilities, comparison of HRVOC measurements with other tracer species such as CO₂, comparison with flux determinations by the Solar Occultation Flux measurement system, and controlling in a more quantitative manner for meteorological variability.

Regarding the long-term auto-GC data sets, further analysis 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 Citations and Information and Data Sources**

Preliminary Response to Question D

Question D
What distribution of anthropogenic and biogenic emissions of ozone and aerosol precursors can be inferred from observations?

Question D Working Group
Co-leaders: David Allen, David Parrish; Participants: Tom Ryerson, Charles Brock, Joost de Gouw, David Sullivan, Mark Estes, John Jolly, Eric Williams, Barry Lefer, Bernhard Rappenglück; Observers: Yulong Xie, Carl Berkowitz, Noor Gillani.

Background
Questions C, D, and E all deal with emissions. Question C specifically addresses highly reactive VOC and NOx emissions in the Houston area. Here, Question D addresses all other ozone and aerosol precursor emissions, biogenic as well as anthropogenic, that are included in emission inventories. Question E addresses evidence for additional, unrecognized sources of precursor emissions.

Preliminary Findings

Preliminary Finding D1: Several rural electric utility power plants in the Houston area and in east Texas have substantially decreased their NOx emissions per unit power generated since the TexAQS 2000 study. With one exception, preliminary analysis suggests that SO2 emissions have not changed appreciably since 2000 for the plants sampled in 2006. Several power plants continue to emit substantially more CO than expected.

NOx, SO2, CO, and CO2 are emitted directly, in varying ratios, from electric generation units (EGUs). Enhancement of the first three species, relative to CO2 enhancements when sampled in plumes immediately downwind of EGU point sources, provide a measure of pollutant emissions per unit energy generated by the plant (e.g., Ryerson et al., 2003). Comparisons of emissions ratios between the TexAQS 2000 and TexAQS 2006 studies permit an assessment of EGU emissions control strategies, intended primarily to reduce NOx emissions, that have been implemented since 2000.

Near-field plumes from numerous rural EGUs in Texas were characterized using aircraft measurements in 2000 and 2006. Data were generated as shown in Figure D1a, which depicts the NOAA WP-3D ground track for a flight designed to assess several large EGU point sources in the East Texas area. The data shown in Figure D1b are taken from the closest transects, within 10 km downwind of the plants, and plotted in Figure D2 as enhancement ratios versus CO2. The slopes of linear fits to these data provide a direct measure of the plant emissions ratios.

Preliminary analyses of rural EGU emissions ratios to CO2 have been performed for Monticello, Welsh, Martin Lake, Big Brown, and the W.A. Parish power plants; analysis of additional EGUs is underway. Table D1 compares derived emission ratios from the 2006 WP-3D preliminary data with the ratios measured from the NCAR Electra aircraft in 2000.

The TexAQS 2000 study demonstrated quantitative agreement between emissions estimates from the Electra aircraft data and the tabulated emissions from Continuous Emissions Monitoring Systems (CEMS) data, for NOx and SO2 at each plant. Some variability is expected on time scales of hours to years, and is reflected in the data in Table D1. Nonetheless, initial conclusions
from the 2006 study can be drawn that are well outside of the uncertainties due to normal emissions variability over time.

Figure D1a. Sept. 16, 2006 WP-3D ground track (green) with observed SO2 enhancements (blue) plotted along the track.

Figure D1b. Time series of CO2, SO2, NOx, and CO measured immediately downwind of Welsh and Monticello.

Figure D2. Emissions ratios of SO2, CO, and NOx derived from linear fits to measured plume enhancement ratios for the Monticello and Welsh power plants on Sept 16, 2006. Uncertainties in the derived emissions ratios are ca. ± 10% for the preliminary data given here (data from Ryerson, Holloway et al.–NOAA).

Table D1. Measured emissions relative to CO2 for EGUs in East Texas.

<table>
<thead>
<tr>
<th>EGU name</th>
<th>NCAR Electra aircraft data 2000</th>
<th>NOAA WP-3D aircraft data 2006</th>
<th>NOx emissions decreased by factor of:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monticello</td>
<td>SO2: 3.5 CO: 6.4 NOx: 1.0</td>
<td>SO2: 1.9 CO: 1.5 NOx: 0.71</td>
<td>—</td>
</tr>
<tr>
<td>Welsh</td>
<td>SO2: 1.5 CO: 1.7 NOx: 0.80</td>
<td>SO2: 1.5 CO: 1.7 NOx: 0.98</td>
<td>(minor increase)</td>
</tr>
<tr>
<td>Martin Lake</td>
<td>SO2: 1.4 CO: 4.0 NOx: 1.3</td>
<td>SO2: 2.8 CO: 6.0 NOx: 0.70</td>
<td>1.9</td>
</tr>
<tr>
<td>Big Brown</td>
<td>SO2: 4.8 CO: 2.9 NOx: 1.5</td>
<td>SO2: 6.9 CO: 6.0 NOx: 0.65</td>
<td>2.3</td>
</tr>
<tr>
<td>W.A. Parish</td>
<td>SO2: 2.1 CO: 2.1 NOx: 2.1</td>
<td>SO2: 2.1 NOx: 2.1</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Emissions values presented as molecules per 1000 molecules of CO2 emitted.
Preliminary conclusions from this body of evidence are:

- **NOx emissions** have decreased substantially in several electric utility power plants, by factors of 2-4, qualitatively consistent with NOx controls implemented since the 2000 study. NOx emissions from other EGUs are essentially unchanged.

- **SO2 emissions** are generally unchanged between 2000 and 2006 in the plants studied to date. The small variability observed is within that expected from CEMS data due to normally changing plant loads. An exception is the Martin Lake plant, where SO2 appears to have increased by a factor of 2 relative to CO2 compared to the 2000 study.

- Unexpectedly large CO emissions, reflecting sub-optimal combustion processes in the plants, are still present for many of these EGUs and are similar to those observed in the 2000 study. These CO emission rates, if shown to be continuous over time, would greatly exceed the annual inventory values for these plants (Nicks et al., 2003).

**Preliminary Finding D2:** On-road mobile emission inventories developed from MOBILE6 have significant shortcomings. MOBILE6 consistently overestimates CO emissions by about a factor of 2. It accurately estimated NOx emissions in the years near 2000, but it indicates decreases in NOx emissions since then, while ambient data suggests NOx emissions have actually increased. Consequently in 2006, NOx to VOC emission ratios in urban areas are likely underestimated by current inventories.

Figure D3 compares CO to NOx ratios from ambient measurements with those from emission inventories. The Dallas and Houston routine ambient data are in excellent agreement with the nationwide AIRS data. The TexAQS 2006 data from Moody tower are in good agreement with the routine monitoring data. Significant differences are seen in El Paso and San Antonio, which have older vehicle fleets.

In most cases the Texas inventories overestimate the CO to NOx ratio, particularly recently, and do not show significant temporal decreases. Parrish (2006) shows that the rapid decrease (6.6%/yr) in the ratio is partially due to a slower decrease in CO emissions (4.6%/yr), which implies a significant increase in NOx emissions (approximately 2%/yr). The large inventory overestimates in the CO to NOx ratio at the present time are attributed to a factor of 2 overestimate in CO emissions, and an underestimate in present NOx emissions. This will cause NOx to CO emission ratios in urban areas, which are often dominated by on-road mobile emissions, to be underestimated by current emission inventories.
Preliminary Finding D3: NOx emissions from ships are a strong function of vessel speed, and inventories based on AP-42 emission factors will significantly overestimate ship NOx emissions in Galveston Bay and the Houston Ship Channel.

Measurements aboard the NOAA R/V Ronald H. Brown (RHB) have been analyzed to characterize marine diesel emissions along the Texas coast, including Galveston Bay and in the Houston Ship Channel. The NOx/CO2 ratios in ship emission plumes, and thus NOx per mass of fuel burned (i.e., NOx emission factor), were determined from linear fits to measured data in plumes from a variety of ships, in a manner similar to that employed for the EGU emissions analysis described above in Finding D1. Figure D4 plots the NOx emission factor as a function of vessel speed, which was determined from the Automatic Identification System ship location database.

The generally increasing trend in NOx emissions per mass of fuel burned with increasing speed suggests that vessels slowly transiting the Ship Channel and Galveston Bay or docked at harbor facilities emit substantially less NOx than expected based on the AP-42 estimates. Further, analysis of the RHB data also shows a dependence of SO2 emission, and thus fuel sulfur content (not shown), on ship speed. This finding is interpreted to mean that higher sulfur fuels, containing between 1-4% S, are usually used offshore, while lower sulfur fuels (less than 1% S) are usually used during Ship Channel transit or while docked.
**Preliminary Finding D4:** Work is in progress to correlate measured mixing ratios of biogenic VOC over NE Texas with emission inventories. Preliminary findings indicate that: (i) there may be an area south of Dallas-Fort Worth in which isoprene emissions were lower than indicated by the inventories, and (ii) monoterpene mixing ratios in general were relatively low.

Isoprene and monoterpenes were measured from the NOAA WP-3D aircraft using PTR-MS, and from the whole air samples (WAS) collected in flight. An example of the results obtained by PTR-MS is given in Figure D5, which shows the results from a flight over an area with high isoprene emissions in northeast Texas. Isoprene is high and highly variable in the boundary layer, and quickly drops off to zero above the boundary layer. The monoterpene levels are relatively low at 60 pptv or less, whereas in other regions of the US, levels over 200 pptv have been observed from the NOAA WP-3D.

