State of the Science of Air Quality in Texas:

Scientific Findings from the Air Quality Research Program (AQRP) and Recommendations for Future Research

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Air Quality Research Program Independent Technical Advisory Committee

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Executive Summary

The goals of the State of Texas Air Quality Research Program (AQRP) are:

(i) to support scientific research related to Texas air quality, in the areas of emissions inventory development, atmospheric chemistry, meteorology and air quality modeling,
(ii) to integrate AQRP research with the work of other organizations, and
(iii) to communicate the results of AQRP research to air quality decision-makers and stakeholders.

Beginning with the 2010-2011 biennium, the Texas Commission on Environmental Quality (TCEQ) contracted with the University of Texas at Austin to administer the AQRP. During the 2010-2011 biennium, the AQRP funded 16 projects, which have now been completed. The purpose of this State of the Science document is to describe the current state of scientific understanding on key issues addressed by the AQRP, to summarize key findings from 2010-2011 AQRP projects and to identify high priority topics for AQRP funded research in the 2012-2013 biennium.

Current scientific understanding of emissions, chemistry, meteorology and modeling of the transport of air pollutants is described through sets of key findings; citations to the scientific literature provide additional details. Because many of the measurements on which findings are based emerge from air quality field programs, a separate section provides a summary of recent field studies conducted in Texas, including studies sponsored by AQRP and studies sponsored by other organizations.

AQRP projects funded in the 2010-2011 biennium made significant contributions to improved scientific understanding of air quality in Texas. Highlights include continuing improvement in characterizing emission sources from industrial operations, deployment of advanced measurement instruments in natural gas production regions near Fort Worth (Barnett Shale), studies of industrial flares, both in production operations and in controlled burn situations, and a variety of improvements to air quality modeling tools.

In 2012-2013, priorities for the AQRP research program will include continuing data analyses for measurements conducted during the 2010-2011 biennium:

- Analysis of data collected in the Dallas-Fort Worth (Barnett Shale) field campaign
- Analysis of flare operating regimes that provide both high combustion efficiency and minimal smoke formation

In addition, several new initiatives will have a high priority:

- Deployment of supplementary measurements in a large field measurement campaign planned by NASA for the summer of 2013
- Analysis of prior Texas field study data and modeling tools to investigate transformation of gas-phase pollutants to aerosol phase
- Investigation of how the temporal resolution of meso-scale meteorology and photochemical grid models must be altered for high spatial resolution modeling; investigation of mesoscale modeling of cloud formation and the effects of clouds upon ozone and PM chemistry;
- Analysis of radical chemistry in Texas cities, especially HONO formation, ozone removal and production by halogen chemistry, and atmospheric chemistry within industrial plumes.
- Analysis of the impact of global and regional transport of air pollutants on Texas

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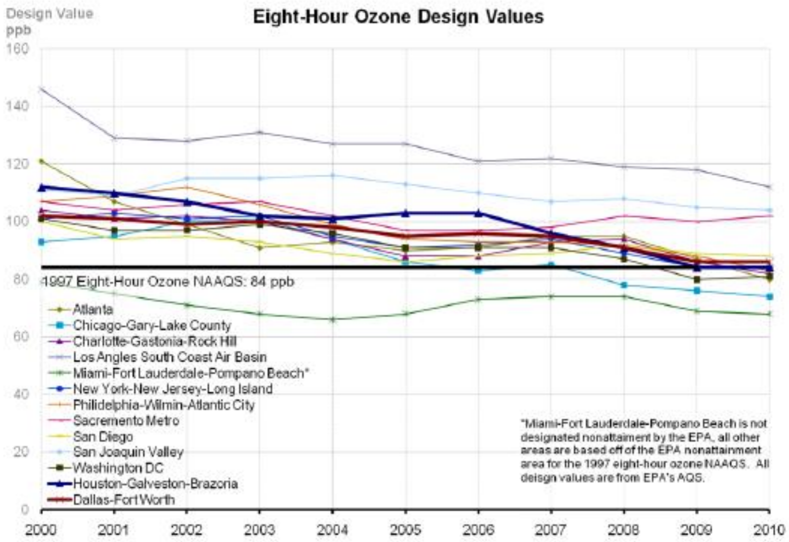
1. Overview of Air Quality Research in Texas

1.1 Issues

Exposure to air pollutants remains a significant public health issue around the world. In Texas, the state's two largest urban areas exceed the National Ambient Air Quality Standard (NAAQS) for ozone and concentrations of air toxics remain a health concern in many communities. Reducing emissions and improving air quality, while supporting economic growth and an increasing population, is challenging, yet over the past decade, substantial improvements in air quality have been made in Texas. Over the decade from 2000 to 2010, average design values of ozone concentrations* at regulatory monitors decreased by 27% in Texas, roughly double the national average rate (Hildebrandt, 2011). The Houston metropolitan area went from, in 1999, having the highest number of days exceeding the NAAQS for ozone of any US city and one of the highest ozone design values*, to meeting the then current NAAQS in 2009 and 2010.

*An ozone design value is the fourth highest daily maximum, 8-hr averaged concentration over the course of a year, averaged over three years. The design value is used to compare measurements at regulatory monitors to the NAAQS.



*Miami-Fort Lauderdale-Pompano Beach is not designated nonattaiment by the EPA, all other areas are based off of the EPA nonattainment area for the 1997 eight-hour ozone NAAQS. All deisgn values are from EPA's AQS.

Figure 1.1.1 Comparison of ozone reductions in the Houston and Dallas-Fort Worth areas to other US cities, 2000-2010.

Source: TCEQ (http://www.tceq.texas.gov/airquality/airsuccess/others)

Identifying the most effective and efficient approaches to improving air quality in Texas requires a sound understanding of the emissions and atmospheric processes that lead to air pollution. One reason for the success that the State has had in reducing ozone concentrations is its investments in air quality research, which have helped to identify focused strategies for emission reductions, designed to be most effective for conditions in the State.

While progress in air quality over the past decade has been impressive, challenges remain as air quality standards become more stringent. More than 10 million Texans live in cities that do not meet new air quality standards for ozone. Continuing to make improvements in air quality will require new strategies which, in turn will require continuing improvements in scientific understanding. For example, it is becoming increasingly recognized that regional, continental and even global factors now have a significant influence on air quality in some parts of Texas

(McDonald-Buller, et al, 2011). Identifying the most effective and efficient balance between local, regional and national air quality improvement actions will require a new body of scientific information. In addition, driven by advances in drilling technology, oil and gas production activities in Texas have seen a substantial resurgence over the past 5 years. These activities have the potential to impact air quality in complex ways. Direct emissions associated with the production activities include ozone precursors and some air toxics. Indirectly, the availability of relatively inexpensive natural gas and natural gas liquids could change emissions associated with electricity generation and chemical manufacturing. Again, identifying the most effective and efficient approaches to reducing emissions, while promoting energy development, will require new scientific information.

These are just a few of the examples of the types of challenges Texas will face as the State strives to continue to improve air quality. This document summarizes the current state of scientific understanding of air quality in Texas. It draws on and builds on previous State of the Science assessments (Allen, et al., 2004). Findings from recent work, particularly work funded by the Texas Air Quality Research Program (AQRP) are summarized and priority topics for additional research are identified.

KEY CITATIONS:

Allen, D.T., Olaguer, E., Nielsen-Gammon, J., Estes, M., Carmichael, G., Carter, W., Sattler, M., Scire, J. State of the Science of Air Quality in Eastern Texas: Major Scientific Findings and Recommendations, July, 2004.

McDonald-Buller, E.C., Allen, D.T., Brown, N., Jacob, D.J., Jaffe, D., Kolb, C. Lefohn, A., Oltmans, S., Parrish, D., and Yarwood, G., “Establishing Policy Relevant Background (PRB) Ozone Concentrations in the United States”, *Environmental Science & Technology,* 45, 9484-9497 DOI: 10.1021/es2022818 (2011).

Update of Air Quality in Texas Susana M. Hildebrand, P.E. Chief Engineer http://www.tceq.texas.gov/agency/air_main.html, May 20, 2010.

1.2 Field Measurement Campaigns

Air pollutant formation and accumulation depends on emissions, meteorology, atmospheric chemistry and other inter-dependent phenomena. Because of the complexity and interdependence of atmospheric processes, experimental studies often involve simultaneous measurements of many chemical and physical features of the atmosphere. These coordinated measurement efforts are referred to as field measurement campaigns.

1.2.1. Field Measurement Campaigns

- Texas Air Quality Study (TexAQS 2000)
- Texas Air Quality Study II (TexAQS 2005-2006)
- Study of Houston Atmospheric Radical Precursors (SHARP, 2009)
- Formaldehyde and Olefin from Large Industrial Sources (FLAIR) measurements (Houston and Texas City, 2009)
- 2010 Flare Study (Controlled, full scale flare tests)
- 2010-date Dallas-Fort Worth Barnett Shale field measurements
- DISCOVER AQ 2013
- Near-road Monitoring 2013

Since 2000, multiple field measurement campaigns have been conducted in Texas (Box 1.2.1), and these measurement campaigns have generally been a focal point for both measurements and modeling done to improve the scientific understanding of air quality in Texas. The campaigns have ranged greatly in size and scope, with the smallest programs involving approximately a dozen investigators, and the largest involving several hundred. One of the largest campaigns was conducted in southeastern Texas in the summer of 2000 and focused on air pollutant formation, accumulation and transport. Known as the Texas Air Quality Study, or TexAQS, this field campaign involved approximately 300 researchers drawn from around the world. TexAQS led to the identification of the role of Highly Reactive Volatile Organic Compounds (HRVOCs, ethene, propene, butenes, 1,3-butadiene) in ozone formation in southeast Texas. Based on the results of TexAQS, the TCEQ substantially revised the air quality management plan (State Implementation Plan, or SIP) for the Houston-Galveston-Brazoria region. A follow-up field campaign was conducted in 2005 and 2006 (TexAQS II) and involved many of the same investigators. This field campaign documented substantial reductions in HRVOC concentrations, relative to the measurements made in 2000. In addition, TexAQS II identified new mechanisms for activation of chlorine in sea salt particles and made measurements to quantify inter-city transport of ozone.

Since 2006, more focused field studies, involving smaller numbers of investigators, have been conducted. Many of these field campaigns focused on issues associated with HRVOCs initially raised during the 2000 TexAQS campaign. For example, two campaigns in 2009 (SHARP and FLAIR) sought better characterization of olefin, formaldehyde and free radical sources in southeast Texas. A series of full scale flare tests conducted in 2010 at an industrial research facility in Tulsa, Oklahoma examined the emissions of flares operating at low flow rates and with low heating value gases as a potential source of HRVOC emissions. All of these studies have provided insights that will be useful in developing plans for reducing ozone formation in southeast Texas.

Beginning in 2010, the focus of field campaigns shifted from the industrial regions of southeast Texas to measurements made in regions with recently expanded oil and gas production activity, particularly production involving hydraulic fracturing of shale formations. The majority of these measurements have been made in the Barnett Shale natural gas production region near

Fort Worth. These measurements are continuing and analysis of data from the campaigns is on-going.

In addition to continuing measurements associated with expanded oil and gas production, future plans for field studies include a joint effort with the National Aeronautics and Space Administration (NASA). A 2013 field campaign titled DISCOVER AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) will use southeast Texas as a test bed for the use of satellite measurements in characterizing air quality. Sub-orbital (aircraft and ground station) measurements will be compared to satellite measurements to assess the limits of current and the needs for future satellite measurement capabilities. In addition, the US EPA has recently required states to deploy near-road monitors in cities with populations larger than 500,000. These near-road monitors will be used to assess compliance with a new National Ambient Air Quality Standard for NO_2. These near-road measurements may have significant air quality management implications for Texas and enhancing scientific understanding of near-road environments could help inform air quality planning.

These field programs are described in more detail in Sections 1.2.1-1.2.8.

KEY CITATIONS:

Web sites describing TexAQS and its principal findings have been maintained by the University of Texas, www.utexas.edu/research/ceer/texaqs www.utexas.edu/research/ceer/texaqsarchive

Summary of TexAQS II: Parrish, D.D., D.T. Allen, T.S. Bates, M. Estes, F.C. Fehsenfeld, G. Feingold, R. Ferrare, R.M. Hardesty, J.F. Meagher, J.W. Nielsen-Gammon, R.B.Pierce, T.B. Ryerson, J.H. Seinfeld, E.J. Williams "Overview of the Second Texas Air Quality Study (TexAQS II) and the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS)", *Journal of Geophysical Research – Atmospheres*, 114, D00F13, doi:10.1029/2009JD011842 (2009).

Reports describing the FLAIR, SHARP, Controlled Industrial Flare, and Barnett Shale field studies are available at the AQRP web site: http://aqrp.ceer.utexas.edu/projects.cfm ; the controlled industrial flare study is also described at: Torres, V.M., Herndon, S., Kodesh, Z., and Allen, D.T. "Industrial flare performance at low flow conditions: Part 1. Study Overview" *Industrial & Engineering Chemistry Research* DOI: 10.1021/ie202674t (2012); Torres, V.M., Herndon, S. and Allen, D.T. "Industrial flare performance at low flow conditions: Part 2. Air and Steam assisted flares" *Industrial & Engineering Chemistry Research* DOI: 10.1021/ie202675f (2012).

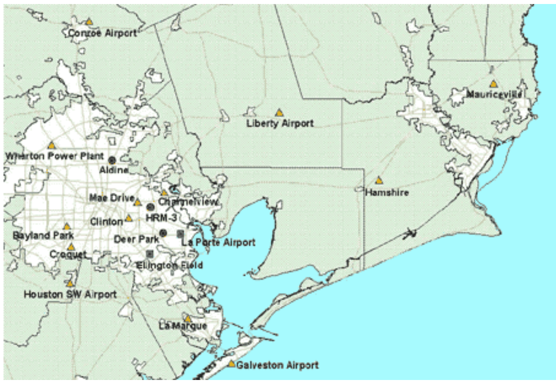
The DISCOVER-AQ program is described at the NASA web site: http://discover-aq.larc.nasa.gov/

The EPA mandated near-road measurement program is described at http://www.epa.gov/ttnamti1/nearroad.html

1.2.1 Texas Air Quality Study (TexAQS 2000)

In August and September of 2000, an international team of more than 300 researchers, drawn from nearly two dozen universities, the National Oceanic and Atmospheric Administration, Brookhaven National Laboratory, Pacific Northwest National Laboratory, and the Environmental Protection Agency, undertook the largest air quality study ever conducted in the State of Texas. The study was designed to improve understanding of the formation, transport and accumulation of air pollutants along the Gulf Coast of southeastern Texas. Measurements were made at approximately 20 ground stations, shown in Figure 1.2.1. Additional sampling was carried out with aircraft that flew over broad regions of eastern Texas.