The correlation between measured isoprene mixing ratios from all flights and the BEIS3 emissions inventory (for nominal, standard meteorology) is shown in Figure D6. It can be seen that measured isoprene was generally higher above areas with higher emissions. An exception is an area to the southeast of Dallas-Fort Worth, where the highest emissions are expected according to the inventory, but where the NOAA WP-3D only measured moderately enhanced mixing ratios. Measurements from the NCAR Electra during TexAQS 2000 are shown for comparison. They show higher isoprene mixing ratios over this area, though not higher than elsewhere in the state. Before final conclusions are reached, several important issues must be investigated including different drought stress on the vegetation between the two study years, and the influence of recalculating the BEIS3 isoprene emissions with the actual meteorology specific to the time of the isoprene measurements.

Figure D5. Flight track of the NOAA WP-3D on September 16, 2006, color-coded by the measured mixing ratio of isoprene. The lower panel shows the time series of isoprene along with that of the monoterpenes and the flight altitude (data from de Gouw et al.–NOAA).
Figure D6. Correlation between the BEIS3 isoprene emission inventory and the isoprene mixing ratios measured from the NOAA WP-3D in 2006 and the NCAR Electra in 2000 (data from de Gouw et al.–NOAA).
Required Additional Analyses
The material presented here is based on preliminary analyses of a few selected data. All findings are tentative at this point. Additional analyses will focus on more comprehensive evaluation of the complete data sets that will put the findings and ultimate conclusions on a more firm foundation. Specific analyses planned include:

1. Comparison of the SO₂, NOₓ, CO, and CO₂ ratios observed from the aircraft, and absolute emissions rates derived from aircraft data, to hourly CEMS data for the plume study periods in 2006. These CEMS data are expected to become available in the next few months.
2. Determining whether NOₓ reductions have been implemented in the non-utility EGUs and co-generation plants in the industrialized Ship Channel region, and comparison to these emissions as observed in the 2000 study.
3. A comparison of WP-3D measurements of isoprene (and its photochemical products) with the BEIS3 inventory using the actual rather than nominal, standard meteorology. The large differences in the region to the southeast of Dallas will be a particular focus.

Key Citations and Information and Data Sources


Preliminary Response to Question E

Question E
Are there sources of ozone and aerosol precursors that are not represented in the reported emissions inventories?

Question E Working Group
Leader: David Parrish; Participants: Tom Ryerson, Charles Brock, Joost de Gouw, David Sullivan, John Jolly, David Allen, Eric Williams, Barry Lefer, Bernhard Rappenglück.

Preliminary Findings

Preliminary Finding E1: The observed concentrations and distribution of ambient formaldehyde are broadly consistent with daytime photochemical production associated with olefin emissions. Primary formaldehyde emissions appear to be significantly less important, with more precise quantification awaiting additional analysis.

Formaldehyde (HCHO) was measured both on the NOAA R/V Ronald H. Brown (RHB) and the NOAA WP-3D research aircraft during TexAQS II. Onboard the RHB, Mark Zahniser and Scott Herndon from Aerodyne Research measured formaldehyde (along with ethene and ammonia) using quantum cascade laser (QCL) absorption. Onboard the WP-3D, Alan Fried and co-workers from NCAR measured formaldehyde using the different-frequency generation (DFG) tunable diode laser absorption method.

Numerous point sources were individually characterized using the aircraft measurements. In some cases (see Figure E1), direct emissions of formaldehyde in very narrow plumes were likely observed.

Figure E1. Results from the flight of the NOAA WP-3D on September 29, 2006. The top panel shows part of the flight track circling four petrochemical plants to the south of Houston. The bottom panel shows the measured results for ethene and formaldehyde. Around Chocolate Bayou, enhancements of formaldehyde were observed that are likely due to direct emission (data from de Gouw et al.–NOAA; Fried et al.–NCAR).
In general, however, the dominant contribution to formaldehyde was associated with photochemical production from olefins. Figure E2 shows an example from October 6, in which high mixing ratios of ethene were observed just downwind from point sources in the Houston Ship Channel, whereas formaldehyde, ozone and APAN, a PAN-type compound from butadiene oxidation, were observed further downwind as ethane was being removed.

Figure E2. Results from the flight of the NOAA WP-3D on October 6, 2006. The top panel shows part of the flight track downwind from the Houston Ship Channel. The flight track is color-coded by the measured formaldehyde and the arrow indicates the wind direction. The two lower panels show the measured results for formaldehyde, ethane, ozone and APAN (data from de Gouw, Ryerson et al.–NOAA; Fried, Flocke et al.–NCAR).
The finding that the dominant source of formaldehyde is photochemical production is consistent with the diurnal variation of formaldehyde and its precursors observed from the RHB, as it was docked at various places in the Houston Ship Channel. Figure E3 shows that ethene, on average, was the highest during the night and early morning and low during the day. During the night, ethene is only slowly removed and builds up in a very shallow boundary layer. During the day, OH radicals rapidly remove ethene, resulting in the formation of formaldehyde. As a result, formaldehyde is the highest during the day. The lowest mixing ratios were observed during the night, indicating that, averaged over a full day, direct emissions of formaldehyde are far less important than photochemical production. This finding is fully consistent with the TexAQS 2000 study results (Wert et al., 2003; Ryerson et al., 2003).

Formaldehyde also was measured at the Moody Tower site (60 m a.g.l.) on the University of Houston campus using the Aero-Laser AL4021 analyzer based on fluorescence initiated by the Hantzsch reaction. High daytime formaldehyde values nicely correlate with peroxyacetic nitric anhydride (PAN) and peroxypropionic nitric anhydride (PPN), which can most likely be ascribed to secondary formation. The preliminary data set indicates background values for formaldehyde of about 3-4 ppbv, but photochemical active daytime periods show maximum values up to more than 40 ppbv. Occasionally, during nighttime, strong fluctuations with peak values up to 20 ppbv were observed.
The observed temporal behavior of formaldehyde at Moody Tower, in conjunction with other trace gases, suggest that secondary formation of formaldehyde accounts for the major fraction of ambient formaldehyde. The occasional episodes of enhanced nighttime formaldehyde may indicate the influence of primary sources during these periods.

**Preliminary Finding E2:** Concentrated plumes of ammonia were observed occasionally in the Houston Ship Channel area.

High time resolution (≈1 s) ammonia measurements were made from the NOAA WP-3D aircraft and R/V Ronald H. Brown during TexAQS 2006. Background concentrations over urban areas were enhanced by 2 to 3 ppbv because of emissions from mobile sources. Occasionally concentrated (10’s of ppbv) plumes of ammonia were encountered in the vicinity of the Houston Ship Channel; Figure E4 shows one example. Concentrations as high as several hundred ppbv were measured from the RHB, also in the Houston Ship Channel. The WP-3D measurements showed that these ammonia plumes were accompanied by the formation of ammonium nitrate produced by reaction of ammonia with ambient concentrations of nitric acid. The air quality implications of these ammonia plumes should be considered, particularly in the cooler wintertime when the ammonium nitrate will make a longer-lived contribution to the PM$_{2.5}$ concentrations.

**Preliminary Finding E3:** Concentrated plumes of gaseous mercury from at least one point source were observed in the Houston Ship Channel area.

High time resolution (≈1 s) measurements of gaseous mercury were made from the NOAA R/V Ronald H. Brown research vessel during TexAQS 2006. Concentrated plumes from at least one major point source were encountered during transects of the Houston Ship Channel under southerly to easterly winds. Figure E5 shows one of the plume encounters, and locates industrial facilities that could be possible sources. The magnitude of the detected plumes varied widely; the plume was detected during each of six transects of the ship channel under southerly to easterly winds, but the magnitude of the plume varied by a factor of approximately 25. Determining how much of the plume variability is due to flux variability of the source will require more work to account for variability of wind speed, boundary layer depth, and other factors.
Required Additional Analyses

All of the material presented here is based on preliminary analysis of a few example data. All findings are tentative at this point. Additional analyses will focus on a much more comprehensive evaluation of the complete data sets that will put the findings and ultimate conclusions on a more firm foundation. Specific analyses planned include:

1. A quantitative analysis of the relative importance of secondary and primary sources of formaldehyde in the east Texas region.
2. A quantitative analysis of mercury flux from source(s) in the Houston Ship Channel area, as well as the identity of the source.

Key Citations and Information and Data Sources


Preliminary Response to Question F

Question F
How do the mesoscale chemical environments (NOx-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?

Question F Working Group
Co-Leaders: Basil Dimitriades, David Parrish; Participants: David Allen, Harvey Jeffries, William Vizuete, Daewon Byun, Mark Estes, Kenneth Schere, Barry Lefer, Bernhard Rappenglück; Observers: Yulong Xie, Carl Berkowitz.

Background
This question is closely related to Question K. Here the focus is on a general discussion of the photochemical environment of the entire east Texas region, and Question K will specifically focus on the distinctive photochemistry of the HGB area that is attributed primarily to the petrochemical industry emissions.

Preliminary Finding

Preliminary Finding F1: At the highest ozone concentrations, the observed relationship between ozone and the products of NOx oxidation indicates less efficient ozone production in the Dallas area than in the Houston area. In the observation-based indicator species approach, this behavior corresponds to less NOx-sensitive and more VOC- or radical-sensitive ozone formation in Dallas compared to Houston.

Figure F1 shows the relationships between ozone and the oxidation products of NOx. These oxidation products include only nitric acid on the left plot and nitric acid plus organic nitrates on the right plot. The generally shallower slopes in the Dallas area indicate less efficient ozone production in that area. From an observation-based indicator approach, this behavior corresponds to less NOx-sensitive and more VOC- or radical-sensitive ozone formation in Dallas compared to Houston. The Question K section gives a more complete discussion of such relationships, and critically assesses the application of the observation-based indicator approach in the Houston area.
Required Additional Analyses
To provide reliable answers to Question F will require a comprehensive modeling effort. This modeling will require both inventory assembly and photochemical modeling:

1. Development of the most nearly realistic emission inventory possible, for the entire east Texas area for both 2000 and 2006. As discussed in the Question K section, the inventory in the Houston area requires particular attention. The biogenic inventory will be particularly important here. The inventory should be compared to the fullest extent possible with available observations (e.g. NOAA WP-3D and Solar Occulation Flux measurements in 2006). An available, open inventory is critical so that the results of different models can be directly compared.

2. Analysis through traditional Eulerian AQ modeling with a focus on 8-hour-averaged ozone and its sensitivities to variation in AVOC, BVOC, HRVOC, OVOC, and NOx emissions. Particular attention must be paid to the ability of the model to resolve the plumes that determine the highest ozone values in the Houston area. Such resolution may be a severe challenge for Eulerian AQ models, especially if they attempt to include the whole east Texas region. When the association of mesoscale chemical environments with high ozone is understood, it will be appropriate to then examine the association with high aerosol concentrations.

3. Verification of the performance of the models through their ability to reproduce the observations collected during TexAQS 2000 and 2006; particular attention should be paid to relationships between ozone and other photochemical products such as aldehydes and organic nitrates, and observed radical concentrations.

Figure F1. Indicator species relationships from the TexAQS 2000 Electra measurements. The gray and blue symbols indicate data collected in the Houston and Dallas areas, respectively (Data from Ryerson, Neuman, Parrish, et al.-NOAA.)
Preliminary Response to Question G

Question 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?

Question G Working Group

Background
Question G is closely related to Question H. Here Question G focuses on characterizing the background ozone and aerosol distributions, and the chemical and physical processes that affect the background concentrations of ozone and aerosol in Texas. Question H focuses on the transport processes and source-receptor relationships of those background concentrations.

Preliminary Finding G1: The maximum background ozone concentrations encountered in 2006 exceeded the 8-hour NAAQS. On average, air of continental origin had higher background concentrations than marine air. The average background O₃ concentrations measured in 2006 in eastern Texas complement a previously developed climatology.

Overview of background ozone in eastern Texas
The NOAA lidar provided mesoscale estimates of background ozone for eastern Texas, and classified backgrounds as either “marine” or “continental” based on synoptic winds and the transect path. Background ozone was measured by averaging lidar ozone profiles between the surface and the top of the boundary layer over a data segment of several tens of kilometers outside of plumes. The blue line segments in Figure G1 indicate the mean marine and continental background ozone values using measurements from all suitable lidar flights. The average marine background (38 ppbv) is close to the average curves for Houston-Galveston-Brazoria (HGA) and Beaumont-Port Arthur (BPA) for the August 1 to September 15 period of the measurements, while the continental average is just below the Dallas-Fort Worth (DFW) average curve for the same time period. The highest observed ozone background value was 97 ppb on September 8 at 18:14 UTC (1:14 p.m. CDT) in east central Texas, after several days of continuous easterly flow conditions.

Daily 8-hour-averaged ozone maxima have been compiled from TCEQ surface monitoring data. The daily 8-hour averages at upwind suburban or rural sites serve as indicators of the local background. The red line segments in Figure G1 indicate the average background for four areas in Texas on days in 2006 with the area maximum 8-hour average at 80 ppb or above. These segments are higher than the corresponding average curves, which are compiled for all days, not just high ozone days. The marine influence in the Houston area accounts for the lower
background (49 ppbv) compared to the Dallas (63 ppbv), Beaumont (61 ppbv), and Northeast Texas (60 ppbv) areas.

![Graph showing ozone levels in different regions of Texas over a year.](Image)

Figure G1. Six-year (1998-2003) average background ozone in various regions in eastern Texas. Curves are smoothed with a 31-point running mean filter. (Figure from Nielsen-Gammon et al., 2005). The blue and red line segments indicate 2006 background ozone as described in the text (2006 data from Senff et al.-NOAA; TCEQ).

**Preliminary Finding G2**: The net ozone flux transported out of Houston averages about a factor of three larger than the corresponding flux from Dallas. The fluxes from these urban areas are significant contributors to the background ozone in the eastern Texas region. The horizontal flux of O₃ downwind of Houston and Dallas was calculated from airborne lidar measurements of O₃. The O₃ flux is computed by integrating excess O₃ in the plume (plume O₃ – background O₃) between the surface and the top of the boundary layer and between the horizontal plume edges. The integrated plume O₃ was then multiplied by the horizontal wind speed (estimated from nearby wind profilers) to yield O₃ flux in molecules per second. Fluxes were computed for the Houston area on three separate days (8/12, 8/14, and 8/30/2006) and the Dallas/Fort Worth area for one day (9/13/2006). Preliminary results, which need further verification, indicate that the ozone flux from Houston was remarkably similar for the three days studied, with measured values ranging from 4 * 10²⁶ to 4.6 * 10²⁶ molec s⁻¹. This flux, emitted over one hour, would increase O₃ levels by about 10 ppb if emitted into a 2-km deep boundary layer over a 3100 km² area. The flux for the one Dallas determination was estimated as 1.4 * 10²⁶ molec s⁻¹, about a factor of 3 smaller than that observed for Houston.
Preliminary Finding G3: Elevated background ozone concentrations for urban areas include the recirculation of local emissions.

A past example provided by the TCEQ is a May 31, 2003 episode in DFW, for which O₃ concentration contours at mid afternoon are shown in Figure G2. In this event, the one-hour-averaged peak O₃ was 161 ppbv, with the eight-hour-averaged peak at 130 ppbv. The event was influenced by a stalled frontal passage – note the contrasting direction at the wind vanes associated with monitoring sites on the north side versus the south side of DFW. The color code for the figure is: Gray 85-99 ppb, Orange 100-124 ppb, Red 125-149, Purple > 149 ppb.

Figure G2. (Left) Surface weather map for 6 CST May 31, 2003 shows stalled front in north Texas (http://weather.unisys.com/archive/index.html). (Right) Mid-day contour of O₃ concentrations shows “pancake” of elevated O₃ between Dallas and Fort Worth. Wind barbs show northerly winds north of the city and southerly winds south of the city, trapping local pollution (TCEQ, 2003).

Preliminary Finding G4: Plumes from Texas urban areas make substantial contributions to the ozone, aerosol, and precursor concentrations in the rural regions of eastern Texas.

Figure G3 shows one example of model output and measurements of transported plumes of emissions from the Houston area to northeastern Texas. The model results are from the FLEXPART Lagrangian parcel tracer model and the measurements are from the NOAA WP-3D aircraft on 16 September 2006. There is excellent agreement between the model and the measurements, with both agreeing that the SO₂ plume, primarily form the Parish power plant, was transported parallel and to the west of the NOₓ and benzene plumes, primarily from the Houston urban and Ship Channel areas. Table G1 shows that these plumes nearly doubled the total aerosol concentrations in rural northeast Texas (for reference, the NAAQS for PM₂.₅ aerosol are 15.0 µg m⁻³ annual mean, and 35 µg m⁻³ 24-hour mean).
Table G1. Summary of impact of Parish and Houston plume on northeast Texas.

<table>
<thead>
<tr>
<th></th>
<th>background</th>
<th>Parish</th>
<th>Houston/Ship Channel</th>
</tr>
</thead>
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<tr>
<td>Total mass (µg m⁻³)</td>
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<tr>
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<tr>
<td>Organic (µg m⁻³)</td>
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<tr>
<td>Black Carbon (µg m⁻³)</td>
<td>0.11</td>
<td>0.13</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Figure G3. Model and measurement of transported plumes from the Houston area to northeast Texas. The upper figures show the FLEXPART model calculations (Cooper et al.–NOAA) for SO₂ and NOₓ plumes, and the lower figures show the measurements from the NOAA WP-3D of sulfate aerosol and benzene concentrations (data from Middlebrook et al., de Gouw et al.–NOAA).
Preliminary Finding G5: Dust of African origin and sulfate aerosol advected into the region, even under southerly flow conditions from the Gulf of Mexico, make significant contributions to the background aerosol in the eastern Texas region.

Figure G4 summarizes the 2006 aerosol chemical composition measurements made on the NOAA R/V *Ronald H. Brown* in the Houston area. Under southerly flow, the sub-micrometer (60% RH) aerosol in the marine boundary layer over the Gulf of Mexico advecting into Texas was composed primarily of (NH₄)HSO₄ (80%). The mean total concentration was 4.0 ± 3.5 µg m⁻³. The NH₄/SO₄ molar ratio was 0.89 ± 0.43. Sulfate concentrations measured in the Houston Ship Channel (HSC) were twice as large as that measured over the Gulf of Mexico under southerly flow. Particulate organic matter (POM) concentrations were a factor of 10 greater in the HSC than that measured under southerly flow over the Gulf of Mexico. African dust was a major component of PM₂.₅ on 4 days during TexAQS 2006 when concentrations averaged 15 ± 1.7 µg m⁻³. These concentrations amount to nearly half of the 24-hour mean NAAQS for PM₂.₅. Scattering from the dust resulted in a white haze and low visibility in Galveston Bay.

Preliminary Finding G6: Nighttime chemistry influences the availability of oxides of nitrogen (NOₓ) and O₃ the next morning.