Figure 1.2.1. Ground sampling sites operated during the Texas Air Quality Study during the summer of 2000.



TexAQS led to the identification of the role of Highly Reactive Volatile Organic Compounds (HRVOCs, ethene, propene, butenes, 1,3-butadiene) in ozone formation in southeast Texas. Key scientific findings were summarized in an Accelerated Science Evaluation (see citation below), and based on these findings, the TCEQ substantially revised the air quality management plan (State Implementation Plan, or SIP) for the Houston-Galveston-Brazoria region. Understanding the sources of HRVOC emissions, which were not well quantified in emission inventories, and reducing HRVOC emissions, became a priority that has continued for more than a decade.

KEY CITATIONS:

Daum, P.H., J. Meagher, D. Allen, and C. Durrenberger. 2002. Accelerated Science Evaluation of Ozone Formation in the Houston-Galveston Area. Summary. 6 pp. http://www.utexas.edu/research/ceer/texaqsarchive/accelerated.htm

Web sites describing TexAQS and its principal findings have been maintained by the University of Texas, www.utexas.edu/research/ceer/texaqs www.utexas.edu/research/ceer/texaqsarchive

1.2.2 Texas Air Quality Study II (TexAQS 2005-2006)

The first Texas Air Quality Study, conducted in the summer of 2000 (Section 1.2.1), was focused primarily on southeast Texas, and helped inform state decisions concerning how to meet then current air quality standards for southeast Texas. After 2000, however, regulations for ozone shifted in emphasis, from concentrations averaged over short periods of time (i.e., the ozone standard with ozone concentrations averaged over one-hour), to concentrations averaged over longer time periods (e.g., ozone concentrations averaged over eight hours). Longer averaging times mean broader geographical regions influence air pollutant concentrations. A second Texas Air Quality Study (TexAQS II) was conducted in 2005 and 2006 to characterize pollutant transport over regional (~100-1000 km) scales. The study also characterized progress that had been made in improving air quality in Houston since 2000.

Among the most significant findings emerging from TexAQS II was the magnitude of ozone transported into Texas. Background ozone in concentrations in eastern Texas, which represent the minimum ozone concentration that is likely achievable through only local controls, can approach or exceed 75 ppbv for an 8 hour average, which is the level of the current National Ambient Air Quality Standard (see Parrish, et al, 2009, cited below).

A second set of major findings were associated with concentrations of Highly Reactive Volatile Organic Compounds (HRVOCs, identified as critical to ozone formation in Houston during TexAQS 2000). Observed concentrations of HRVOCs in southeast Texas were lower in 2006 than in 2000, however, despite improvements in inventory estimates since the TexAQS 2000 study, significant discrepancies were still observed between reported emissions and observed concentrations (see Parrish, et al, 2009, cited below). This finding led to additional field programs related to potential sources of HRVOCs (FLAIR and the 2010 Controlled, full-scale industrial flare study)

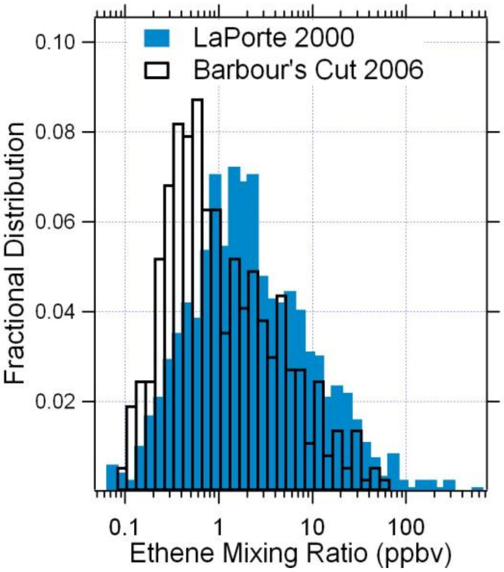


Figure 1.2.2. Comparison of ethylene concentrations made at similar locations in the Houston Ship Channel region in 2000 (LaPorte) and 2006 (Barbour's Cut). A significant decrease in average and extreme ethylene concentrations was observed.

KEY CITATION:

Parrish, D.D., D.T. Allen, T.S. Bates, M. Estes, F.C. Fehsenfeld, G. Feingold, R. Ferrare, R.M. Hardesty, J.F. Meagher, J.W. Nielsen-Gammon, R.B.Pierce, T.B. Ryerson, J.H. Seinfeld, E.J. Williams "Overview of the Second Texas Air Quality Study (TexAQS II) and the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS)", *Journal of Geophysical Research – Atmospheres*, 114, D00F13, doi:10.1029/2009JD011842 (2009).

1.2.3 Study of Houston Atmospheric Radical Precursors (SHARP, 2009)

The chemistry of atmospheric radicals, especially the hydroxyl radical (OH) and hydroperoxyl radical (HO_2), together called HOx, is deeply involved in the formation of ozone and other photochemical air pollutants. Radical precursors, such as nitrous acid (HONO) and formaldehyde (HCHO), significantly affect the HOx budget in urban environments such as Houston. The Study of Houston Atmospheric Radical Precursors (SHARP), in the spring of 2009, examined sources and sinks for free radicals and the impact of radical sources and sinks on the sensitivity of ozone formation to emissions of oxides of nitrogen (NOx) and volatile organic compounds (VOCs). Both measurements and modeling were performed and reconciling model predictions and observations has been a major focus of the study.

Among the HONO formation mechanisms that have been considered are gas-phase photolysis of nitrophenols, heterogeneous conversion of NO_2 on fresh and aged soot particles and soil surfaces, photolysis of surface adsorbed nitric acid, and heterogeneous conversion of HNO_3 on the surface of primary organic aerosol. HO_x production during the SHARP campaign in Houston was dominated by the photolysis of HONO in the early morning and by photolysis of O_3 in the midday; at night, OH production occurred mainly via O_3 reactions with alkenes. On average, the daily HO_x production rate was 23.8 ppbv day^{-1} in the region, of which 31% was from O_3 photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O_3 reactions with alkenes (Lefer et al., 2011).

Daytime observed HONO mixing ratios are often far larger than expected. Statistically significant vertical gradients of HONO throughout the day, with smaller mixing ratios aloft, have suggested that a likely source of daytime HONO could be photocatalytic conversion of NO_2 on the ground surfaces in Houston. Although daytime mechanisms for HONO formation have been a subject of exploration, it is evident that uncertainty remains and further studies are needed.

KEY CITATIONS:

Lefer, B.L., W.H. Brune, D.R. Collins, J.E. Dibb, R.J. Griffin, S.C. Herndon, L.G. Huey, B.T. Jobson, W.T. Luke, J. Mellqvist, G.A. Morris, G.H. Mount, S.W. North, E.P. Olaguer, B. Rappenglück, X. Ren, J. Stutz, X. Yu, R. Zhang, Overview and Major Findings of the Study of Houston Atmospheric Radical Precursors (SHARP) Campaign. American Geophysical Union, Fall Meeting 2010b, abstract #A34C-05.

Lefer, B., J. Stutz, X. Ren, W. Brune, J. Dibb, Study of Houston Atmospheric Radical Precursors (SHARP) data analysis. Air Quality Research Program, TCEQ Grant No. 582-10-94300, November 2011.

1.2.4 Formaldehyde and Olefin from Large Industrial Sources (FLAIR) measurements (Houston and Texas City, 2009)

The goal of the FLAIR program was to use a variety of remote sensing and direct field measurements to assess the strength of industrial sources of formaldehyde and olefins. Measurements were made in Texas City, and the Houston Ship Channel region. The study was motivated by a variety of divergent analyses of the relative contribution of primary sources and secondary chemical production to ambient formaldehyde concentrations and fluxes in Houston.

Among the sources examined in the study were flares. Consistent with controlled flare studies done in 2010 (described in Section 1.2.5), a variety of measurement techniques used in the FLAIR study found that formaldehyde is not directly emitted by un-ignited flare stacks, but burning flares emit formaldehyde at the flare tip. Emission rates of burning flares observed during FLAIR varied between 0.3-2.5 kg/h. Also consistent with results from controlled flare studies, combustion efficiencies were found to vary from 0 (unlit) to 0.7 (over-assisted) to 0.999 (presumably operating as intended).

The FLAIR study also identified a large source of primary formaldehyde emissions in the Texas City refinery complex with a strength of 18 ± 5 kg/h. Analysis of the $HCHO/SO_2$ ratio revealed that during most of the time this source(s) co-emitted with a ratio of roughly 0.1. However, some of the formaldehyde emissions were not correlated with SO_2. Analysis of the emission inventory in Texas City, as well as triangulation and wind field analysis revealed that the most likely source of HCHO is a Fluid Catalytic Cracking Unit (FCCU) regeneration unit.

While the measurements made during the FLAIR study in 2009 indicate that some formaldehyde is directly emitted from flares and from FCCU catalyst regeneration units, most of the formaldehyde observed in Houston (~92%) is associated with secondary formation from the oxidation of VOCs (Parrish et al., 2012). Photochemical modeling studies indicate that directly-emitted formaldehyde associated with over-assisted flares does not accentuate ozone formation as greatly as originally hypothesized.

The olefin measurements made during the FLAIR campaign continued to show discrepancies between reported emissions and observations with observations exceeding levels expected from inventories by a factor of 2 orders of magnitude or more at many sites.

KEY CITATIONS:

Parrish, D.D., T.B. Ryerson, J. Mellqvist, J. Johansson, A. Fried, D. Richter, J.G. Walega, R.A. Washenfelder, J.A. de Gouw, J. Peischl, K.C. Aikin, S.A. McKeen, G.J. Frost, F.C. Fehsenfeld, S.C. Herndon, Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region. Atmospheric Chemistry and Physics 12 (2012), doi:10.5194/acp-12-3273-2012.

Stutz, J. O. Pikelnaya, G. Mount, E. Spinei, S. Herndon, E. Wood, O. Oluwole, W. Vizuette, E. Causo, Quantification of hydrocarbon NOx and SO2 emissions from petrochemical facilities in Houston: Interpretation of the 2009 FLAIR dataset, Quality Research Program, TCEQ Grant No. 582-10-94300, November 2011.

1.2.5 Flare Study (Controlled, full scale flare tests, 2010)

One of the potential sources of HRVOCs in the Houston area is industrial flaring operations. Flares are safety devices that must be able to combust large emergency releases of hydrocarbons. These emergency events are rare, however, and most flare operations occur at flow rates much lower than the maximum flare capacity. Achieving complete combustion at low flow rates, particularly with low heating value gases, can be challenging, but little data existed on flare combustion efficiencies at these conditions. In response to this, the TCEQ contracted with the University of Texas to perform a series of full scale flare tests at low flow conditions with low heating value gases. A 24” diameter air-assisted flare with a flow capacity of 144,000 lb/hr and a 36” steam-assisted flare with a flow capacity of 937,000 lb/hr were employed in the testing. The range of flared gas flow rates was 0.1% to 0.25% of the flare’s design capacity and heating values of the flared gases were in the range of 300-600 BTU/scf.


Figure 1.2.3. Full scale flare tests

Destruction/removal efficiencies (DRE, fraction of vent gas reacted) for steam-assisted flares dropped rapidly when combustion zone heating values fell below 250 BTU/scf. Air-assisted flares showed a linear drop in DRE as a function of air flow. While DREs of 98-99% were observed in some experiments, many operating conditions produced DREs of substantially less than 99%. Since standard methods for estimating emissions would have allowed a 98-99% DRE for all the tests, some test conditions resulted in the production of flare emissions multiple times the value that would be calculated using the standard methods. (from Torres, et al., 2012a, cited below) Air quality modeling of theoretical scenarios associated with low flaring destruction efficiencies have shown that the majority of the ozone formation associated with low destruction efficiency flares is due to the unburned gases sent to the flare, rather than products of incomplete combustion (e.g., formaldehyde).

KEY CITATIONS:

Torres, V.M., Herndon, S., Kodesh, Z., and Allen, D.T. “Industrial flare performance at low flow conditions: Part 1. Study Overview” *Indus. Eng. Chem.Res.* DOI: 10.1021/ie202674t (2012a);

Torres, V.M., Herndon, S. and Allen, D.T. “Industrial flare performance at low flow conditions: Part 2. Air and Steam assisted flares” *Indus. Eng. Chem. Res.* DOI: 10.1021/ie202675f (2012b).

Al-Fadhli, F.M., Kimura, Y., McDonald-Buller, E.C., and Allen, D.T. Impact of flare destruction efficiency and products of incomplete combustion on ozone formation in Houston, Texas, *Industrial & Engineering Chemistry Research*, DOI: 10.1021/ie201400z (2011).

1.2.6 Dallas-Fort Worth Barnett Shale field measurements (2010-date)

Driven by advances in drilling technology, oil and gas production activities in Texas have seen a substantial resurgence over the past 5 years. The use of hydraulic fracturing and other technologies has enabled significantly expanded oil and gas production in the Barnett Shale formation near Fort Worth, the Eagle Ford formation south of San Antonio, the Haynesville formation in east Texas, and in other formations throughout the state. These activities have the potential to impact air quality in complex ways. Direct emissions associated with the production activities include ozone precursors (nitrogen oxides, volatile organic compounds), and some air toxics (e.g., benzene). Indirectly, the availability of relatively inexpensive natural gas and natural gas liquids could change emissions associated with electricity generation and chemical manufacturing.

A series of field campaigns have been undertaken since 2010, primarily to characterize direct emissions of volatile organic compounds and air toxics in the Barnett Shale formation. With funding provided by the TCEQ and cities in the Barnett Shale region, hourly and daily measurements of concentrations of volatile organic compounds were made at multiple sites. In addition, the Texas Air Quality Research Program funded the deployment of an augmented set of measurements in and around Eagle Mountain Lake in the summer of 2011. These measurements assessed emissions from individual well and processing sites and examined, in detail, the ozone formation chemistry in the Barnett Shale region.

Results from the studies are just becoming available, but should help to clarify the role of direct emissions associated with renewed oil and gas production activities on ozone formation.

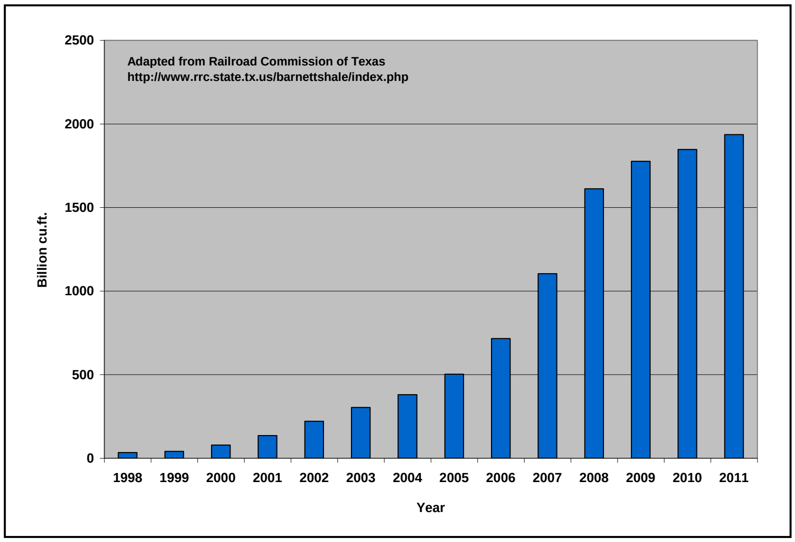


Figure 1.2.4. Natural gas production in the Barnett Shale region near Fort Worth. Significant expansion in production activities has occurred over the past 5-10 years

KEY CITATIONS:

Eastern Research Group and Sage Environmental Consulting, Final Report, City of Fort Worth Natural Gas Air Quality Study, prepared for the City of Fort Worth, July 13, 2011.

Final Reports of AQRP funded projects for the DFW field campaign are available at: http://aqrp.ceer.utexas.edu/projects.cfm

1.2.7 DISCOVER AQ (2013)

"DISCOVER-AQ, a NASA Earth Venture program funded mission, stands for Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality.

In recent years, progress in reaching air quality goals has begun to plateau for many locations. Furthermore, near-surface pollution is one of the most challenging problems for Earth observations from space. However, with an improved ability to monitor pollution from satellites from DISCOVER-AQ, scientists could make better air quality forecasts, more accurately determine the sources of pollutants in the air and more closely determine the fluctuations in emissions levels. In short, the more accurate data scientists have at hand, the better society is able to deal effectively with lingering pollution problems.

The campaign will employ NASA aircraft to make a series of flights, with scientific instruments on board to measure gaseous and particulate pollution, beginning in 2011. The series of flights -- which will be made by NASA Langley's King Air and NASA's P-3B – will commence over Baltimore-Washington, D.C. in 2011. Other future flights may include Houston (2013); Sacramento (2013); and a final site in 2014 to be determined. The measurements will be taken in concert with ground observations in order to shed light on how satellites could be used to make similar, consistent measurements over time, with the ultimate goal of putting better data in the hands of policymakers and elected officials." (From NASA Discover AQ web site: http://discover-aq.larc.nasa.gov/science.php)

The State of Texas, through the TCEQ and the Air Quality Research Program, is working with NASA to develop sampling strategies for the 2013 field measurement campaign in Houston. The field campaign will involve coordinating ground measurements and instrumented aircraft flights with satellite overpasses. The field measurements have the potential to benefit the State both through improved capabilities for the use of satellite measurements and through availability of a new set of measurements that can assess progress in southeast Texas air quality since TexAQS II in 2006.

KEY CITATION:

The DISCOVER-AQ program is described at the NASA web site: http://discover-aq.larc.nasa.gov

1.2.8 Near-road sampling for NO_2 NAAQS compliance

The U.S. Environmental Protection Agency (EPA) recently established a new National Ambient Air Quality Standard for NO_2 (100 ppb, 1 hour averaged concentrations, 98th percentile averaged over 3 years). It is anticipated that the highest concentrations of NO_2 will be observed in near-roadway environments, therefore the EPA has also mandated the deployment of a national near-roadway monitoring network for NO_2. The network is to be deployed by January of 2013. Every city with a population greater than 500,000 will have at least one monitor that will be located at positions anticipated (e.g., due to traffic volume and type) to lead to high NO_2 concentrations.

The TCEQ has supported a series of pilot studies designed to characterize near-roadway concentrations of NO_2 and other traffic related air pollutants, and to determine the rate at which pollutant concentrations decrease with distance from roadways. These studies have indicated that near-roadway emissions and chemistry are complex, especially for NO_2.

In current vehicles, most NOx is emitted as NO. New generation diesel control technologies reduce NOx emissions, but may increase the NO_2/NO ratio, suggesting that fleet mix and age will have complex impacts on near-road NO_2 emissions. Studies near Texas roadways have further demonstrated that within tens of meters of a roadway, ozone reactions with NO can significantly increase NO_2 concentrations, making the positioning of monitors and ambient ozone concentrations potentially critical factors in NAAQS compliance.

Currently only NO_2 and CO measurements are mandated in the near-road monitoring requirements due to be implemented in 2013, however, the draft Technical Assistance document developed by the EPA suggests a variety of additional measurements that could be added to the network. These include meteorological variables, traffic counts and vehicle types, ozone concentrations, and other measurements that can improve understanding of NO_2 sources.

Should Texas near-road monitors detect exceedances of the NAAQS, additional near-road measurements could help inform appropriate responses.

KEY CITATIONS:

EPA near roadway monitoring program website: (http://www.epa.gov/ttnamti1/nearroad.html) and technical assistance document (http://www.epa.gov/ttnamti1/files/nearroad/20111221tad.pdf)

Zhu, Y., J. Pudota, D. Collins, D. Allen, A. Clements, A. Denbleyker, M. Fraser, Y. Jia, E. McDonald-Buller, E, Michel “Air pollutant Concentrations near 3 Texas Roadways, Part 1: Ultrafine Particles, *Atmospheric Environment,* 43, 4513-4522 (2009).

Jia, Y., A. Denbleyker, E. McDonald-Buller, M. Fraser, D. T. Allen, E, Michel, D.R. Collins, J. Pudota, Y. Zhu “Air pollutant Concentrations near 3 Texas Roadways, Part 2: Chemical Characterization and Transformation of Pollutants, *Atmospheric Environment,* 43, 4523-4534, doi:10.1016/j.atmosenv.2009.06.044 (2009).

Wang, Y.J., DenBleyker, A., McDonald-Buller, E., Allen, D., and Zhang, K.M. “Modeling the chemical evolution of nitrogen oxides near roadways”, Atmospheric Environment, 45, 43-52 (2011).

2. State of the Science: Emissions, Chemistry, and Meteorology and Transport/Modeling

2.1 Overview and methods for developing state of the science findings

Scientific findings emerging from large field campaigns and data analysis programs, of the type that have occurred in Texas over the past decade, are multifaceted. Many of the scientific findings have direct and immediate policy relevance. For example, scientific findings from TexAQS were used to guide the development of the approaches used to attain the National Ambient Air Quality Standard for ozone in Houston. Other scientific findings have longer-term policy relevance. For example, scientific findings that improve understanding of emissions and chemistry associated with natural gas production may help inform the direction of air quality policies in regions such as the Dallas-Fort Worth area. Better understanding of how flare operating practices influence emissions can guide emission reduction strategies. This document summarizes the scientific findings emerging from air quality studies performed in Texas. Findings with both immediate and longer-term relevance are summarized.

Scientific findings have varying degrees of certainty. The findings reported in this document are not limited to those for which there is a high degree of certainty; in many cases highlighting critical areas where uncertainty exists can be important in determining the likelihood that a policy will be effective, and identifying areas where uncertainty exists is critical to continued progress in scientific understanding. However, when uncertainty or areas of disagreement concerning the implications of scientific findings exist, this document clearly characterizes the uncertainties.

Initial drafts of this report were written by AQRP staff (David Allen, Elena McDonald-Buller and Gary McGaughey of the University of Texas). The draft findings and recommendations for future work were reviewed by both the Texas Commission on Environmental Quality.

The findings are divided into four sections corresponding to the areas where the AQRP performs research: emissions, chemistry, and atmospheric transport/modeling. In each section, there is a brief statement of major findings; citations to the scientific literature provide additional details.

2.2 Ozone Precursor Emissions

2.2.1 Overview of Emission Inventories

Emission inventories are used for a variety of purposes and at a variety of spatial and temporal scales. Inventories are used at state and national spatial scales and at annual and multi-year temporal scales to establish trends in air quality. They are also used as inputs to air quality models that require kilometer-level spatial resolution and hourly temporal resolution. These variable applications of emission inventories lead to very different information needs. This State of the Science assessment focuses on emission inventories that are used in air quality models that are used to evaluate air quality management plans for ozone. These models must predict atmospheric processes on days when extreme ozone concentrations have been observed, therefore emission inventories resolved at kilometer-level spatial scales and at hourly temporal scales are of greatest interest. Findings are reported for motor vehicle emissions, point source emissions, and emissions associated with oil and natural gas production. Biogenic emissions are discussed in the section on atmospheric chemistry. Other categories of emissions (e.g., off-road equipment) are significant sources but have not been the focus of AQRP research activities and therefore are not summarized here, but have been described in previous scientific assessments (Allen and Durrenberger, 2003).

Data summarized in this assessment indicate that emissions of ozone precursors from some sources can vary significantly on a daily, even an hourly basis (Murphy and Allen, 2005). Consequently, both the magnitude and the variability in ozone precursor emissions are reported.

KEY CITATIONS:

Allen, D., Durrenberger, C. and Texas Commission on Environmental Quality, Technical Analysis Division. 2003. Accelerated Science Evaluation of Ozone Formation in the Houston-Galveston Area: Emission Inventories Version 3, February, 2003, available at http://www.utexas.edu/research/ceer/texaqsarchive/accelerated.htm

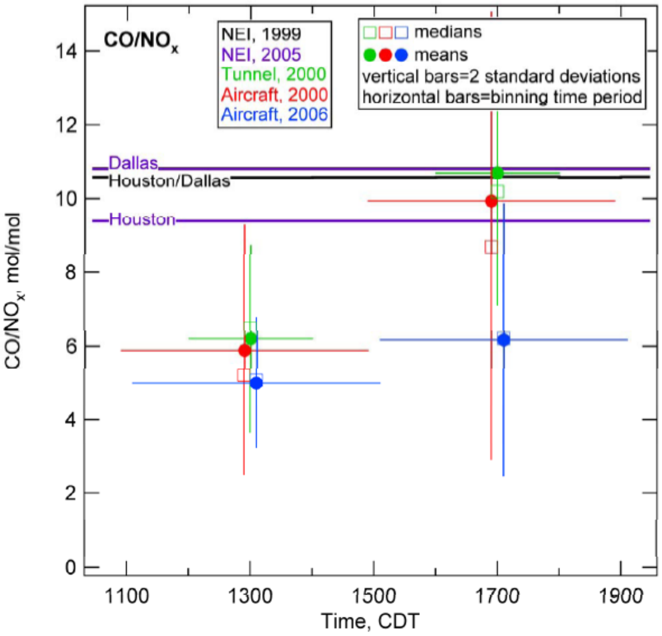
Murphy, C. F. and D. T. Allen "Hydrocarbon Emissions from Industrial Release Events in the Houston-Galveston Area and their Impact on Ozone Formation," *Atmospheric Environment*, 39, 3785 – 3798 (2005).

2.2.2 Motor Vehicles

1. On-road mobile source emissions have historically been obtained using the MOBILE model, which overestimates CO/NO$_x$ ratios in eastern Texas urban areas.

Observational evaluation of CO/NOx ratios from airborne sampling and tunnel studies during TexAQS II has indicated that emissions inventories based on the MOBILE6 model overestimate CO/NO$_x$ ratios in eastern Texas urban areas. Figure 2.2.1 (Frost et al., 2008) compares measured CO/NO$_x$ ratios during the morning and evening rush hours obtained from airborne sampling and tunnel studies during TexAQS and TexAQS II with those obtained from the 1999 and 2005 National Emissions Inventories (NEIs). In addition, CO/NOx emission ratios of 5.81 ±0.94 were observed during the morning rush hour from the Moody Tower supersite (Luke et al., 2010) during the 2006 TexAQS-II Radical and Aerosol Measurement Project (TRAMP). Discrepancies between observed and MOBILE predicted CO/NOx ratios have become more pronounced over time and have been attributed to a factor of 2-3 overestimate in CO emissions (Parrish, 2006; Frost et al., 2008) and an underestimate of NO$_x$ emissions (Parrish, 2006) in the more recent emissions inventories. The Texas Roadway Study (Denbleyker et al., 2007; Zhu et al., 2009; Clements et al., 2009) characterized ambient concentrations of CO and NO$_x$, as well as other vehicular emitted pollutants, and chemical processes in the microenvironments of three Austin roadways. Comparisons between MOBILE6 predictions and observations from the Texas Roadway Study suggested that MOBILE6 overpredicts CO/NO$_x$ ratios, but is generally within a factor of three of observed ratios.

Figure 2.2.1. Mobile source CO/NO$_x$ emission ratios from airborne and tunnel studies during TexAQS and TexAQS II and from the 1999 and 2005 National Emissions Inventories (ref. Frost et al., 2008).



2. Estimates of vehicular emitted pollutants in Texas will change with the transition from the MOBILE model to MOVES.

The U.S. EPA (2003) and the TCEQ have utilized versions of the MOBILE model to obtain estimates of vehicular emitted pollutants since 1978. The Motor Vehicle Emissions Simulator (MOVES) was released as a replacement to the MOBILE model in March 2010 with a minor update (MOVES2010a) in September 2010 (EPA, 2010a). MOVES2010b is the most recent version and was released in April 2012. MOVES offers a substantially improved understanding of the relationship between vehicle activity, environmental variables and emissions and includes new emissions test data, while accounting for recent changes in vehicle technology and regulations. Preliminary analyses with MOVES have indicated that PM, NO_x, and CO_2 emissions rates are higher than MOBILE6.2, while VOC and especially CO emissions rates are lower (Bai et al., 2008, Beardsley, 2009). Tables 2.2.1 and 2.2.2 present summaries of 2006 and 2018 HGB area on-road emissions inventories developed by the Texas Transportation Institute under contract to the TCEQ using local area travel demand model (TDM) output coupled with emission rates from MOBILE6.2, MOVES2010, and MOVES2010a. Relative to MOBILE6.2 estimates, MOVES predictions are substantially greater for NO_x, slightly higher for VOC, and slightly lower for CO.