Nocturnal measurements of key nitrogen oxide species, NO₃ and N₂O₅, were made on the NOAA R/V *Ronald H. Brown* and WP-3D. Modeling based on these observations will be required to determine the correct partitioning and rates of reactions involving NOₓ, Oₓ (= O₃ + NO₂), NO₃, VOC, and N₂O₅ at night. For example, in the relatively warm Houston area, the partitioning between NO₃ and N₂O₅ favors NO₃. This may have the effect of slowing down nocturnal NOₓ and O₃ loss in this region. Large variability in nocturnal chemical processing of NOₓ and O₃ was observed, particularly between surface measurements on the R/V Brown and aircraft.
measurements on the P-3. While surface loss rates of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} were generally consistent with rapid loss of NO\textsubscript{x} and O\textsubscript{3}, some of the aircraft measurements showed transport of these compounds in the form of N\textsubscript{2}O\textsubscript{5} overnight. Therefore, further analysis will be needed to determine accurate NO\textsubscript{x} and O\textsubscript{3} loss rates at night, and the factors that govern the variability in these loss rates. Concentrations of NO\textsubscript{3} sufficient to induce rapid loss of highly reactive volatile organic compounds (HRVOC) at night also were observed intermittently, both at the surface and aloft. Consequently, further analysis will also be required to determine the conditions under which nocturnal HRVOC removal is significant.

**Preliminary Finding G7:** Low rural nighttime ozone concentrations have been observed at some, but not all, rural locations in northeast Texas; these low nighttime ozone concentrations are not replicated in the regulatory modeling. Photochemical models fail to reproduce the low nighttime ozone concentrations observed at some rural sites. Possible causes of this discrepancy include the presence of: 1) shallower nighttime boundary layers than predicted by the model at the affected sites, and 2) larger local NO emissions than included in emission inventories. If the latter possibility is the case, then corrections to the emissions inventory may be needed to accurately assess NO\textsubscript{x} concentrations and atmospheric chemistry upwind of northeast Texas cities and the Dallas-Fort Worth area.

**Required Additional Analyses**
All of the material presented here is based on preliminary analysis of a few example data. All findings are tentative at this point. Additional analysis will focus on a much more comprehensive evaluation of the complete data sets that will put the findings and ultimate conclusions on a more firm foundation.

Analysis of the cause of the low nighttime ozone observed at some rural sites in northeast Texas should be pursued.

**Key Citations and Information and Data Sources**

Preliminary Response to Question H

Question H
Which areas within Texas adversely affect the air quality of non-attainment areas in Texas?
Which areas outside of Texas adversely affect the air quality of non-attainment areas in Texas?

Question H Working Group

Background
Question H is closely related to Question G. Here Question H focuses on the source-receptor relationships that determine the background concentrations of ozone and aerosol in Texas and the meteorologically driven transport processes. Question G focuses on characterizing the background concentrations and the chemical and physical processes that affect those background concentrations.

Preliminary Findings

Preliminary Finding H1: Ozone can be transported into the Dallas area from the Houston area.
During 4-8 September 2006, there was a regional buildup of background ozone in eastern Texas, indicated by Dallas-Fort Worth (DFW) surface station ozone monitors (not shown) and airborne ozone lidar measurements (Figure H1). From 4–7 September, large-scale winds tended to be northerly to easterly. While the ozone was building up in Dallas, Houston also experienced a daily increase in ozone, resulting in 8-hr ozone averages up to 110 ppbv in Houston on 7 September (not shown). Between 7 and 8 September, a shift in the position of a synoptic-scale high caused the transport winds to Dallas to change from a weak northeasterly component to a stronger southerly component. This major shift in transport had a strong impact on Dallas, as 24-hour forward trajectories from Houston, beginning at 3 pm local time, indicated transport from Houston to Dallas (Figure H2). Also, elevated overnight O₃ concentrations were measured at two rural O₃ stations sited for TexAQS II (Palestine, and Italy). This transport brought additional ozone to a region that was already approaching 8-hr exceedance levels, resulting in 3 stations exceeding the 80 ppbv 8-hr-averaged O₃ in the DFW network.
Figure H1. Airborne ozone lidar measurements on 4 and 8 September 2006, showing the large increase in background ozone in eastern Texas between the two days (data from Senff et al.–NOAA).

Figure H2. Forward trajectories starting at 3 pm local time in Houston, 7 September, and ending at 3 pm local time on 8 September 2006. The trajectories show direct transport from Houston to Dallas. 7 September was an exceedance day in Houston, 8 September was an exceedance day in Dallas. (The trajectory map was created using the NOAA Physical Science Division (PSD) upper air back-trajectory tool [http://www.etl.noaa.gov/programs/2006/texaqs/traj/]).
Preliminary Finding H2: *High ozone concentrations in eastern Texas result from both in-state sources and transport of continental air from the east and northeast.*

Ensembles of historic Hysplit (see citations) 5-day back trajectories have been run from major Texas cities on high ($\geq 75$ ppb 8-hr max) and low $O_3$ days to characterize the upwind “dirty” and “clean” typical fetches. A residence time analysis of these trajectories yields high $O_3$ air residence maps for northeast Texas as exemplified in Figure H3. These maps (particularly the left one) show that transport of air from the east and northeast support many high $O_3$ episodes in August through October, but this analysis also shows that on high $O_3$ days in eastern Texas, the upwind air is resident within the state for several days, potentially building up background pollutants from in-state sources.

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Preliminary Finding H3: *A synthesis of satellite and in situ measurements with photochemical modeling and Lagrangian trajectory analyses provides a quantification of regional influences and distant sources on Houston and Dallas air quality during TexAQS 2006.*

Chemical assimilation/forecasts from the NASA Realtime Air Quality Modeling System (RAQMS) ([http://rossby.larc.nasa.gov/RAQMS/](http://rossby.larc.nasa.gov/RAQMS/)) accessed October 2006, with corroboration from satellite observations and aircraft data, provide a means to quantify regional influences on local air quality in Texas. A time series depiction of the RAQMS back-trajectory analysis of regional influences on Houston and Dallas $O_3$ is shown in Figure H4. Periods of enhanced regional $O_3$ production preceded 3 out of 6 Houston periods and 4 out of 6 Dallas periods with elevated $O_3$ during TexAQS 2006. The red line graph shows the observed mean and variability of surface $O_3$ measurements in the urban area at 18 UTC extracted from EPA’s AIRNOW data system ([http://www.airnow.gov/](http://www.airnow.gov/)) accessed October 2006). The blue line graphs show the RAQMS predictions with the solid blue for the predicted AIRNOW mean (bias corrected), and the dashed blue for the predicted background mean (bias corrected) immediately prior to entering the urban area. The color bar along the upper part of each time series indicates the regional influence classification code for the modeled extent of $O_3$ production and loss upwind (see key).
Case studies are being conducted to investigate the processes responsible for enhanced regional O₃ production rates during the TexAQS II period. One such case is early September 2006. Twelve-day boundary layer back trajectories were initialized at locations where the High Spectral Resolution Lidar (HSRL) instrument (used to look down from the NASA King Air airplane to assess the aerosol loading of the vertical column of air below) observed enhanced aerosol optical depths (AOD) indicating the presence of elevated particulate matter concentrations in the vicinity of Houston on September 04, 2006. Based on calculations of regional 24-hour rolling averages of TCEQ’s hourly PM₂.₅ concentrations, September 4 was one of only three days in the TexAQS II intensive period with widespread rolling 24-hour concentrations above 20 μg m⁻³. In addition, a speciation monitoring site in Deer Park showed elevated sulfate and carbon material for that date. The back trajectories link the local HSRL measurements to satellite column and profile measurements from various sensors on low-earth orbit satellites (see Table H1) on August 23, 2006.
Table H1. Satellite sensors and resulting data products.

<table>
<thead>
<tr>
<th>NASA Sensor</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>MODIS - Moderate Resolution Imaging Spectro-radiometer</td>
<td>Aerosol optical depth</td>
</tr>
<tr>
<td>CALIPSO - Cloud-Aerosol LIDAR and Infrared Pathfinder Satellite Observation</td>
<td>Aerosol optical depth profile</td>
</tr>
<tr>
<td>TES - Tropospheric Emission Spectrometer</td>
<td>Carbon monoxide profile estimate</td>
</tr>
<tr>
<td>AIRS - Atmospheric Infrared Sounder</td>
<td>Carbon monoxide</td>
</tr>
</tbody>
</table>

The 12-day back trajectories indicated two primary source regions: Southern Canada and the Eastern US. The MODIS sensor and AIRS sensor show column AOD and carbon monoxide (CO) enhancements associated with Pacific Northwest wild fire emissions within the Canadian branch, and CO enhancements associated within the Eastern US branch of the back trajectories. CALIPSO attenuated aerosol backscatter cross-sections through the central US show an elevated aerosol layer associated with wild fire emissions and boundary layer aerosol enhancements over the Eastern US. TES CO vertical cross-sections, which follow the same orbit as CALIPSO, show...
both lower and upper tropospheric CO enhancements. This case study illustrates the influence of remote emissions from the southeastern US and Pacific Northwest on Houston air quality. This analysis underscores the importance of integrating of satellite, aircraft, and surface measurements of aerosol and trace gases in conjunction with advanced modeling techniques for characterizing the impact of emissions from remote sources on local Texas air quality.

Additional case studies are presented on the TCEQ-Website, and a detailed case study is available from the Workshop for a July 20, 2004 O3 and PM2.5 episode in the Dallas area.

**Preliminary Finding H4:** Ozone transport modeling for the Dallas area shows that local emissions and transport each contributed about equally to the average 8-hr ozone exceedance in 2002.

Transport contributions to Dallas area O3 were quantified for June – September, 2002 using the CAMx photochemical model with emissions from EPA’s 2002 National Emissions Inventory (NEI) (updated by the Central Regional Air Planning (CENRAP) consortium) and meteorology from the MM5 model. The Dallas area had 35 days in 2002 with monitored 8-hour ozone levels of 85 ppb or higher. Averaged over these days, Dallas area emissions contributed about 48 ppb and other sources 54 ppb to the total modeled ozone 8-hour maximum of 102 ppb on the average exceedance day. The modeled average transport contribution from other parts of Texas was 6 ppb, and there were days when Northeast Texas, Houston/Beaumont, South Texas and Central Texas individually contributed 9 ppb or more. The average modeled transport contribution from other US states was 28 ppb, and the largest contributing states were Louisiana, Arkansas, Mississippi, Alabama, and Tennessee. These findings are consistent with back trajectory and residence time analyses. The example figure below compares CAMx O3 transport contributions to back trajectories for August 7, 2002. The 5-day back trajectories cross NE Texas, Arkansas, and Tennessee, extending to the mid-Atlantic region; the CAMx modeling finds these same regions contributing to the Dallas area O3 exceedance at the Ft. Worth NW monitor on August 7, 2002.
Required Additional Analyses
All of the material presented here is quite preliminary. All findings are tentative at this point. Additional analyses will focus on a much more comprehensive evaluation of the complete data sets that will put the findings and ultimate conclusions on a more firm foundation.

Key Citations and Information and Data Sources


Acknowledgment
The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.html) used in this report.
Preliminary Response to Question I

**Question I**

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, Bill Carter, David Parrish, Stu McKeen, Joost de Gouw, William Vizuete, Daewon Byun, Barry Lefer, Bernhard Rappenglück; Observers: Mark Estes, Noor Gillani.

**Background**

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 US EPA and are updated periodically to incorporate new experimental findings. For most urban areas, the CB mechanism, version IV (CB-IV) and SAPRC mechanism yield similar results, but for conditions found in Houston, the SAPRC mechanism leads to concentrations of ozone that are 30-50 ppb higher than in CB-IV and is more sensitive to reductions in NOx emissions, especially on days with high predicted ozone concentrations. These differences in the sensitivity of chemical mechanisms to the emission reductions 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.

Figure I1. Predictions of domain-wide maximum O₃ concentrations in CAMx on August 30, 2000 (analysis by Allen et al.–U. Texas).
Preliminary Findings

Preliminary Finding I1: Air quality modeling for both 2000 and 2006 shows substantial differences in the ozone concentrations predicted by the SAPRC and CB-IV chemical mechanisms.
Simulations performed using multiple modeling packages (CAMx and CMAQ), and multiple emissions preprocessing systems (SMOKE and EPS2) for 2000 and for 2006 predict higher ozone concentrations when the SAPRC mechanism is used than when the CB-IV mechanism is used. The differences in predicted ozone concentrations are greatest when predicted ozone concentrations are high.

Preliminary Finding I2: Comparison of environmental chamber experiments with mechanism predictions indicates that both SAPRC and CB-IV under-predict ozone concentrations under conditions with high NOx availability.
Based on comparisons of mechanism predictions with a wide range of chamber experiments, Carter (2004) concludes that the under-prediction of ozone concentrations in SAPRC under NOx-rich conditions is less than in CB-IV. When the ratio of reactive organic gas (ROG) concentrations to NOx is greater than the ratio that leads to maximum ozone concentration, both SAPRC and CB-IV mechanisms lead to modest under-predictions of ozone formation, when compared to environmental chamber experiments conducted at the University of California, Riverside (UCR). When NOx is available in excess, however, as it is in some portions of the Houston Ship Channel, the under-predictions of ozone concentrations in the CB-IV model are two to three times as large as the under-predictions in SAPRC. Detailed comparisons of the chamber conditions to Houston conditions still need to be performed to assess which of the chamber experiments reported in Figure I2, and experiments from other chambers such as the University of North Carolina, are most relevant to Texas conditions.

Figure I2. Comparison of CB4 and SAPRC-99 model errors for UCR EPA surrogate runs.
**Preliminary Finding 13:** In regions with very high hydrocarbon reactivity, near high NOx emission density, differences in ozone formation and accumulation predictions between the SAPRC and CB-IV mechanisms are due to differences in: (1) the chemistry of mono-substituted aromatics (e.g., toluene), (2) nitric acid formation rates, and (3) the rates of free radical source terms in the SAPRC and CB-IV mechanisms.

Under conditions relevant to Houston, the CB-IV mechanism predicts a higher proportion of ring-retaining products, such as cresols, than SAPRC, when mono-substituted aromatics react. These ring-retaining products are less reactive than the ring opening products. The CB-IV mechanism also predicts more extensive nitric acid formation, and less peroxyacetyl nitrate (PAN) than the SAPRC model, reducing radical concentrations, and the SAPRC mechanism has several source reactions for higher aldehydes that are not present in CB-IV. The enhanced free radical production in SAPRC, as compared to CB-IV, leads to higher radical concentrations.

**Preliminary Finding 14:** Ozone productivities predicted by the SAPRC mechanism are generally higher than those predicted by CB-IV.

Ozone productivity is defined as ozone formed per NOx converted to less reactive chemical forms. In the plumes from isolated petrochemical facilities, ozone productivities of 10-15 moles of ozone formed per mole of NOx consumed have been observed. Ozone productivities are typically 5-7 in Ship Channel plumes. The SAPRC model, with current estimates of emission inventories, predicts ozone productivities that are approximately 25-50% higher than those predicted by CB-IV. A systematic comparison of model predictions with ambient observations of ozone productivities needs to be performed.

**Required Additional Analyses**

Systematic comparisons of SAPRC and CB-IV predictions with ambient observations from both 2000 and 2006, and with environmental chamber experiments, are still required. These comparisons between predictions and observations should include ozone productivities, nitric acid concentrations, cresol concentrations, higher aldehyde concentrations, and free radical concentrations, under a variety of atmospheric conditions.

Predictions of mechanisms that currently are under development (CB05 and SAPRC-2006) should be compared to the predictions of CB-IV and SAPRC-99, as the new mechanisms become available.

Recognizing that it may be difficult to unambiguously define the most appropriate mechanism for use in Houston, the effectiveness of proposed control strategies should be evaluated using multiple chemical mechanisms.

**Key Citations and Information and Data Sources**


Preliminary Response to Question J

Question J
How well do air quality forecast models predict the observed ozone and aerosol formation?
What are the implications for improvement of ozone forecasts?

Question J Working Group

Background
A preliminary assessment of nine air quality forecast models (AQFMs) operating in real-time during TexAQS 2006 focuses on skill at predicting maximum 8-hour-average O₃ and 24-hr-average PM₂.₅ levels at 14 CAMS sites in east Texas based on bulk statistical parameters. These models include the NCEP CMAQ-WRF model, three versions of the NOAA/ESRL WRF-Chem model, the Canadian CMC AURAMS and CHRONOS models, two versions of the Baron-AMS MAQSIP-RT model, and the University of Iowa STEM model. Only three bulk statistical parameters, Mean Absolute Error (MAE), Root Mean Square Error (RMSE), and correlation coefficients have been evaluated in this preliminary work. Skill for these three statistics is measured relative to persistence forecasts, or the forecast that tomorrow’s AQ levels are the same as today’s observed levels. In addition, bias-corrected model forecast values are calculated based on the mean O₃ or PM₂.₅ bias at each site at each hour of the day, averaged over the previous 7 days. The statistical parameters are also calculated from the ensemble of the models, and the ensemble of bias corrected models. The summary statistics for the models and their ensemble are shown in Fig. J1 for O₃, and Figure J2 for PM₂.₅. Also shown are MAE and RMSE for persistence and climatology forecasts, and correlation coefficients for persistence.

The University of Houston also made nine AQ forecasts using three model resolutions and three emission scenarios with the MM5/CMAQ model. Detailed statistical summaries for O₃ and PM₂.₅ for each forecast, and for each of the CAMS surface monitors can be found at the University of Houston web page: [http://www.imaqs.uh.edu/ftp/AQF_usa/](http://www.imaqs.uh.edu/ftp/AQF_usa/) (password protected).
Figure J1. Summary statistics for 8-hour maximum ozone for nine models and their ensemble mean (analysis by McKeen et al.–NOAA).
Preliminary Findings

**Preliminary Finding J1:** Photochemical model ensembles, particularly when they are combined in an optimal manner, outperform any individual forecast model overall.

General features that emerged from the assessment of these nine air quality forecast models are:

- No model beats persistence MAE and RMSE by a significant amount.
- Bias correction usually improves forecasts.
- Models tend to forecast O₃ better than PM₂.₅.
- The ensemble is better than all individual models.
- The ensemble beats persistence for ozone correlation, but not for PM₂.₅.
- The bias-corrected ensemble provides the best forecast for both ozone and PM₂.₅.
Daytime planetary boundary layer (PBL) heights from seven of the models were compared to those derived from wind profiler measurements at several sites in east Texas. Some models show persistent bias in daytime PBL, and no model appears to stand out in terms of significantly better comparisons. The different definition or diagnostic evaluation of PBL depth within each model precludes final evaluation and comparisons to features in the observations, such as spatial gradients in PBL depth.

**Preliminary Finding J2:** Sophisticated data assimilation of meteorological and even chemical observations is essential for improving photochemical model forecasts.

Spatial and temporal accuracy of AQ forecasts are to a large degree limited by the accuracy of the underlying meteorological forecasts within the AQ models. Most models rely on the available NCEP/NAM model product for initialization and boundary conditions, which may contribute to model biases in AQ model wind fields and pressure patterns documented throughout the field study. Retrospective forecasts and sensitivity studies are needed to assess the impact of the NAM forecasts available in the summer of 2006 to AQFMs, particularly in light of recent upgrades to the WRF-NMM model used in the NAM forecasts. Assimilation of wind profiler data (Nielsen-Gammon et al., 2006) has been shown to improve forecast meteorology in the Houston area. Similar research related to the assimilation of photochemical and aerosol data within AQFMs should be encouraged, utilizing the comprehensive data sets from the TexAQS 2006 field study.