Table 2.2.1 Comparison of 2006 Summer Weekday On-Road Emission Inventory Estimates for the HGB Area Using MOBILE6.2, MOVES2010, and MOVES2010a

Model Version and Level of Effort	**Development Date**	**Daily VMT**	**2006 Summer Weekday Emissions** (tpd)		
			NO_X	**VOC**	**CO**
MOBILE6.2 SIP-Quality	Summer 2007	133,868,661	206.74	90.71	1,115.28
MOVES2010 Sensitivity	Summer 2010	133,868,661	292.65	107.57	1,013.21
MOVES2010a SIP-Quality	Summer 2011	143,408,584	270.00	104.74	1,024.03

Table 2.2.2. Comparison of 2018 Summer Weekday On-Road Emission Inventory Estimates for the HGB Area Using MOBILE6.2, MOVES2010, and MOVES2010a

Model Version and Level of Effort	**Development Date**	**Daily VMT**	**2018 Summer Weekday Emissions** (tpd)		
			NO_X	**VOC**	**CO**
MOBILE6.2 SIP-Quality	Spring 2009	180,993,087	52.55	45.97	733.18
MOVES2010 Sensitivity	Summer 2010	180,993,087	109.07	48.10	617.79
MOVES2010a SIP-Quality	Winter 2012	180,955,402	103.34	50.13	656.24

For any future studies involving ambient measurements near roadways, careful attention must be paid to the mix of vehicle types being monitored. Many on-road emission inventories are based on either daily or annual average vehicle miles traveled (VMT) distributions by vehicle category. However, these distributions can vary significantly by individual roadway segment, time-of-day, day-of-week, etc. If VOC and/or CO were the only pollutants of concern, then the focus of a study could be primarily limited to the light-duty gasoline fleet, which dominates both VMT and emissions of these two pollutants. However, NO_x emission totals are heavily dependent on the VMT split between the light-duty gasoline passenger fleet and “eighteen-wheeler” heavy-duty diesel trucks. Comparisons between ambient measurements and emission inventory estimates must pay special attention to this split if CO/NO_x ratios are being evaluated.

3. In-use characterization of heavy-duty diesel vehicle (HDDV) exhaust emissions suggests variability in MOVES performance among classes and model years.

Johnson et al. (2012) conducted driving and idling emission testing on 30 selected HDDV from the City of Houston fleet to characterize their emissions with respect to vehicle classes, types (high emitting or non-high emitting), and model years. Measurements were compared with MOVES2010a (refer to p.27 in Johnson et al. 2012) estimates, as well as among vehicle classes and types. CO and NO_x emissions from potential high emitting vehicles, which were generally older, were highly consistent with MOVES estimates. Randomly selected vehicles, which were of newer model years (2003 and 2006), exhibited greater variability with respect to divergence from MOVES estimates. These results may be associated with the limited field data used in MOVES for HDDVs. Total hydrocarbon (THC) emissions from potential high emitting Class 8 vehicles, i.e., heavy duty trucks with a gross vehicle weight rating (GVWR) above 33,000 pounds, were generally higher than MOVES estimates, but were lower than MOVES for all other vehicle types. Observed PM emissions for all test vehicles were significantly lower than MOVES estimates, which could have been associated with differences in measurement methods between the study of Johnson et al. (2012) and those used for the development of MOVES.

4. Strong spatial gradients in concentrations exist and chemical processing of vehicular emitted air pollutants occurs in the near-roadway microenvironment. Characterization of near-roadway processes is required to respond to new ambient monitoring requirements and to assess human exposure patterns.

The Texas Roadway study (Denbleyker et al., 2007; Zhu et al., 2009; Clements et al., 2009; Wang et al., 2011) measured the spatial gradients of vehicular emitted air pollutants in the vicinity of three roadways, with varying traffic volume counts and fractions of heavy-duty vehicles, near Austin, Texas. Regardless of roadway type or wind direction, ultrafine particulate (UFP; number, surface, and volume), CO, NO, and NO_x concentrations increased between the upwind and downwind side of the roadways with return to background levels within a few hundred meters of the roadway. The behavior of particle-bound organic species was complex. $PM_{2.5}$ mass concentrations, PAHs, hopanes, and EC concentrations generally exhibited concentrations that decreased with distance downwind. Relative to upwind concentrations, concentrations of OC increased immediately downwind and continued to increase further downwind, which may have resulted from the condensation of vehicular emitted semi-volatile organic species. The decay rate for NO was more than a factor of two greater than for CO, and it comprised a larger fraction of NO_x closer to the roadways than further downwind suggesting the potential significance of near roadway chemical processing, as well as atmospheric dilution. Wang et al. (2011) suggested that the chemical evolution of NO_2 and NO may not be well simulated by historically utilized Gaussian dispersion models, such as CALINE4. Comparisons of the performance of CALINE4 with a computational fluid dynamics model, CFD-VIT-RIT, that couples a standard k - ε turbulence model for turbulent mixing and the Finite-Rate model for chemical reactions, with observations from the Texas Roadway Study indicated that CFD-VIT-RIT was capable of predicting both NO_x and NO_2 profiles downwind. Although CALINE4 captured near-roadway NO_x profiles, it underpredicted NO_2 concentrations under high wind velocities. In addition, Wang et al. (2011) found that initial NO_2/NO_x ratios must be carefully selected based on traffic conditions in order to assess NO_2 concentrations near roadways. Commonly assumed NO_2/NO_x ratios by volume of 5% or 10% may not be suitable for most roadways, especially those with a high fraction of heavy-duty truck traffic. Recognition that the majority of ambient exposures to peak NO_2 concentrations (EPA, 2011) are associated with roadways has led to the requirement for near-road monitoring in U.S. metropolitan areas. Understanding near-roadway spatial gradients in NO_2 concentrations and chemical processes and atmospheric modeling capabilities will be critical as Texas responds to forthcoming deadlines for site selection and configuration.

Unlike MOBILE6.2 that only estimated total NO_X, the MOVES2010a model estimates NO and NO_2 emission rates separately. The NO_2 portion of total NO_X can be as low as 1% for some gasoline vehicles in the cold start mode, and as high as 40% for newer technology diesel vehicles in the hot stabilized running mode. For the on-road emission inventories developed to date with MOVES2010a, the TCEQ has been estimating and processing NO and NO_2 separately when preparing air quality modeling inputs. The recently released MOVES2010b version of the model has added nitrous acid (HONO) emissions as a subset of NO_X, so that NO + NO_2 + HONO = NO_X. MOVES2010b currently assumes that HONO comprises 0.8% of total NO_X for all combinations of vehicle type, fuel type, and mode of engine operation. Until an updated version of MOVES is released, TCEQ will be using MOVES2010b for all future on-road inventory development, and will estimate NO, NO_2, and HONO separately for air quality modeling purposes.

5. The use of catalyzed Diesel Particulate Filters (DPFs) and Diesel Oxidation Catalysts (DOCs) in on-road and off-road diesel equipment have the potential to increase NO_2 emissions.

Modern diesel engines are increasingly incorporating DOC and catalyzed DPF, which have the potential to form additional NO_2 emissions, in on-road and off-road vehicles, to meet PM emissions standards (Bar-Ilan et al., 2009; Carslaw, 2005). Bar-Ilan et al. (2009) examined the potential impacts of these additional NO_2 emissions on ozone formation in the DFW area for two scenarios. One scenario assumed a maximum penetration, in which there was significant turnover to newer model year on-road vehicles and higher Tier non-road equipment, and a second scenario, which is more realistic, considered the fractional usage of DOC/DPF devices in the 2009 fleet of heavy-duty on-road trucks, buses and some construction equipment. In order to achieve the maximum penetration scenario, highly accelerated turnover of the fleet to newer vehicles and equipment was required, that resulted in decreases in total NO_x emissions. Air quality modeling showed that the maximum penetration scenario resulted in a decrease in ozone due primarily to reductions in total NO_x emissions, despite increase in NO_2. The realistic scenario analysis, which did not consider equipment turnover, resulted in a modest increase in total NO_2 emissions and ozone increases within the DFW area of less than 1ppb. Bar-Ilan et al. (2009) noted that manufacturers of these devices are investigating strategies to mitigate the excess NO_2 formation. Future studies are needed to consider the impacts of these devices on NO_2 concentrations and human exposure patterns in near-road microenvironments in Texas.

6. Retrofit devices aimed at reducing tailpipe and crankcase emissions from diesel vehicles may also improve cabin air quality by reducing vehicle self-pollution.

Rim et al. (2008) examined the effects of a staged installation of a Spiracle Crankcase Filtration System followed by a DOC, on cabin pollutant concentrations in Central Texas school buses. Following installation of the Spiracle Crankcase Filtration System, in-cabin concentration decreases ranged from 24 to 37% for NO_x and 26 to 62% and 6.6 to 43% for $PM_{2.5}$ and ultrafine PM, respectively. Following installation of the Spiracle, the DOC provided negligible or only small additional reductions of in-cabin pollutant levels.

7. The air quality benefits of increasing the penetration of plug-in hybrid electric vehicles (PHEVs) in the Texas fleet will be influenced by the temporal pattern of battery charging.

Thomson et al. (2011) examined the air quality impacts of replacing approximately 20% of the gasoline-powered light duty vehicle miles traveled (VMT) with electric VMT by the year 2018 for four major cities in Texas: Dallas/Ft Worth, Houston, Austin, and San Antonio. Three charging scenarios, occurring on the Electricity Reliability Council of Texas (ERCOT) grid, were compared: nighttime charging, charging to maximize battery life, and charging to maximize driver convenience. Net impacts of PHEVs included an increase in NO_x emissions from EGUs during times of day when the vehicle was charging, and a decrease in NO_x from mobile emissions. In general, PHEVs were predicted to lead to an increase in ozone during nighttime hours and a decrease in ozone during daytime hours. Larger increases in ozone for the convenience charging scenario relative to the other scenarios were predicted at the locations of a few ambient monitoring sites. Nighttime charging was found to most likely reduce a measure of ozone exposure potential versus the other two scenarios.

References

Bai, S., D. Eisinger, D. Niemeier, MOVES vs. EMFAC: A Comparative Assessment based on a Los Angeles County Case Study. Transportation Research Board Annual Meeting, Washington, DC, January 2009.

Bar-Ilan, A., J. Johnson, A. DenBleyker, L. Chan, G. Yarwood, Potential Ozone Impacts of Excess NO2 Emissions From Diesel Particulate Filters For On- and Off-Road Diesel Engines, Final Report, Project Number H93, prepared for the Houston Advanced Research Center, April 2009.

Beardsley, M., J. Warila, G. Dolce, J. Koupal, Air Pollution Emissions from Highway Vehicles: What MOVES Tells Us. The 18th Annual International Emission Inventory Conference, Baltimore, MD, April 2009.

Carslaw, D.C., Evidence of an increasing NO_2/NO_X emissions ratio from road traffic emissions, Atmospheric Environment, 39 (2005) 4793-4802.

Clements, A., Y. Jia, A. Denbleyker, E. McDonald-Buller, M. Fraser, D. Allen, D. Collins, E. Michel, J. Pudota, D. Sullivan, Y. Zhu, Air pollutant concentrations near three Texas roadways, Part II: Chemical characterization and transformation of pollutants, Atmospheric Environment 43 (2009), 4523-4534.

Cowling, E.B., C. Furiness, B. Dimitriades, D. Parrish et al., 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, TCEQ Contract Number 582-4-65614
31 October 2006 [8 November revision].

DenBleyker, A., D. Allen, E. McDonald-Buller, S. Fincher, S. Kishan, Assessment of CO and NOx Emission Estimates from MOBILE6 with Ambient Concentrations from Texas Roadways, Final Report
Submitted to The Texas Joint Center for Transportation and Air Quality Houston Advanced Research Center, Contract Number: 20-23016-UT0707, July 2008.

ENVIRON, Prepared by A.K. Pollack, C. Lindhjem, T.E. Stoeckenius, C. Tran, G. Mansell, M. Jimenez, G. Wilson, S. Coulter-Burke, Evaluation of the U.S. EPA MOBILE6 Highway Vehicle Emission Factor Model, Final Report, CRC Project E-64, 2004.

Frost, G., S. McKeen, M. Trainer, K. Aikin, J. Peischl, T. Ryerson, J. Holloway, G. Pétron, P. Tans, Observational Evaluation of Mobile Source Emissions, EPA 17th International Emission Inventory Conference, Portland, Oregon, June 3-5, 2008.

Johnson, J., D. Lee, R. Farzaneh, J. Zietsman, L. Yu, Characterization of Exhaust Emissions from Heavy-Duty Diesel Vehicles in the HGB Area – Final Report, Project No. 0-6237 in cooperation with the Texas Department of Transportation and the Federal Highway Administration, February 2012.

Kockelman, K., G. McGaughey, B. Nichols, D. Fagnant, Technical Memorandum, Development of a Performance Measurement Based Methodology to Objectively Compare Operational Improvements with Capacity Additions, TxDOT Project #0-6487, February 2012.

Kite, C., MOVES2010a Update of the 2006 and 2018 On-Road Emission Inventories for Houston/Galveston/Brazoria (HGB). Presented to the Southeast Texas Photochemical Modeling Technical Committee, Houston, Texas, April 2012., which is available at http://www.tceq.state.tx.us/assets/public/implementation/air/am/committees/pmt_set/20120425/20120425-kite.pdf

Luke, W.T., P. Kelley, B. L. Lefer, J. Flynn, B. Rappenglück, M. Leuchner, J. E. Dibb, L. D. Ziemba, C. H. Anderson, M. Buhr, Measurements of primary trace gases and NO_Y composition in Houston, Texas, Atmospheric Environment 44 (2010) 4068–4080.

Parrish, D.D., Critical evaluation of US on-road vehicle emission inventories. Atmospheric Environment 40 (2006), 2288-2300.

Rim, D., J. Siegel, J. Spinhirne, A. Webb, E. McDonald-Buller, Characteristics of cabin air quality in school buses in Central Texas, Atmospheric Environment 42 (2008) 6453–6464.

Thompson, T., C. King, D. T Allen, M. E. Webber, Air quality impacts of plug-in hybrid electric vehicles in Texas: evaluating three battery charging scenarios, Environmental Research Letters 6 (2011) doi:10.1088/1748-9326/6/2/024004.

Wang, Y, A. Denbleyker, E. McDonald-Buller, D. Allen, K. Zhang, Modeling the chemical evolution of nitrogen oxides near roadways, Atmospheric Environment 45(2011), 43-52.

Zhu, Y., J. Pudota, D. Collins, D. Allen, A. Clements, A. Denbleyker, M. Fraser, Y. Jia, E. McDonald- Buller, E. Michel, Air pollutant concentrations near three Texas roadways, Part I: Ultrafine particles, Atmospheric Environment 43 (2009), 4513-4522.

2.2.3 Point Sources

1. Emissions of highly reactive VOCs (HRVOCs) and nitrogen oxides (NOx) declined between the time periods of the TexAQS2000 and TexAQS II studies, but discrepancies between observations and reported emissions inventories remain.