Deficiencies in AQ forecasts from several of the models appear to be related to the formulation of PBL height, particularly the characterization of the stable boundary layer. The misrepresentation of the stable PBL often affects model-predicted offshore pollutant transport and pollution precursor buildup from emissions along the coastlines. Persistent errors in the forecast of the low-level nocturnal jet are also characteristic of many models. Preliminary sensitivity studies with the MM5/CMAQ model also have demonstrated a case of over-predicted O₃ associated with a missed forecast of widespread precipitation (August 24, 25). The collection of available satellite, radar, and surface network data sets for comparing cloudiness, precipitation, and radiation with model output are needed to perform further evaluations of these parameters, and their relationships to O₃ and PM₂.₅ forecasts.

**Preliminary Finding J3:** Model performance evaluations and intercomparisons need a comprehensive, best-guess emissions inventory for the TexAQS 2006 Field Intensive.

Ozone and PM₂.₅ forecasts are highly dependent on the emissions inventories of precursor emissions, and PM₂.₅ forecasts are also dependent on primary emissions at many of the urban and suburban CAMS locations. A high priority in the model evaluation effort should be placed on using TexAQS 2006 field data to determine the accuracy of the inventories that drive AQ forecasts. Ozone forecasts are particularly sensitive to emissions estimates of highly reactive VOC, such as ethylene and propylene, from large petrochemical facilities, especially in the Houston ship channel region. The release of quality-assured VOC measurements from the various platforms precludes the evaluation of the model emissions inventories. Two preliminary sensitivity results from the University of Houston MM5/CMAQ model relate directly to emissions inventory validation. That model shows generally improved NO₂ and O₃ comparisons with CAMS site data using an emission inventory based on projections to 2005 as opposed to an inventory based on 2000 estimates. A narrow plume of extremely high O₃ observed downtown and west of Houston (September 7) that was significantly under-predicted by the original
forecast was found to be replicated accurately in retrospective runs that included a large VOC source in the ship channel region, presumably from an upset release not included in the base emissions inventory.

**Key Citations and Information and Data Sources**

Preliminary Response to Question K

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?

Question K Working Group

Background
This question is closely related to Question F. Here the focus is on the distinctive photochemistry of the HGB area that is attributed primarily to the petrochemical industry emissions, and Question F will focus on a more general discussion of the entire east Texas region.

Both observation and modeling based approaches to determining the sensitivity of high ozone to VOC and NOx emissions have been applied to the HGB non-attainment area. Both have focused on the year 2000.

Preliminary Findings

Preliminary Finding K1: Both Eulerian and Lagrangian plume modeling approaches indicate that in 2000 the high ozone in the HGB area was sensitive to both VOC and NOx emission reductions (Wert et al., 2003; TCEQ, 2004, 2006).

Simple Lagrangian plume model
Wert et al. (2003) present a Lagrangian plume model designed to closely reproduce emissions, ozone formation and plume dispersion observed during the TexAQS 2000 study. The model accurately reproduced the rapid production of ozone and formaldehyde observed in a highly polluted plume (200+ ppbv ozone and 30+ ppbv formaldehyde) originating from the ship channel region of Houston. The model required only two NMHCs, ethene and propene. Two factors were both critical in successfully modeling the highest ozone levels: a high ozone production efficiency as shown by observations (e.g. Figures A2 and A3 of this report), and a rapid rate of ozone production. High ozone production efficiency assures that high ozone can be produced from the emitted precursors, and the rapid rate of ozone production assures that high ozone is produced before the plumes of emissions have a chance to dilute and disperse. In the plumes from the industrial facilities in the Houston Ship Channel region, the HRVOC loading is high enough that the ozone production efficiency is maximized. Under these conditions, the ozone is NOx-sensitive, because reducing NOx emissions reduces the NOx available for oxidation at that high ozone production efficiency. The high HRVOC loading also is necessary for rapid ozone production. Under these conditions the ozone is also VOC-sensitive, because reducing HRVOC emissions reduces the maximum amount of ozone that can be formed while the plume is being diluted and dispersed during transport. Wert et al. (2003) concluded that targeted reductions in either or both emission categories would effectively reduce the highest observed ozone levels.
**Eulerian modeling**
TCEQ (2004, 2006) has conducted Eulerian modeling of the entire HGB nonattainment area in order to determine which controls are necessary to reach attainment. This modeling indicates that both VOC and NOx controls are effective in reducing ozone in 2000.

In particular, two tests have indicated sensitivity to both VOC and NOx in Houston: reductions of biogenic VOC emissions by 30%, and modeling of weekend/weekday differences in mobile source emissions. However, in both cases, the effects on ozone concentrations varied by location within the HGB area, and meteorological conditions, suggesting that VOC and NOx sensitivity in HGB varies spatially and temporally.

In future case modeling scenarios, TCEQ modeling indicates in HGB that VOC controls become less and less effective as NOx controls are increased. Consequently, the modeling shows that attainment would require substantial NOx cuts, and cannot be reached with VOC cuts alone. In this respect, it matches the situation in the DFW nonattainment area.

**“Radical Starvation” in selected modeling scenarios**
A photochemical grid modeling scenario has shown that under certain conditions with high concentrations of highly reactive VOCs, ozone formation can be inhibited by "radical starvation". The radical starvation can be alleviated by adding large quantities of primary formaldehyde emissions, CO emissions, or aromatic emissions, or by changing to the SAPRC99 chemical mechanism. It is unclear at this point which, if any, of these solutions are appropriate for Houston modeling.

**Preliminary Finding K2:** An observation-based approach to determine the sensitivities of high ozone in the HGB non-attainment area to the precursor VOC and NOx emissions has been investigated; it has yielded ambiguous results.

**Observation-based approach**
The observation-based approach selected is based upon the relationships between indicator species developed by S. Sillman (http://www-personal.engin.umich.edu/~sillman/obm.htm). This approach was selected because: 1) it addresses integrated total O3 produced (not instantaneous rate of O3 production), and is thus designed to answer the question of how maximum O3 responds to changes in VOC versus changes in NOx emissions; 2) it is arguably the most fully developed observation-based method and is widely used; 3) it is related to the ozone production efficiency relationships exemplified in Figures A2 and A3 of this report; and 4) it utilizes measurements made with high precision and accuracy on the NOAA-operated Electra during TexAQS 2000 and the NOAA WP-3D and R/V Ronald Brown during TexAQS 2006.

Figure K1 compares the measurements made from the Electra during TexAQS 2000 with the modeled indicator species relationships of Sillman. These two relationships are those discussed most thoroughly by him. The data shown include all 5-second average measurements made in the greater Houston area (94.3-96.3 deg. E Long., 28.7-30.7 deg. N. Lat.), which includes the entire urban area, all petrochemical facilities including the isolated Gulf Coast facilities, and the Parish power plant.
The indicator species relationships in Figure K1 give ambiguous results. In both figures the data are predominately localized in the predominately NOx-sensitive region, but some points are in the mixed and predominately VOC-sensitive regions. Further, the model results themselves are interspersed between regions. Definitive conclusions cannot be drawn from these figures. This ambiguity is particularly clear in the examination of ozone data above 200 ppbv. These data were collected on three days: August 25 and 30 and September 1 (see Figure A2). The relationship of ozone with HNO₃ suggests that all three days represent NOx-sensitive conditions, while the relationship of ozone with NOy - NOx suggests that the three days span the full range from NOx-sensitive to VOC-sensitive. It is clear that no definitive conclusions can be drawn. It may be that the indicator species relationships may be most useful as a basis of comparison of models with measurements.
Required Additional Analyses

The issue of NOx vs VOC sensitivity in the HGB area is central to the even more important SIP-relevant question of “direction of control” – that is, should ozone control efforts in the HGB ozone non-attainment area be focused on: a) decreasing emissions of NOx alone, b) decreasing emissions of VOC alone, or c) decreasing emissions of both NOx and VOC. It is clear from the discussions that already have taken place within the Rapid Science Synthesis Team about the Preliminary Findings for Question K, that developing a scientific consensus about suitable methods to resolve these issues is likely to be a long and probably contentious process. Thus, it is desirable that the requisite discussions and debates about this issue should be undertaken in earnest.

Providing reliable answers to Question K will require a comprehensive modeling effort. This modeling will require both inventory assembly and photochemical modeling:

1. Development of the most nearly realistic emission inventory possible, for the HGB area for both 2000 and 2006. The inventory must include HRVOC, AVOC, BVOC, OVOC, and NOx; must pay particular attention to appropriate magnitude and spatial distributions (i.e. co-emission with NOx) of HRVOC emissions; and be compared to the fullest extent possible with available observations (e.g. NOAA WP-3D and Solar Occulsion Flux measurements in 2006). An available, open inventory is critical so that the results of different models can be directly compared.

2. Analysis through traditional Eulerian AQ modeling with a focus on 8-hour-averaged ozone and its sensitivities to variation in AVOC, BVOC, HRVOC, OVOC, and NOx emissions. Particular attention must be paid to the ability of the model to resolve the plumes that determine the highest ozone values. Such resolution is easily treated by the simple Lagrangian plume model, but may be a severe challenge for Eulerian AQ models.

3. Verification of the performance of the models through their ability to reproduce the observations collected during TexAQS 2000 and 2006; particular attention should be paid to relationships between ozone and other photochemical products such as aldehydes and organic nitrates, and observed radical concentrations.

Key Citations and Information and Data Sources


S. Sillman Observation-based methods (OBMs) for analyzing urban/regional ozone production and Ozone-NOx-VOC sensitivity ([http://www-personal.engin.umich.edu/~sillman/obm.htm](http://www-personal.engin.umich.edu/~sillman/obm.htm))


Response to Question L

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

Background
In order to address this question, databases that are potentially useful to individuals performing air quality modeling for Texas, including both permanent measurements and enhanced measurements from TexAQS II deployments, were compiled. The databases were evaluated based on several criteria, including quality control, accessibility, regional coverage, and time resolution. Web links to the databases are shown below. The full Question L report, including evaluations, can be found in Appendix 1.

Findings

Surface Meteorology and Chemistry Data

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

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

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

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

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

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

Soil Climate Analysis Network, US Agriculture Department
http://www.wcc.nrcs.usda.gov/scan/

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

Louisiana Universities Marine Consortium weather network.
http://weather.lumcon.edu/
CAMS (TCEQ organized surface meteorological and chemical data)
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)
http://www.nndc.noaa.gov/cgi-bin/ndc/buyOL-001.cgi

Oklahoma air quality monitors
http://www.deq.state.ok.us/AQDnew/monitoring/index.htm

Upper Air Data

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

NOAA National Profiler Network graphical display
http://www.profiler.noaa.gov/npn/

Rapid Update Cycle (RUC) soundings
http://rucsounding.noaa.gov/

University of Wyoming sounding page
http://weather.uwyo.edu/upperair/sounding.html

ACARS aircraft observations
http://amdar.noaa.gov/

Coastal and Buoy Data

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

NDBC (National buoy data)
http://www.ndbc.noaa.gov/Maps/WestGulf.shtml

Houston/Galveston Port Meteorological Office
http://www.srh.noaa.gov/hgx/marine/pro.htm

Satellite Data

Space Science and Engineering Center, University of Wisconsin, Madison
http://www.ssec.wisc.edu/

TES step and stare observations
http://tes.jpl.nasa.gov
NOAA and DoD satellite images
http://www.class.noaa.gov/nsaa/products/welcome;jsessionid=1C0E54F015C2813E5A9ACFC22C675F90

NASA Earth Observatory natural hazards
http://earthobservatory.nasa.gov/NaturalHazards/

MODIS Rapid Response System images
http://rapidfire.sci.gsfc.nasa.gov/realtime/2006297/

AIRS retrieved CO profiles
http://asl.umbc.edu/pub/mcmillan/www/index.html#calendar

Solar Radiation Data

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

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

Large, Multi-field Data Sets

MADIS
http://madis.noaa.gov/

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

EDAS (NCEP grid reanalysis)
http://www.cdc.noaa.gov/cdc/reanalysis/reanalysis.shtml

NCEP/NCAR Reanalysis
http://dss.ucar.edu/pub/reanalysis/
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Question L Final Report

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

Background
In order to address this question, databases that are potentially useful to individuals performing air quality modeling for Texas, including both permanent measurements and enhanced measurements from TexAQS II deployments, were compiled. The databases were evaluated based on several criteria, including quality control, accessibility, regional coverage, and time resolution. Web links to the databases are given, followed by a brief description and evaluation.

Findings

Surface Meteorology and Chemistry Data

COOP observations
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
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
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 quality-controlled). 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 is 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
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
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
http://texaset.tamu.edu/weatherstns.php
This one would be useful for Texas meteorological comparisons of precipitation (not many CAMS sites have precipitation), temp, RH, wind speed, wind direction, and solar radiation. Pretty good coverage in East Texas. Hourly data should be simple to download and compare with model results.

Soil Climate Analysis Network, US Agriculture Department
http://www.wcc.nrcs.usda.gov/scan/
This site only gives soil parameters - no standard met. There is only one site (Prairie View) in the region of Texas that may be useful to TexAQS 2006 participants. Nonetheless, it may useful for comparison of soil models and parameterizations in meteorological models, since soil data is so sparse in the east Texas region.

Louisiana agricultural weather data network
http://www.agctr.lsu.edu/subjects/weather/
This site is specific to the state of Louisiana. It gives meteorological and soil parameter data at about 20 sites evenly distributed throughout Louisiana. The data are not so convenient to download. But the soil parameters may be useful for meteorological model soil data comparisons.

Louisiana Universities Marine Consortium weather network.
http://weather.lumcon.edu/
This web site includes measurements from 5 sites in Louisiana run by LUMCOM (Louisiana Universities Marine Consortium). Four of the sites are on platforms over water. The 5th site is somewhat inland, but looks like it’s in a marshy/wetlands type of area. The Lake Pontchartrain station is in the northern part of the lake. Meteorological data include: atmospheric pressure, humidity, temperature, winds, solar radiation, and precipitation. Hydrographic instrumentation include: chlorophyll probe, conductivity probe, and a sonde, 6600. Three other sites have the same instruments: Tambour Bay, Southwest Pass/Miss River and LUMCOM. The Tambour Bay and Southwest sites are off the LA coast, on platforms. LUMCOM is the slightly inland site and also has a co-located 915-mHz wind profiler with RASS. The Audubon/Miss River site is on a floating structure near the coast (from the picture is looks like it’s in a harbor). It only has atmospheric pressure, humidity, and temperature for meteorological measurements. It has the same hydrographic measurements as Lake Pontchartrain, plus a wet chemical in-situ nitrate analyzer.

The web site is comprehensive, with a map and much information for each station. There are records regarding calibrations and inspections, implying that these sites are well maintained. These appear to be good sites for modelers to obtain coastal meteorological data for Louisiana. The archived files are easy to access.
CAMS (TCEQ organized surface meteorological and chemical data)
http://www.tceq.state.tx.us/nav/eq/mon_sites.html
This website includes information regarding the details of the TCEQ measurements sites. Many sites have both meteorology and chemistry measurements. Some have just one or the other. All chemistry sites appear to have ozone measurements, but some also include NO, NO2, and perhaps other important constituents. Those with meteorology tend to have temperature and winds, perhaps precipitation. This site has two links:

1) TCEQ’s Air Monitoring Sites (Regional Map) provides details about the TCEQ's air monitoring sites and air pollution, weather and other parameters measured at each site.

2) Air Monitoring Sites (Table)
Provides a user interface to view sortable list of locations and descriptions of monitoring sites operated by the TCEQ and other entities around the state as well as link to photos of sites, lists of parameters monitored, and current measurements.

This is useful for modelers who want to know the locations of monitoring stations, and what is monitored at each station.

http://www.tceq.state.tx.us/compliance/monitoring/air/monops/historical_data.html
This page provides access to two sources of pollutant and weather data. The first source, the Texas Commission on Environmental Quality (TCEQ) and local monitoring networks, provides hourly pollutant and weather data from 1972 to 2004. The second source, the U.S. Environmental Protection Agency (EPA), provides data summaries and hourly data collected since 1982 on numerous pollutants and meteorological parameters in Texas and other states.

A useful site for modelers to download hourly surface data for model evaluation.

METARs (NWS surface data)
http://www.nndc.noaa.gov/cgi-bin/nndc/buyOL-001.cgi
The Unedited Surface Weather Observations product consists of unedited hourly observations from over 700 U.S. locations. There is a charge to access this data online, but not if your domain is .gov, .mil, or .edu. (More details on the web site.) The time range of the available data is from July 1, 1996 to two days ago. A useful site for obtaining surface observations for model evaluation.

Oklahoma air quality monitors
http://www.deq.state.ok.us/AQDnew/monitoring/index.htm
This site has the details of the air quality monitoring stations in Oklahoma. There are several monitoring sites north of the Texas-Oklahoma border that would be useful for southerly flow events (e.g., looking at transport from Dallas to Oklahoma). For a graphical display, the site links to the EPA site http://www.airnow.gov/index.cfm?action=airnow.currentconditions, where the user can click on the state of Oklahoma to see the Oklahoma observations. Text data includes real-time data (for today and yesterday). The user can sort by pollutant or by station. Archived data includes 8-hour averages of ozone and CO, organized by year. Within each year is the date and amount of the 4 highest readings for each station. One-hour ozone exceedances are also available in this format. It does not appear that data other than the 4 highest readings per year are available via the web. This site is probably somewhat useful for modelers.
Upper Air Data

ESRL (formerly ETL) Profiler Network, South Central Texas
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 include 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
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
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 are 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
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
http://amdar.noaa.gov/
ACARS observations are in situ meteorological observations made by commercial aircraft. The data include temperature, wind, and often dew point. The wind precision is not very good, but the temperature and dew point 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 are not freely available in real time on the web, but they are 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

Texas Coastal Ocean Observation Network, Texas A&M Corpus Christi, Conrad Blucher Institute
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.

Possibly useful for improving resolution of model validations for simple parameters.

NDBC (National buoy data)
http://www.ndbc.noaa.gov/Maps/WestGulf.shtml
Provides listings of hourly meteorological data (air and sea-surface temperature, winds, pressure, etc.) and wave data for each meteorological buoy in the Gulf of Mexico (and elsewhere around the U.S.). Meteorological data are archived back as far as 1990 for some sites. Also a section gives data on ocean currents as a function of depth. Buoy and other instrument locations are displayed on a map, and data are obtained by clicking on the site of interest. Recent ship observations are also listed at this site, and the tri-annual *Mariners Weather Log*.

Houston/Galveston Port Meteorological Office
http://www.srh.noaa.gov/hgx/marine/pro.htm
Houston/Galveston Port Meteorological Office

Site includes a description of needs for maritime meteorological data and the role of this office in facilitation of the Voluntary Observing Ship (VOS) Program. The office also “works within the framework of the Shipboard Environmental (Data) Acquisition System (SEAS), by which meteorological data are collected and transmitted to NCEP, for inclusion in the major data bases. Under *Past Weather*, this site has climatological data and daily information for several Texas land stations around the Gulf of Mexico, including daily high and low temperatures, wind, precipitation, and some other meteorological data. The monthly Texas Climatic Bulletins and other climatological products and information are available at this site. We were unable to locate any actual shipboard data from this site (however, some current data could be found on the NDBC site).
**Satellite Data**

**Space Science and Engineering Center, University of Wisconsin, Madison**

[http://www.ssec.wisc.edu/](http://www.ssec.wisc.edu/)

Comprehensive archive of data, products, and downloadable processing software for geosynchronous and polar-orbiting satellites, including GOES-11 and -12 and MODIS data from Terra and Aqua. A host of real-time satellite images and products are also available, some stored for 7 days. Routine meteorological data are also available for McIdas users.