Observational evidence has indicated substantial reductions in emissions of ozone precursors in the Houston area during the time period between the TexAQS 2000 and TexAQS II field campaigns,. Washenfelder et al. (2010) measured reductions of 29% ± 20% in NO_x emissions between August 2000 and September 2006 in the Houston industrial area that were consistent with reductions in NO_x emissions at larger point sources throughout the southeastern United States that have implemented controls. Temporal trends in the ratios of the HRVOCs, ethene and propene, respectively, to oxides of nitrogen (i.e., C_2H_4/NO_x and C_3H_6/NO_x) over the same time period indicated decreases by 30% ± 30%; median ambient concentrations of ethene and propene within the Houston urban area decreased by 52% and 48%, respectively.

However, even with declines in emissions and ambient concentrations, this study and others conducted during TexAQS II have suggested that discrepancies between reported VOC emissions inventories and observations remain. Washenfelder et al. (2010) found that measured ratios of C_2H_4/NO_x and C_3H_6/NO_x exceeded emission inventory values by factors of 1.4–20 and 1–24, respectively. Mellqvist et al. (2010) found that emission flux estimates from Solar Occultation Flux (SOF) measurements in the Houston area were, in some locations, an order of magnitude larger than a 2006 daily emission inventory from the TCEQ, which are similar to the findings of de Gouw et al. (2009). Mellqvist et al. (2010) also found large variability in alkene emission flux estimates, especially propene, downwind of petrochemical plants. These facilities reported highly variable emissions from flaring during August and September of 2006 that periodically dominated their alkene emissions.

2. Temporal variability in industrial emissions can affect ozone formation in the Houston-Galveston-Brazoria (HGB) area and should be characterized for air quality models.

Studies performed in the HGB area indicate that some industrial emissions sources exhibit high temporal emissions variability, with emissions changing by orders of magnitude over hourly to daily time periods (Murphy and Allen, 2005; Nam et al., 2006; Webster et al., 2007; Nam et al., 2008). These temporal variations in emissions can lead to very rapid ozone formation, especially when emissions are composed of highly reactive volatile organic compounds (HRVOCs, defined as ethene, propylene, 1,3-butadiene, and butenes), and consequently, may have a significant impact on ozone generation in the HGB region (Kleinman et al., 2003; Allen et al., 2004; Vizuete et al., 2008; Olaguer et al., 2009; Henderson et al., 2010).

Recognition of the importance of industrial emission variability motivated the collection of hourly emissions data from 141 industrial locations in the HGB area over 32 days during the time period of TexAQS II (August 15 through September 15, 2006). This emissions database, which is the largest collection of hourly industrial emissions in a single area of the United States, was incorporated into the 2006 Special Inventory (2006 SI) by the Texas Commission on Environmental Quality (2008). Flares constituted 45% of all VOC and 77% of all HRVOC emissions in the SI, followed by stacks and cooling towers (41% VOC and 18% HRVOC), and finally fugitives (14% VOC and 5% HRVOC).

Pavlovic et al. (2009; 2012a) categorized emissions from refinery and olefin production flares, the largest sources of VOC in the 2006 SI. Flares were categorized by industrial process, chemical composition, and the temporal patterns of their emissions. Stochastic representations of emissions were developed using a Markov process model for each flare subcategory based on the earlier work of Nam et al. (2006) and Webster et al. (2007). Industrial flare emission temporal patterns were comprised of multiple components, including as nearly constant, routinely variable or episodic emissions. The stochastic models provided a representation of flare emissions that were used to explore the effects of the variable emissions inventory, relative to a typical ozone season day inventory, on ozone formation using the Comprehensive Air Quality Model with extensions (CAMx). The temporal variability in flare emissions from the 2006 SI was found to lead to localized differences in ozone concentrations of as much as 27 ppb in the HGB area relative to the ozone season daily inventory (Pavlovic et al., 2010; Pavlovic et al., 2012b). The ozone impacts associated with the temporal variability in emissions typically lasted a few hours, consistent with the length of large flaring events (Pavlovic et al., 2012b). This finding was consistent with those of an earlier study by Nam et al. (2008), which indicated that strategies that eliminate the infrequent largest emissions are more effective at reducing the highest localized ozone concentrations than changes in nearly constant emissions. Use of a fine model horizontal grid resolution (2 km x 2km) was necessary to capture the impacts on ozone predictions.

3. Ensuring high destruction removal efficiencies (DREs) during flaring operations can be important for regional air quality.

Most flares are designed to have destruction removal efficiencies (DREs), defined as the percentage of waste gas fed to the flare that is destroyed by complete or partial combustion, of 98% or 99%. Flares are also designed to operate over a very large range of flow rates. Recent observations have indicated that DRE can fall substantially below the target range of 98-99% under low flows and high steam or air assist rates, for some types of flares (Strosher, 2000; Mellqvist, 2001; Allen and Torres, 2011; Torres et al., 2012a; Torres et al., 2012b). In addition, recent measurements have characterized products of incomplete combustion (PICs) in flares, which include both highly reactive gases, such as formaldehyde and acetaldehyde, and less reactive gases, such as CO (Allen and Torres, 2010; Herndon, 2011). Al-Fadhli et al. (2011) examined the impacts of flare DRE (95, 90, 75 and 50% versus a base case with 98% or 99%) and PICs (a scenario that accounted for PICs, consistent with Allen and Torres (2011) versus a base case that did not consider PICs) on predicted ozone formation in southeastern Texas using CAMx. Of the five flares examined in the study, two flares showed predicted increases in ozone concentrations in excess of 15 ppb when the DRE was reduced, while the others showed more modest effects on predicted ozone concentrations. The flare DRE impact on ozone concentrations depended on the amount of flare emissions and chemical composition of the emissions. Accounting for the PICs had a relatively modest impact on ozone concentration because most of the mass was carbon monoxide which had a low chemical reactivity to form ozone. The analyses were intended to represent upper bounds on the ozone formation potential of flare emissions. Overall, the results indicated the potential effects of flare DRE on regional air quality.

4. Field tests in a semi-controlled environment indicate that the most efficient flare operation, as measured by the DRE and combustion efficiency (CE), are achieved at or near the incipient smoke point (ISP). Minimum levels of steam or air assist that comply with the flare manufacturer's recommendations should be used when possible.

Recent studies, sponsored by the TCEQ and led by the University of Texas at Austin with Aerodyne Research, Inc. and other collaborators, have focused on the measurement of emissions and the collection of process and operational data from full-scale industrial design flares in a semi-controlled environment at John Zink, LLC in Tulsa, Oklahoma, in order to determine the relationship between flare design, operation, vent gas lower heating value (LHV), flow rate, destruction and removal efficiency (DRE), and combustion efficiency (CE; percentage of the total hydrocarbon stream entering the flare that burns completely to form only carbon dioxide and water) (Allen and Torres, 2011). A key assumption has been that flares operating over the range of requirements stated in Title 40 Code of Federal Regulations (CFR) § 60.18 achieve the assumed hydrocarbon DRE of 98-99 percent at varying vent gas flow rate turndown, assist ratios and vent gas heat content, although limited observational evidence in southeastern Texas has suggested that HRVOC flares routinely do not meet the assumption of 99% DRE (Herndon et al., 2011). Given the significance of flaring emission to the total VOC and HRVOC inventories in the region, these recent studies have led to new insights regarding efficient flare operational conditions that potentially minimize emissions.

As an example, at low vent gas flow rates (nominally 937 lb/hr and 2,342 lb/hr) and low LHVs (nominally 350 Btu/scf and 600 Btu/scf), the flare performance curve of DRE versus steam assist had a very short to non-existent "shelf" before the DRE fell off to less than 98%. Beyond this point, the DRE and CE decrease as steam assist increases. For nominal LHVs of 350 Btu/scf and 600 Btu/scf and vent gas flow rates of 359 lb/hr and 937 lb/hr, air flare test data showed that an air assist quantity of up to 6 times the stoichiometric air-to-fuel ratio (lb/lb) produced a DRE > 99%. Higher levels of air assist produced lower DREs.

The most efficient flare operation, as measured by the DRE and CE, for the flare operating conditions tested, was achieved at or near the incipient smoke point. Higher efficiencies could have been achieved with steam or air assist slightly less than the ISP assist value but this condition, i.e., a smoking flare, would not have been in compliance with 40 CFR § 60.18.(f) Therefore, no more than the minimum levels of steam or air assist that comply with the flare manufacturer's recommendations should be used when possible. Further development of remote sensing technologies, such as Passive and Active Fourier Transform Infrared (PFTIR, AFTIR) Spectroscopy (Allen and Torres, 2011), and modeling techniques, such as Multivariate Image Analysis (MIA; Rawlings et al., 2011), may offer approaches for improving the detection, monitoring, and evaluation of flare operational conditions in the future.

Options for controlling routine emissions using methods other than flaring must be addressed on a case-by-case basis. However, Pavlovic et al. (2009) describe that several approaches have been utilized in the Houston area, including implementation of process and operating changes that eliminate flows to the flare; use of higher efficiency control devices during normal operating conditions; and/or flare gas recovery for reprocessing or use as a fuel. Individually or in combination, these techniques could potentially be used to effectively eliminate emissions from flaring during normal or routine operations.

References

Al-Fadhli, F. MS Thesis, University of Texas at Austin, May 2010.

Al-Fadhli, F.M., Y. Kimura, E. McDonald-Buller, D. Allen, Impact of flare combustion efficiency and products of incomplete combustion on ozone formation in Houston, Texas. Industrial & Engineering Chemistry Research, 2011, doi:10.1021/ie201400z.

Allen, D.T., C. Murphy, Y. Kimura, W. Vizuete, T. Edgar, H. Jeffries, B. Kim, M. Webster, M. Symons, Variable industrial VOC emissions and their impact on ozone formation in the Houston Galveston Area. Houston Advanced Research Consortium (HARC); Project H-13, 2004.

Allen, D. T., V.M. Torres, 2010 TCEQ Flare Study Project, Final Report. Available: http://www.tceq.texas.gov/assets/public/implementation/air/rules/Flare/TCEQ2010FlareStudyDraftFinalReport.pdf, August 2011.

B.C. Rawlings, O.A. Ezekoye, T. F. Edgar, Air Quality Research Program. TCEQ Grant No. 582-10-94300. Additional Tests Days for TCEQ 2010 Flare Study Project 10-009 (Task 2) Modeling of Flare Performance Using Multivariate Image Analysis and Computational Fluid Dynamics, AQRP Project Air Quality Research Program, TCEQ Grant No. 582-10-94300, December 2011.

de Gouw , J.A. , S. Telintelhekkert, J. Mellqvist, C. Warneke, E. L. Atlas, F. C. Fehsenfeld, A. Fried, G. J. Frost, F. J. M. Harren, J. S. Holloway, B. Lefer, R. Lueb, J. F. Meagher, D. D. Parrish, M. Patel, L. Pope, D. Richter, C. Rivera, T. B. Ryerson, J. Samuelsson, J. Walega, R. A. Washenfelder, P. Weibring, X. Zhu. Airborne measurements of ethene from industrial sources using Laser Photo-Acoustic Spectroscopy. Environmental Science & Technology 43(2009), 2437–2442.

Henderson, B. H., H.E. Jeffries, B.-U. Kim, W. G. Vizuete, The influence of model resolution on ozone in industrial volatile organic compound plumes, Journal of the Air & Waste Management Association 60 (2009), 1105–1117.

Herndon, S. C., E. C. Wood, E. Fortner, W. B. Knighton, C. E. Kolb, V. Torres, F. Al-Fadhli, E. McDonald-Buller, D. Allen. Connecting top down and bottom up methods for characterizing VOC emissions from petrochemical facilities. American Geophysical Union Annual Meeting, San Francisco, CA, December 2011.

Herndon, S. C., Products of incomplete combustion from full scale industrial flares under low flow conditions Industrial & Engineering Chemistry Research, in press 2012.

Kleinman, L.I., P.H. Daum, D. Imre, Y.N. Lee, L.J. Nunner-Macker, S.R. Springston, J. Weinstein-Lloyd, J. Rudolph, Correction to ozone production rate and hydrocarbon reactivity in 5 urban areas: A cause of high ozone concentration in Houston, Geophysical Research Letters 30 (2003) 1639.

Mellqvist, J., Chalmers: Flare testing using the SOF method at Borealis Polyethylene in the summer of 2000, 2001.

Mellqvist, J., J. Samuelsson, J. Johansson, C. Rivera, B. Lefer, S. Alvarez, J. Jolly. Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method. Journal of Geophysical Research 115 (2010), doi:10.1029/2008JD011682.

Murphy, C. F., D. T. Allen, Hydrocarbon emissions from industrial release events in the Houston-Galveston area and their impact on ozone formation, Atmospheric Environment 39 (2005), 3785-3798.

Nam, J., Y. Kimura, W. Vizuete, C. Murphy, D.T. Allen, Modeling the impact of emission events on ozone formation in Houston, Texas, Atmospheric Environment 40 (2006), 5329-5341.

Nam, J., M. Webster, Y. Kimura, H. Jeffries, W. Vizuete, D.T. Allen, Reductions in ozone concentrations due to controls on variability in industrial flare emissions in Houston, Texas, Atmospheric Environment 42 (2008) 4198-4211.

Nam, J., M. Webster, Y. Kimura, H. Jeffries, W. Vizuete, D. T. Allen. Reductions in ozone concentrations due to controls on variability in industrial flare emissions in Houston, Texas. Atmospheric Environment 42 (2008) 4198–4211.

Olaguer, E. P., B. Rappenglück, B. Lefer, J. Stutz, J. Dibb, R. Griffin, W.H. Brune, et al. Deciphering the role of radical precursors during the Second Texas Air Quality Study, Journal of the Air & Waste Management Association 59(2009), 1258–1277.

Pavlovic, R.T., E. McDonald-Buller, E., D. T. Allen, G. Yarwood, G. TERC Project No. H-95: Estimating Future Year Emissions and Control Strategy Effectiveness based on Hourly Industrial Emissions, submitted to the Houston Advanced Research Consortium (HARC), Project No. H-95, 2009.

Pavlovic, R.T., E.C. McDonald-Buller, F. Al-Fadhli, Y. Kimura, D.T. Allen, Impacts of refinery flare operations and emissions variability on ozone formation in the Houston-Galveston-Brazoria Area. Extended Abstract 2010-A-132-AWMA, Air & Waste Management Association Annual Meeting, Calgary, Alberta, Canada, June 2010.

Pavlovic, R.T., D. T. Allen, E. C. McDonald-Buller. Temporal variability in flaring emissions in the Houston-Galveston area, Industrial & Engineering Chemistry Research, in press 2012a.

Pavlovic, R.T., F. M. Al-Fadhli, Y. Kimura, D. T. Allen, E. C. McDonald-Buller, Impacts of emission variability and flare combustion efficiency on ozone formation in the Houston-Galveston-Brazoria area Industrial & Engineering Chemistry Research, in press 2012b.