**NASA Aura TES step and stare observations**


TES is an infrared, high resolution, Fourier Transform spectrometer covering the spectral range 650 - 3050 cm\(^{-1}\) (3.3 - 15.4 \(\mu\)m) at a spectral resolution of 0.1 cm\(^{-1}\) (nadir viewing) or 0.025 cm\(^{-1}\) (limb viewing). Launched into a polar sun-synchronous orbit (13:38 hrs local mean solar time ascending node) on July 15, 2004, the TES orbit repeats its ground track every 16 days (233 orbits), allowing global mapping of the vertical distribution of tropospheric ozone and carbon monoxide along with atmospheric temperature, water vapor, surface properties (nadir), and effective cloud properties (nadir). TES has a fixed array of 16 detectors, which in the nadir mode, have an individual footprint of approximately 5.3 x .5 km. In order to increase the signal-to-noise ratio, these detectors are averaged together to produce a combined footprint of 5.3x8.4 km. TES has two basic observational modes: the global survey mode, where observations are taken 1.3 degrees apart in latitude, and the "step-and-stare" mode, where the separation between observations is approximately 35 km along the orbit. This step-and-stare mode was used extensively throughout the TexAQS 2006 campaign.

Maps of these profiles can be found at [http://tes.jpl.nasa.gov/TexAQS_2006/main_SS_TEXAQS_2006.html](http://tes.jpl.nasa.gov/TexAQS_2006/main_SS_TEXAQS_2006.html)

Contact information: [kevin.bowman@jpl.nasa.gov](mailto:kevin.bowman@jpl.nasa.gov)

**NASA CALIPSO observations**


The Cloud-aerosol lidar and Infrared Pathfinder satellite Observations (CALIPSO) satellite mission was launched on April 28, 2006 for a planned 3-year mission. CALIPSO is flying in formation with Aqua, Aura, CloudSat, and Parasol satellites as part of the Afternoon Constellation or A-train. The CALIPSO payload consists of three instruments: the Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP); the Infrared Imaging Radiometer (IIR) and the Wide Field Camera (WFC). CALIPO is a nadir-pointing instrument which provides profile measurements of aerosol backscatter at 532 and 1064 nm and depolarization at 532 nm. The IIR provides calibrated radiances at 8.65 \(\mu\)m, 10.6 \(\mu\)m, and 12.05 \(\mu\)m over a 64 km swath centered on the lidar footprint and a pixel resolution of 1 km. The WFC consists of a single channel covering the 620 nm to 670 nm spectral region providing images of a 61 km swath with a spatial resolution of 125 m in a band 5 km about the nadir track and 1000 m elsewhere. For TexAQS 2006 campaign, CALIPSO quick turn-around browse images were produced to identify aerosol and cloud layers for flight planning activities. Observations were also synthesized into aerosol modeling systems to better understand the origin of surface and elevated aerosol features from regions outside the experiment domain.
Examples of aerosol browse images used during TexAQS can be found at [http://www-calipso.larc.nasa.gov/products/lidar/](http://www-calipso.larc.nasa.gov/products/lidar/)

Contact information: [Charles.R.Trepte@nasa.gov](mailto:Charles.R.Trepte@nasa.gov)

**NOAA and DoD satellite images**

[http://www.class.noaa.gov/nsaa/products/welcome;jsessionid=1C0E54F015C2813E5A9ACFC22C675F90](http://www.class.noaa.gov/nsaa/products/welcome;jsessionid=1C0E54F015C2813E5A9ACFC22C675F90)

The National Oceanic and Atmospheric Administration (NOAA) Comprehensive Large Array-data Stewardship System (CLASS) is NOAA's premier on-line facility for the distribution of NOAA and US Department of Defense (DoD) Polar-orbiting Operational Environmental Satellite (POES) data and derived data products. CLASS is operated by the Information Processing Division (IPD) of the Office of Satellite Data Processing and Distribution (OSDPD), a branch of the National Environmental Satellite, Data and Information Service (NESDIS).

CLASS maintains an active partnership with NOAA's National Climatic Data Center (NCDC). NCDC, the permanent US Archive for POES data and derived data products, supports CLASS through a user-interactive Help Desk facility and through the provision of POES supporting documentation, including the NOAA Polar Orbiter Data (POD) User's Guide and the NOAA KLM User's Guide. Additionally, NCDC and CLASS share data distribution responsibilities for Defense Meteorological Satellite Program (DMSP) data under a Memorandum of Understanding with the National Aeronautics and Space Administration (NASA) for the Earth Observing System (EOS) Program.

CLASS provides data free of charge. Anyone can search the CLASS catalog and view search results through CLASS's World Wide Web (WWW) site. Users who wish to order data are required to register with their names and email addresses. CLASS distributes data to those users via FTP services.

CLASS (originally called Satellite Active Archive), was established as a demonstration prototype for electronic distribution of POES data in 1994, and became operational in July 1995. During that first month, 379 Advanced Very High Resolution Radiometer (AVHRR) Level 1b data sets were distributed to 27 customers via the emerging Internet. During the first five years of operation, the average monthly volume of data distribution increased to 65,000 data sets with a total size of 1.2 TB, and the SAA customer base grew to more than 10,000 registered customers. The active archive was expanded during that period to include TIROS Operational Vertical Sounder (TOVS) data, Defense Meteorological Satellite Program (DMSP) data, Radarsat Synthetic Aperture Radar (SAR) imagery, operational (near-term) satellite-derived products, and climatic (time-series) satellite-derived products.

**NASA Earth Observatory natural hazards**

[http://earthobservatory.nasa.gov/NaturalHazards/](http://earthobservatory.nasa.gov/NaturalHazards/)

This is a NASA site that has awesome satellite images due to the following natural phenomena: crops & drought; dust & smoke, fires, floods, severe storms, and volcanoes. The images are organized by event, and are free to all. They just ask for proper acknowledgment. This site is probably of limited value to modelers, but for certain events, such as the Saharan dust events that occurred during TexAQS II, the images may add some visual interest for a case study presentation.
NASA MODIS Rapid Response System images
http://rapidfire.sci.gsfc.nasa.gov/realtime/2006297/
This site has images from MODIS (Terra and Aqua). Images are archived by day, and can be downloaded. This site may be somewhat useful for modelers.

NASA Aqua AIRS retrieved CO profiles
http://asl.umbc.edu/pub/mcmillan/www/index.html#calendar
AIRS output for the TexAQS II field campaign. There is a clickable calendar for a view of the data. Please work with Dr. Wallace McMillan if interested in using the data (contact information is on the web site).

**Solar Radiation Data**

Texas Solar Radiation data, from a solar energy research group at UT
http://www.me.utexas.edu/~solarlab/tsrdb/
This site has solar radiation data for 15 sites throughout Texas. The data intervals and times of coverage vary by station, ranging from 15 minute data to monthly averages. Data stops in 2003 or earlier for many of the stations. Data reported: Global horizontal, direct normal, and diffuse horizontal (W m$^{-2}$). Monthly averages include temperature (degrees C). Data are easy to access. This site may be moderately useful for modelers.

National Renewable Energy Lab (solar radiation data)
http://rredc.nrel.gov/solar/new_data/confrrm/
Cooperative Networks for Renewable Resource Measurements (CONFRRM). This network was designed to capture long-term solar radiation and wind measurements. There are 5 sites in Texas, however the last month showing data for all sites is March 2000. Therefore, data on this site are not useful for modelers working on summers 2000 – 2006.
Large, Multi-field Data Sets

MADIS
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 very 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. 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
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)**
http://www.cdc.noaa.gov/cdc/reanalysis/reanalysis.shtml
It is a website for the NCEP/NCAR Reanalysis Project at the NOAA/ESRL Physical Sciences Division
This page points you to information on the NCEP/NCAR Reanalysis project and the implementation of a netCDF-based, internet-accessible, data service at NOAA/ESRL PSD for this set of data products.

* The 6-hourly and daily data currently available on-line.
* The monthly and other derived data currently available on-line.
This site also has links to other reanalysis project sites (e.g., ECMWF).

**NCEP/NCAR Reanalysis**
http://dss.ucar.edu/pub/reanalysis/
This site includes the following NCEP/NCAR REANALYSIS databases.

* DSS Reanalysis archives.

Project Overview

* Project Description -

    The project motivation and objectives, cooperative arrangement between NCEP and NCAR, and other published documentation are outlined

* Model Description
* Project Status
* Other Related Sites

Data Product Description

More than 20 different data products are output from the Reanalysis data assimilation, model run, and model forecast. These products are defined in terms of the NCAR archive names, physical variables, resolutions (temporal and spatial), and media storage size. CDROMs are also used to distribute selected reanalysis products.
This web site includes much detail on all of the data bases used, etc.

* 2006AUG10 --All 1948-2006JUL pgb.f00 and grb2d files are now available on line for registered users.

* 2006AUG10 --JUL 2006 data files are released. All 1948-2006JUL reanalysis files are available.

* 2006APR20 --Public (non-restricted) version of 200309-200602 prepqm files are released.

* 2006APR11 --2005 annual cdrom is released. All 1950-2005 reanalysis annual cdroms are available.

* 2006MAR28 --2005OCT-2006FEB reanalysis forecasts are released.

* 2005Apr20 --2004OCT-2004DEC reruns to fix sea-ice problems are released.

* 2005Apr19 --2004AUG and 2004SEP reruns to fix sea-ice problems are released.

* 2005Apr08 --There will be a rerun from 2004080100 to 2005032212 due to sea-ice data problem. The 200501 and 200502 results are in.


* DSS Reanalysis archives.

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