Strosher, M., Characterization of emissions from diffusion flare systems. Journal of the Air & Waste Management Association 50 (2000), 1723-1733.

Texas Commission on Environmental Quality (TCEQ), TexAQS II emissions inventory files modeled for intensive period of August 15 through September 15, 2006, 2008, ftp://amdaftp.tceq.texas.gov/pub/HGB8H2/ei/point/2006/special_inventory/ (Accessed Jan 2008)

Torres, V. M., D. T. Allen, S. C. Herndon, Emissions measurements from full-scale industrial flares under low flow conditions: Steam assisted flares, Industrial & Engineering Chemistry Research, in press 2012a.

Torres, V. M.; Allen, D. T.; Herndon, S. C., Emissions measurements from full-scale industrial flares under low flow conditions: Air assisted flares. Industrial & Engineering Chemistry Research, in press 2012b.

Vizuete, W., B. Kim, H. Jeffries, Y. Kimura, D. T. Allen, M. Kioumourtzoglou, M.; L. Biton, B. Henderson, Modeling ozone formation from industrial emission events in Houston, Texas. Atmospheric Environment 42(2008), 7641–7650.

Washenfelder, R.A., M. Trainer, G. J. Frost, T. B. Ryerson, E. L. Atlas, J. A. de Gouw, F. M. Flocke, A. Fried, J. S. Holloway, D. D. Parrish, J. Peischl, D. Richter, S. M. Schauffler, J. G. Walega, C. Warneke, P. Weibring, W. Zheng, Characterization of NO_x, SO_2, ethene, and propene from industrial emission sources in Houston, Texas. Journal of Geophysical Research 115 (2010), D16311, doi:10.1029/2009JD013645.

Webster, M.; J. Nam, J., Y. Kimura, H. Jeffries, W. Vizuete, D.T. Allen, The effect of variability in industrial emissions on ozone formation in Houston, Texas, Atmospheric Environment 41 (2007), 9580-9593.

2.2.4 Oil and Natural Gas Production

1. Texas oil and gas production is associated with substantial emissions of NOx and VOC that impact predicted ozone concentrations.

NOx (and VOC) emissions occur from compressor stations that produce and move natural gas in pipelines as well as during drilling, hydraulic fracturing, and well completions; VOC is emitted from additional processes such as dehydration of natural gas, venting from oil and condensate tanks, and production and transmission fugitives (Armendariz, 2009; Grant et al., 2009). Emissions from individual oil and gas production sites are typically small, but collectively may become a significant source of emissions (Pring et al., 2010). As shown in Figure 2.2.2, there were over 400,000 active oil and gas wells in Texas during 2011 (http://www.dallascityhall.com/pdf/GasDrilling/ DallasGasDrillingTaskForce_TCEQ.pdf). With recent advancements in exploration and production technology such as the hydraulic fracturing and horizontal drilling of natural gas wells (ERG and SAGE, 2011), oil and gas exploration and production is increasingly taking place in populated areas, including the DFW nonattainment and Tyler-Longview-Marshall (TLM) near nonattainment areas. For example, Figure 2.2.3 shows that Barnett Shale (North Texas) natural gas production increased 540% during 2003 - 2011 (http://www.rrc.state.tx.us/barnettshale/ NewarkEastField_1993-2011.pdf).

In 2012, NOx and VOC emissions in the 9-county DFW area are predicted to be 19 tons/day and 114 tons/day, respectively (TCEQ, 2011a). Although shale gas is projected to play an increasingly important role in meeting US energy needs, studies of the ozone impacts associated with shale gas development are uncommon (Kemball-Cook et al., 2010). Ozone analysis using Anthropogenic Precursor Culpability Assessment (APCA) in support of the DFW SIP suggested that oil and gas emissions during 2012 may contribute up to 3.5 ppb to 8-hour ozone concentrations at some monitoring locations on some days (TCEQ, 2011b). High ozone days in Tyler-Longview-Marshall are often characterized by stagnant winds (Kemball-Cook et al., 2008; Stoeckenius and Yarwood, 2004), which would tend to keep Haynesville ozone precursor emissions near TLM (Grant et al., 2009). Ozone studies for 2012 predicted that increases in the 8-hour ozone design values of up to 5 ppb occurred over some portions of Northeast Texas and Northwest Louisiana resulting from development in the Haynesville Shale (Kemball-Cook et al., 2010).

2. Emissions from oil and gas production have substantial uncertainty.

The oil and gas exploration and production industry in Texas is extensive with many potential sources of emissions. Emissions sources at the larger “downstream” transmission/distribution stations, processing plants, and refineries are reported as major point sources to the TCEQ so they are generally well-handled in annual inventories (ERG, 2007). With the recent advancements in hydraulic fracturing of shale rock, the amount of oil and gas drilling is increasing rapidly in portions of the US including Texas. Emissions from these “upstream” shale oil and gas production sites are subject to substantial uncertainty (Thoma, 2009). Recently, TCEQ has expended significant resources to improve emissions inventories for the predominant oil and gas exploration and production NOx sources such as drilling rigs (ERG, 2009; ERG, 2011) and other internal combustion engines such as natural gas compressor stations and pumpjacks (Grant et al., 2009; Pring et al., 2010). The accuracy of the emission inventories is limited by the availability of county-specific data and the absence of sufficient data often requires substantial assumptions. For example, since the Haynesville Shale is in the initial stages of development and site-specific data were not yet available from many gas producers, historical data for the Barnett Shale were utilized to estimate current and future activity in the Haynesville Shale (Grant et al., 2009).

Figure 2.2.2. Locations of active oil and gas wells in Texas (Source: TCEQ, http://www.tceq.state.tx.us/assets/public/implementation/barnett_shale/bs_images/txOilGasWells.png)

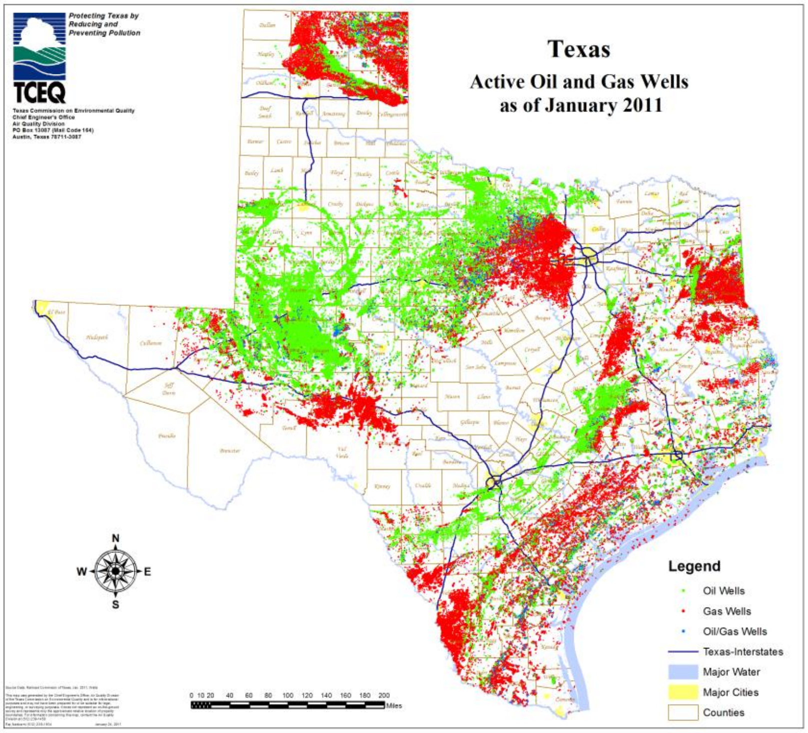
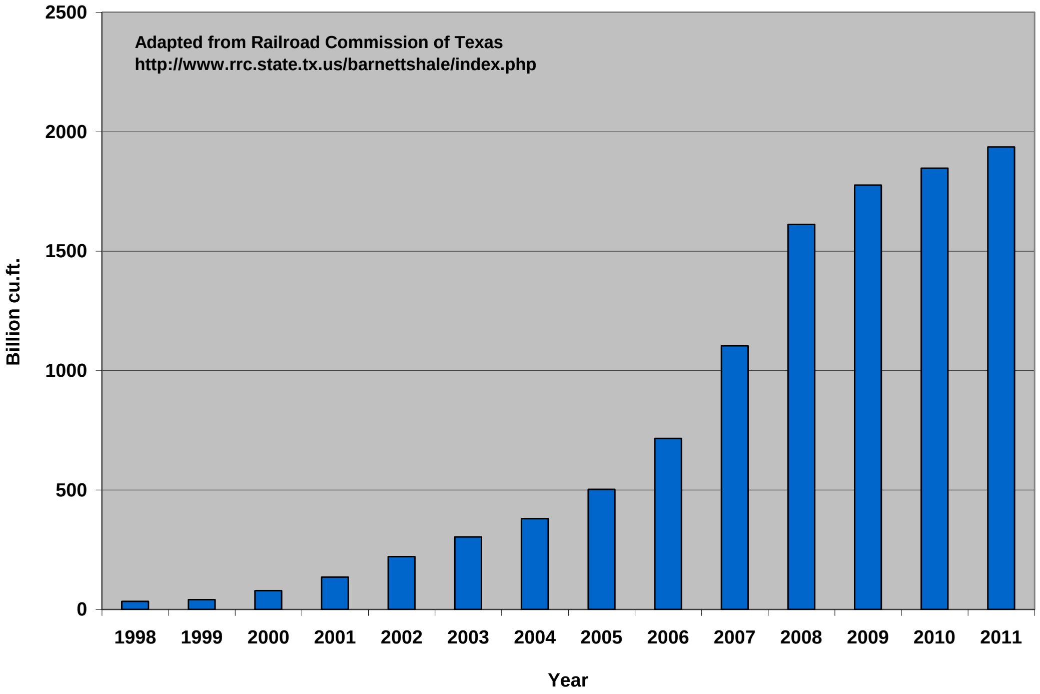


Figure 2.2.3. Barnett Shale natural gas production (billion cubic feet) for 1998 – 2011. Adapted from Railroad Commission of Texas (http://www.rrc.state.tx.us/ barnettshale/index.php).



Emissions inventories show that VOC is primarily associated with oil and condensate storage tanks and production/transmission fugitives in the Barnett Shale (Pring, 2010) and engine exhaust, pneumatic devices, and completion venting in the Haynesville Shale (Grant et al., 2009). An intensive study of oil and gas sources in the Forth Worth area found that the majority of VOC emissions occur at well pads and that compressor engines can be a significant contributor to emissions at natural gas-related facilities (ERG and SAGE, 2011). Important sources of emissions included faulty tank thief hatches and pneumatic valve controllers, both of which could be controlled under an appropriate maintenance program. Emission factors for VOC components are often not available or are associated with substantial uncertainty since the site-specific composition of the gas production stream is often unknown (Grant et al., 2009; Pring et al., 2010). Over the past few years, TCEQ has supported a number of field studies that have investigated emissions rates for specific VOC source types. These studies have included sampling of emissions from oil and condensate storage tanks (Hendler et al., 2009; Gidney and Pena, 2009; ENVIRON, 2010a), water storage tanks (ENVIRONb, 2010), fuel oil tanks (Boczek et al., 2010), and pipelines (ERG, 2010). The results of these recent Texas field studies are often limited in scope and large variability in results is sometimes indicated even at a single site. As such, additional work is necessary to evaluate the general applicability of these studies to other locations (e.g., ENVIRON, 2010c).

3. Recent field studies in the Barnett Shale have focused on the measurement of speciated hydrocarbon compounds associated with oil and gas production.

Several studies were conducted in the Fort Worth area during 2010 – 2011 that included the measurement of speciated hydrocarbons from natural gas production. The City of Fort

Worth, City of Arlington and the Barnett Shale Energy Education Council (BSEEC) engaged TITAN Engineering, Inc. to collect ambient air samples in the vicinity of two compressor stations and eight completed well pads projected to have the relatively high emissions rates of compounds such as benzene and formaldehyde as well as sulfur compounds (TITAN, 2010). Concentrations of compounds such as isopentane, xylene, and toluene were elevated downwind of one completed well site, including a maximum 24-hour average benzene concentration of 1.96 ppbv; however, the study concluded that natural gas operations at most sampling locations made a negligible contribution to downwind concentrations. A second study in Fort Worth focused on a number of potential sampling locations such as compressor stations, condensate tanks, and well pads (Zielinska et al., 2010). For a representative condensate tank adjacent to gas wells, the most abundant non-methane hydrocarbon species were ethane, propane, butanes, and pentanes; aromatic compounds such as benzene, toluene, and xylenes accounted for approximately 0.1-0.2% of non-methane emissions. There was no evidence suggesting that emissions from any natural gas facilities contributed to measured carbonyl compounds such as formaldehyde and acetaldehyde.

A third study performed in Forth Worth included the collection of more than 15,000 ambient air samples at eight different locations (ERG and SAGE, 2011). It was estimated that 98% of the associated hydrocarbon emissions were methane, ethane, propane, and butane, with the majority (75%) occurring at well pads. Individual compounds such as benzene, toluene, and propene were measured at most locations and times at concentrations above the detection limit; however, benzene concentrations were clearly elevated at a location nearby to a well pad and compressor station (average of 0.686 ppbv) compared to concentrations measured at the other sites (0.1 – 0.3 ppbv). Overall, the measurements demonstrated that carbonyl compounds such as formaldehyde (0.70 – 1.14 ppbv) were not unusually elevated when compared to levels measured by TCEQ elsewhere in Texas; however, results from dispersion modeling using measured and/or estimated emissions rates suggested that formaldehyde concentrations could be significant downwind of large (>1500 Hp) compressor engines so that further study was warranted.

During summer 2011, the University of Houston (UH) flew five complete low-level flights over the Barnett Shale to investigate the potential contribution of emissions associated with natural gas production to ozone concentrations (Alvarez et al., 2011). The results of the aircraft measurements did not indicate enhancements in ozone concentrations clearly associated with oil and gas emissions, but the UH team noted that the persistent southerly winds (~10 mph) may not have favored localized ozone production. On some occasions, elevated concentrations of reactive alkenes and formaldehyde (4-6 ppbv compared to background concentrations of 2-3 ppbv) were measured over the Barnett Shale, such as immediately downwind of a large compressor station in the Eagle Mountain Lake area. A FTIR and canister sampling analysis performed in the Barnett Shale by Johansson, et al. (2011) estimated significant rates of ethene emissions from large compressor stations (0.4 kg/hr) and from flash venting from a single condensate tank (2 kg/hr). High ethene concentrations have not been observed in other recent mobile sampling studies (e.g., Sullivan, 2010); however, given the large numbers of oil and condensate tanks and the potential importance of ethene in ozone formation, Johansson et al. (2011) suggested that additional studies to verify these results are warranted since flash venting is an important but intermittent emissions activity.

References

Alvarez, S.L., G.P. Roberts, G. Zanin, M.E. Shauck, B. Rappenglück, Airborne measurements to investigate ozone production and transport in the Dallas Forth Worth (DFW) area during the 201 ozone season. Air Quality Research Program, TCEQ Grant No. 582-10-94300, November 2011.

Armendariz, A, Emissions from natural gas production in the Barnett Shale area and opportunities for cost-effective improvements. Prepared for Ramon Alvarez, Environmental Defense Fund, Version 1.1, January 26, 2009.

Baker, R., M. Pring, Drilling rig emissions inventory for the State of Texas. Prepared by Eastern Research Group, Inc. (ERG) for Greg Lauderdale, Texas Commission on Environmental Quality (TCEQ), July 8, 2009.

Baker, R., D. Preusse, Development of Texas statewide drilling rigs emission inventories for the years 1990, 1993, 1996, and 1999 throughout 2040. Prepared by Eastern Research Group, Inc. (ERG) for Kritika Thapa, Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-11-99776-FY11-05, 2011.

Boczek, B., Z. Willenberg, A. Dindal, Fuel oil tank emissions testing feasibility study. Prepared by Battelle for Eastern Research Group, Inc. (ERG), August 31, 2010.

ENVIRON, Control of VOC flash emissions from oil and condensate storage tanks in East Texas. Prepared by ENVIRON International Corporation for Texas Commission on Environmental Quality (TCEQ), TCEQ Project 2010-43, August 2010, 2010a.

ENVIRON, Emission factor determination for produced water storage tanks. Prepared by ENVIRON International Corporation for Texas Commission on Environmental Quality (TCEQ), TCEQ Project 2010-29, August 2010, 2010b.

ENVIRON, Upstream oil and gas tank emission measurements. Prepared by ENVIRON International Corporation for Texas Commission on Environmental Quality (TCEQ), TCEQ Project 2010-39, August 2010, 2010c.

ERG, Emissions from oil and gas production facilities. Prepared by Eastern Research Group, Inc. (ERG) for Bertie Fernando, Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-7-84003, August 31, 2007.

ERG, Ethylene, propylene, and 1,3-butadiene pipeline emissions inventory. Prepared by Eastern Research Group, Inc. (ERG) for Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-07-83984-FY10-02, August 16, 2010.

ERG and SAGE, City of Fort Worth Natural Gas Air Quality Study. Prepared by Eastern Research Group, Inc. (ERG) and SAGE (Sage Environmental Consulting, L.P.) for City of Fort Worth, July 13, 2011.

Gidney, G., S. Pena, Upstream oil and gas storage tank project flash emissions models evaluation. Prepared for Danielle Nesvacil, Texas Commission on Environmental Quality, and Rick Baker, Eastern Research Group, Inc., July 16, 2009.

Grant, J., L. Parker, A. Bar-Ilan, S. Kemball-Cook, G. Yarwood, Development of emissions inventories for natural gas exploration and production activity in the Haynesville Shale. Prepared for The East Texas Council of Governments, August 31, 2009.

Hendler, A., J. Nunn, J. Lundeen, VOC emissions from oil and condensate storage tanks. Prepared for Texas Environmental Research Consortium (TERC) and Houston Advanced Research Consortium (HARC), Project H-51C, October 31, 206, Revised April 2, 2009.

Johansson, J., J. Mellqvist, J. Samuelsson, B. Offerle, B. Rappenglück, D. Anderson, B. Lefer, S. Alvarez, J. Flynn, Quantification of industrial emissions of VOCs, NO2 and SO2 by SOF and mobile DOAS. Air Quality Research Program, TCEQ Grant No. 582-10-94300, November 2011.

Kemball-Cook, S., J. Johnson, E. Tai, M. Jimenez, G. Mansell, G. Yarwood, Modeling Northeast Texas ozone for May-June 2005. Prepared for East Texas Council of Governments, August 31, 2008.

Kemball-Cook, S., A. Bar0Llan, J. Grant, L. Parker, J. Jung, W. Santamaria, J. Mathers, G. Yarwood, Ozone impacts of natural gas development in the Haynesville Shale. Environmental Science & Technology 44 (2010), doi:10.1021/es1021137.

Pring, M., D. Hudson, J. Renzaglia, B. Smith, S. Treimel. Characterization of oil and gas production equipment and develop a methodology to estimate statewide emissions. Prepared for Martha Maldonado, Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-7-84003-FY10-26, November 24, 2010.

Stoeckenius, T., G. Yarwood, Conceptual model of ozone formation in the Tyler/Longview/Marshall near nonattainment area. Prepared for The East Texas Council of Governments, January 2004.

Sullivan, D., Final report satisfying task 6, Proposal for grant activities under the grant umbrella from TCEQ to the University of Texas at Austin, Prepared for Texas Commission on Environmental Quality (TCEQ), TCEQ Grant Number 582-8-86245-FY09-03, January 31, 2010.

TCEQ, Revisions to the State of Texas air quality implementation plan for the control of ozone air pollution, Dallas-Fort Worth eight-hour ozone nonattainment area, Project Number 2010-022-SIP-NR. Available: http://m.tceq.texas.gov/airquality/sip/dfw_revisions.html, December 7, 2011, 2011a.

TCEQ, Revisions to the State of Texas air quality implementation plan for the control of ozone air pollution, Dallas-Fort Worth eight-hour ozone nonattainment area, Appendix C, Project Number 2010-022-SIP-NR. Available: http://m.tceq.texas.gov/airquality/sip/dfw_revisions.html, December 7, 2011, 2011b.

Thoma, E., Measurement of emissions from produced water ponds: Upstream oil and gas study #1. Environmental Protection Agency, Air Pollution Prevention and Control Division, Research Triangle Park, NC, EPA/600/R-09/132, October 2009.

TITAN, Ambient air quality study, natural gas sites, Cities of Forth Worth & Arlington, Texas. Prepared by TITAN Engineering, Inc. for Barnett Shale Energy Education Council (BSEEC), July 2010.

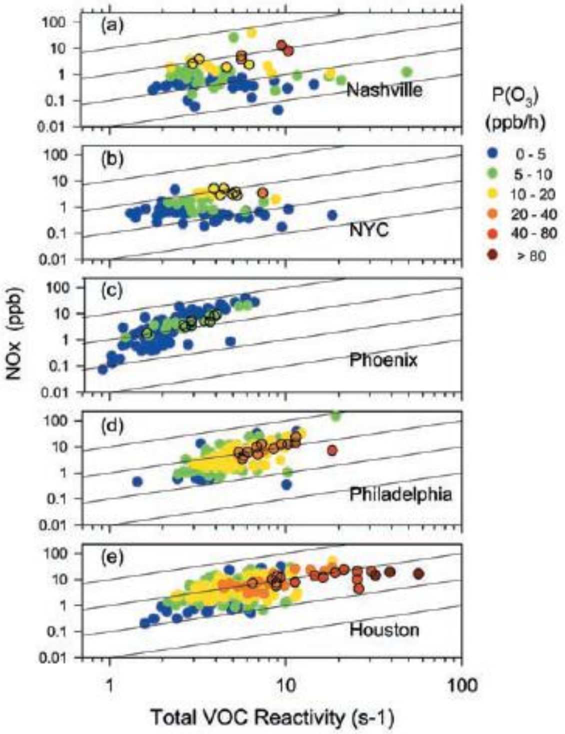
Zielinska, B., E. Fujita, D. Campbell, Monitoring of emissions from Barnett Shale natural gas production facilities for population exposure assessment. Prepared by Desert Research Institute (DRI) for Mickey Leland National Urban Air Toxics Research Center (MLNUATRC), November 11, 2010.

2.3 Tropospheric Chemistry

1. Ozone production rates and efficiencies in the Houston area are similar between the Texas 2000 and TexAQS II studies and indicate the continued importance of co-located emissions of highly reactive VOCs and NO_x in the Houston Ship Channel.

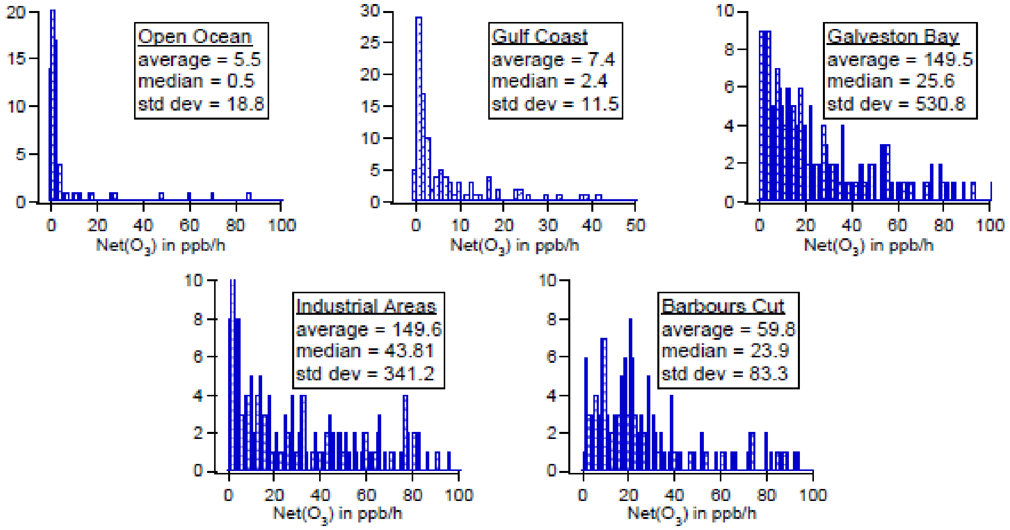
The proximity of NO_x and reactive VOC- rich plumes in Houston's extensive petrochemical complex lead to conditions that favor rapid ozone formation. During TexAQS2000, ozone production rates and ozone production efficiencies (OPE; the integrated number of O_3 molecules formed for each NO_x or observed $(\Delta O_3/\Delta(NO_y - NO_x))$, in plumes originating from the Houston Ship Channel industrial complex were found to be greater than those for the Houston urban core and others areas of the United States (Ryerson et al., 2003; Daum et al., 2003; Berkowitz et al., 2004; Kleinman et al., 2005). For example, comparison of ozone production rates for five U.S. cities by Kleinman et al. (2005), shown in Figure 2.3.1, indicates that the top 10% of the distribution of ozone production rates for Houston are substantially higher than those in Philadelphia, Phoenix, New York City, and Nashville.

Figure 2.3.1. Ozone production rates for five U.S. cities in the style of an ozone isopleths diagram from Kleinman et al. (2005). Samples comprising the top 10% of the distribution in each city are outlined in bold.



During TexAQS 2000, strong spatial gradients in the rates of ozone formation were found across the Houston area (Berkowitz et al., 2005) with levels between 3 and 18 ppb h^{-1} over downtown Houston and 3 and 80 ppb h^{-1} in the eastern industrial plume (Daum et al., 2003). Net ozone production rates by Sommariva et al. (2011), shown in Figure 2.3.2, during TexAQS II varied spatially throughout the Houston/Galveston region and Gulf Coast. Ozone production efficiencies from Neuman et al. (2009) and Cowling et al. (2007) obtained during TexAQS II were similar to those during TexAQS 2000, although maximum observed ozone concentrations and concentrations of highly reactive VOCs in Houston area have decreased over the same time period (Cowling et al., 2007). Similar to TexAQS 2000, ozone production during TexAQS II was found to be NO_x- limited with the influence of reactive hydrocarbons, especially alkenes and their oxidation products, to be of continued importance (Sommariva et al., 2011).

Figure 2.3.2. Frequency distributions of *Net*(O3) at locations during the NOAA R/V Brown cruise in the summer of 2006 as part of TexAQS II from Sommariva et al. (2011). The bin size is 0.1 ppb h-1 for the open ocean and 1 ppb/h for all other locations. Values on the y-axis are the number of data points in each bin.



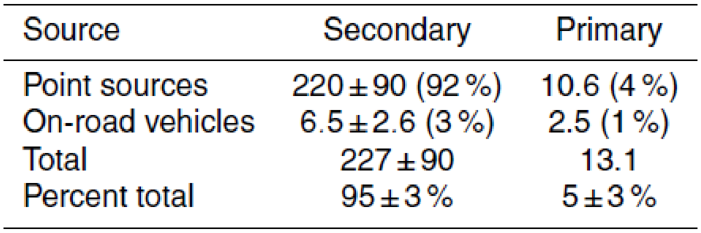
2. Formaldehyde (HCHO) and nitrous acid (HONO) are radical precursors and their characterization is important for understanding atmospheric radical budgets.

Formaldehyde (HCHO) and nitrous acid (HONO) represent critical precursors for the formation of hydroxyl radical (OH). Atmospheric radicals, notably OH and hydroperoxyl radical (HO_2), which collectively are known as HO_x, have important roles in the formation of ozone and fine particulate matter. Over the past decade, field campaigns, such as the Second Texas Air Quality Study (TexAQS II) and 2006 TexAQS-II Radical and Aerosol Measurement Project (TRAMP), the Study of Houston Atmospheric Radical Precursors (SHARP) in 2009, and Formaldehyde and Olefins from Large Industrial Releases (FLAIR), have sought to improve the characterization of HCHO and HONO and the understanding of their influence on radical budgets, primarily in the Houston-Galveston-Brazoria airshed.

As described in detail by Seinfeld and Pandis (1998) and others (e.g., Parrish et al., 2012), formaldehyde originates from primary emissions sources as well as from secondary chemical production through the oxidation of biogenic and anthropogenic volatile organic compounds (VOCs), including alkenes, alkanes, and aromatic compounds. Secondary production of formaldehyde occurs via photochemical oxidation of precursor VOCs initiated by OH during the day; while at night, oxidation of precursor VOCs occurs via ozone and nitrate radical. Atmospheric loss of formaldehyde can occur by photolysis, reaction with OH, and deposition.

The relative contribution of primary sources and secondary chemical production to ambient formaldehyde concentrations and fluxes in Houston has been a topic of focus and divergent analysis during the past several years (Olaguer et al., 2009a; Olaguer et al., 2009b; Olaguer, 2010; Lefer et al, 2010a; Cowling et al., 2007; Parrish et al., 2012). Nonetheless, there is recognition by air quality stakeholders that understanding formaldehyde sources is critical to defining effective ozone control strategies in the Houston area. During TexAQS II, formaldehyde concentrations in excess of 50 ppb were observed in the Houston Ship Channel (Eom et al., 2008). In addition to vehicular emissions, which are common to many urban areas, industrial emissions from Houston's petrochemical complex are expected to have an important contribution to measured formaldehyde concentrations that may be atypical relative to other urban areas. Most recently, Parrish et al. (2012) undertook a reanalysis of the quantification of primary and secondary sources of formaldehyde in the Houston area using archived data from airborne, mobile, and elevated surface (i.e., Moody Tower) studies collected during 2000-2009 and a measurement constrained inventory based upon the 2005 National Emissions Inventory (NEI). In contrast to earlier studies, their analysis indicated that secondary production of formaldehyde from alkenes emitted by petrochemical facilities and on-road vehicles is the major source of formaldehyde in the Houston-Galveston-Brazoria area, as shown in Table 2.3.1 below; primary emissions from these sources represent a much smaller amount of formaldehyde in the region and are well represented by current emissions inventories. The authors argue that although there are cases where targeted reductions of primary formaldehyde emissions may be warranted, for example from the Texas City area where a single primary formaldehyde source was identified (Stutz et al., 2011), on-going efforts to reduce highly reactive VOC (HRVOC) emissions from Houston industrial facilities and VOCs from on-road vehicles should result in control of secondary formaldehyde formation in the region.

Table 2.3.1. Rates of secondary production and primary emissions (kmol h^{-1}) of formaldehyde in the Houston-Galveston-Brazoria area as 24-hour averages from Parrish et al. (2012). Uncertainties of primary emissions are estimated as ±30%.



Source	Secondary	Primary
Point sources	220 ± 90 (92 %)	10.6 (4 %)
On-road vehicles	6.5 ± 2.6 (3 %)	2.5 (1 %)
Total	227 ± 90	13.1
Percent total	95 ± 3 %	5 ± 3 %

As described by Lefer et al. (2011), the calculated HO_x production during SHARP was dominated by the photolysis of HONO in the early morning and by photolysis of O_3 in the midday; at night, OH production occurred mainly via O_3 reactions with alkenes. On average, the daily HO_x production rate was 23.8 ppbv day^{-1} in the region, of which 31% was from O_3 photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O_3 reactions with alkenes (Lefer et al., 2011). Finlayson-Pitts (2003) and others (e.g. Wong et al., 2011) describe that HONO formation in the nocturnal boundary layer is thought to occur via heterogeneous conversion of NO_2 on humid surfaces. Accumulation of HONO in the nocturnal boundary layer and rapid photolysis at sunrise drives morning OH production. Recent measurements have indicated though that daytime observed HONO mixing ratios are often far larger than the expected photostationary state with OH and NO in locations throughout the world (Wong et al., 2012; Acker et al., 2006a; Acker et al., 2006b, Zhou et al., 2007; Carter and Seinfeld, 2012). For example, HONO concentrations in Houston can exceed 2 ppb close to sunrise, and remain at several hundred ppt during much of the day with winds from the Houston Ship Channel (Olaguer et al., 2009b; Wong et al., 2012). During the SHARP campaign, Wong et al. (2012) found that observed HONO mixing ratios were often ten times larger than expected from the photostationary state with OH and NO.

Daytime formation mechanisms that account for enhanced HONO formation have been a focal point of studies over the past several years (e.g., Olaguer et al., 2009b; Wong et al., 2012). Both gas-phase and heterogeneous mechanisms on aerosol surfaces have been investigated, including gas-phase photolysis of ortho-nitrophenols (Bejan et al., 2006), heterogeneous conversion of NO_2 on fresh and aged soot particles (Zhang et al., 2009, Lefer et al., 2010b), humic acids, and soil surfaces (Stemmler et al., 2006), photolysis of surface adsorbed nitric acid (Zhou et al, 2011), and heterogeneous conversion of HNO_3 on the surface of primary organic aerosol (Ziemba et al., 2010). In the Houston area during SHARP, Wong et al. (2012) and Lefer et al (2011) found statistically significant vertical gradients of HONO throughout the day, with smaller mixing ratios aloft, and suggested that a likely source of daytime HONO could be photocatalytic conversion of NO_2 on the ground.

Although daytime mechanisms for HONO formation have been a subject of exploration, it is evident that uncertainty remains and further studies are needed. As further progress is made, incorporation into air quality models will be important. For example, comparisons of CAMx predictions by the TCEQ with radical budgets obtained by Mao et al. (2009) and Chen et al. (2009) during the TRAMP study indicated good agreement in HOx radical production from HCHO photolysis, but poor agreement in HOx formation from HONO photolysis (http://www.tceq.state.tx.us/assets/public/implementation/air/sip/hgb/hgb_sip_2009/09017SIP_ado_Appendix_I.pdf). Czader et al. (2010) found the incorporation of HONO formation via heterogeneous chemistry in CMAQ simulations improved the correlation with measured values in the Houston area.

3. Nitryl chloride ($ClNO_2$) can affect tropospheric oxidation capacity and ozone formation in coastal and inland regions.

Dinitrogen pentoxide (N_2O_5) is a nocturnal reservoir of NO_x, formed from the reaction of nitrate radical (NO_3^-) and NO_2. Heterogeneous reaction of N_2O_5 can proceed via two pathways: (1) hydrolysis to form soluble nitrate, the rate of which depends on the availability of aerosol surface area and on the heterogeneous uptake coefficient of N_2O_5 to aerosol (Brown et al., 2009; Parrish et al., 2009), or (2) reaction with chloride to form nitryl chloride and nitrate, which depends on, among other factors, particulate chloride (PCl) availability (Finlayson-Pitts et al., 1989; Behnke et al., 1997; Kercher et al., 2009; Osthoff et al., 2008; Thornton et al., 2010). At sunrise, $ClNO_2$ photolysis can affect the cycling of oxidants by providing a source of chlorine atoms that enhance VOC oxidation (Osthoff et al., 2008; Knipping and Dabdub, 2003; Tanaka et al., 2003). During the past several years, the presence of nitryl chloride has been characterized in the coastal environment of Houston during the 2006 TexAQS/Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS) (Osthoff et al., 2008), as well as for the inland region of Boulder, Colorado (Thornton et al., 2010).

Simon et al. (2009) used the Comprehensive Air Quality Model with extensions (CAMx) to examine the effects of observed nitryl chloride concentrations on ozone chemistry in southeast

Texas. Predicted $ClNO_2$ increased total reactive chlorine mass by 20–40%. Modest increases in predicted ozone concentrations (up to 1.0–1.5 ppb when baseline 1-h average ozone concentrations were between 60 and 85 ppb) were found to be affected by vertical dispersion and local VOC and NO_x mixtures. These results suggested the potential importance of NO_x emissions reductions on chlorine cycling.

Recently, Koo et al. (2012) undertook an analysis of nitryl chloride formation in Houston, using data from TexAQS II and SHARP (on the top of Moody Tower), and in Los Angeles, using data from the CalNex study in 2010. In addition, the authors implemented the chemistry in CAMx and conducted simulations that included reactive and particulate chloride emissions inventories. Overall, CAMx simulated, but underpredicted, $ClNO_2$ formation, and underpredicted HCl and PCl, which was thought to be due to missing sea salt aerosols in the model. Further CAMx studies suggested that reaction of a fraction of coarse mode sea salts in addition to fine mode sea salts, in combination with a reduced dry deposition velocity for HCl, would improve model performance. The study suggested the need for additional measurements of nitryl chloride and related chlorine species in coastal and inland areas, better estimation of the HCl dry deposition velocity, and inclusion of other chlorine/chloride emission sources in the inventory.

4. NO_x sink and recycling reactions should be represented in atmospheric chemical mechanisms for photochemical modeling of ozone.

As described by Yarwood et al. (2012a), most VOCs can remove NO_x by forming NO_x sink compounds, including organic nitrates, peroxy nitrates, or nitro compounds, that reduce the availability of NO_x for ozone formation. These NO_x sink species may eventually react to return NO_x back to the atmosphere, known as NO_x recycling, potentially causing additional ozone production in NO_x-limited regions. Reactions of NO_x-sink compounds that return sequestered NO_x to an active form are referred to as NO_x-source reactions.

Using novel environmental chamber experiments performed at the University of California at Riverside, Yarwood et al. (2012a) demonstrated the importance of NO_x sinks for toluene and isoprene. The product o-cresol and furan (a precursor to 2-butenedial, which is a major ring-opening product of toluene) had an important influence in producing the observed NO_x sink for toluene. Experimental data were used to test and to improve the mechanisms for isoprene and aromatics in version 6 of the Carbon Bond mechanism (CB6), resulting in the creation of a revised mechanism known as CB6r1. Although CB6r1 performed better than CB6 in simulating experiments for toluene, xylenes and mixtures combining aromatics with other VOCs, aspects of the aromatics chemistry are still not fully understood. Experiments strongly supported the occurrence of NO_x-recycling in the photolysis reactions of the NO_x-source compounds isopropyl nitrate, isobutyl nitrate and 2-nitrophenol; CB6r1 includes NO_x-recycling from photolysis of alkyl nitrates and nitrocresols. Additional experiments are needed to test for the occurrence of NO_x recycling from alkyl nitrates larger than isopropyl and isobutyl.

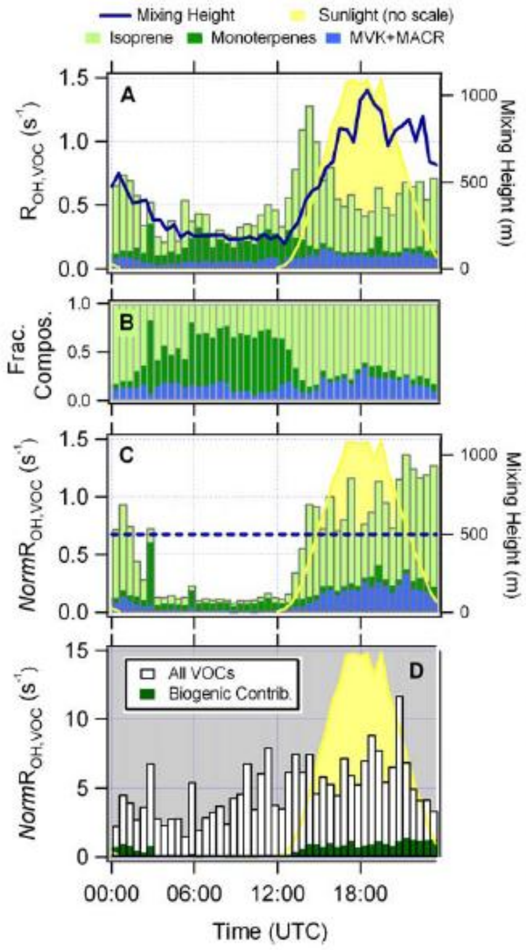
5. Biogenic VOCs have an important contribution to regional atmospheric chemistry in eastern Texas. Ambient measurements, characterization of land use and land cover, and modeling of biogenic emissions have continued to evolve over the past decade.

Biogenic VOCs, including isoprene and monoterpenes, and their oxidation products have important influences on the formation of ozone and secondary organic aerosol. Emissions of biogenic VOCs exhibit strong diurnal variability with temperature and sunlight and spatial gradients due to differences in land use/land cover. Figure 2.3.3 from measurements by Gilman et al. (2009) aboard the NOAA R/V Brown during TexAQS II/GoMACCS, shows the relative fraction and diurnal profiles of isoprene, its oxidation products (methyl vinyl ketone and methacrolein), and monoterpenes (alpha-pinene, beta-pinene, and limonene), as well as the hydroxyl radical reactivity (R_{OH}) as a quantification of the contribution to potential ozone formation in the Houston-Galveston-Brazoria area. Similar to observation during TexAQS 2000, isoprene had the largest overall contribution to biogenic $R_{OH,\ VOC}$; during the afternoon, biogenic VOCs accounted for up to 20% of the VOC reactivity (Gilman et al., 2009).

Using a regional chemical transport model with emissions during an eight day period of TexAQS 2000, Li et al. (2007) found that isoprene emissions had an important role in ozone formation when the ozone plume occurred in the afternoon over the urban Houston area. When isoprene emissions were decreased or increased by 50%, predicted ozone concentrations decreased or increased by 5–25 ppb over the urban Houston area, but less than 5–10 ppb over the Houston Ship Channel industrial area. Differences in ozone concentrations were primarily attributed to local emissions of isoprene, but transport from regions north of Houston were important on selected episode days (Li et al., 2007).

Accurate local and regional characterizations of land use/land cover data are essential for estimating biogenic emissions and have been an area of research for the State of Texas for the past 10 – 15 years (e.g., Wiedinmyer et al., 2001; Feldman et al., 2010; Popescu, 2010). In recent revisions to the State Implementation Plans for the Dallas Fort Worth and Houston-Galveston-Brazoria area, the TCEQ has utilized the Global Biosphere Emissions and Interactions System (GloBEIS3.1), available from http://www.globeis.com/, for estimating biogenic emissions (http://www.tceq.texas.gov/assets/public/implementation/air/sip/dfw/ad_2011/AppB_EI_ado.pdf ;http://www.tceq.state.tx.us/assets/public/implementation/air/sip/hgb/hgb_sip_2009/09017SIP_ado_Appendix_B.pdf.). Comparisons of predicted emissions estimates from GloBEIS, the EPA's Biogenic Emissions Inventory System 3 (BEIS3), and the Model of Emissions of Gases and Aerosols from Nature version 2 (MEGAN2), with measurements of isoprene and monoterpenes have generally shown agreement within a factor of two (Song et al., 2008; Warneke et al., 2010). Drought, the influence of inter-annual variability in emissions, and evaluation of inventories over large spatial scales (Warneke et al., 2010) remain areas for further research.

Figure 2.3.3. (a) Average diurnal profiles of mixing height, sunlight, and $\mathrm{R}_{\mathrm{OH,VOC}}$ for all biogenic VOCs for the Houston-Galveston-Brazoria area; (b) the fractional contribution of isoprene, monoterpenes, and methyl vinyl ketone (MVK) and methacrolein (MACR) to $\mathrm{R}_{\mathrm{OH,VOC}}$; (c) the average diurnal profile of *Norm*$\mathrm{R}_{\mathrm{OH,VOC}}$ for the biogenics; (d) a comparison of the average diurnal profile of *Norm*$\mathrm{R}_{\mathrm{OH,VOC}}$ for all VOCs (biogenic + anthropogenic + oxygenated VOCs) and the contribution solely from biogenic VOCs from Gilman et al. (2009). *Norm*$\mathrm{R}_{\mathrm{OH;VOC}}$ is the normalized OH reactivity for which the dependence of VOC mixing ratios on mixing heights is considered by normalization with a constant mixing height of 500 m.



6. Characteristics of fine particulate matter composition and sources between the time periods of the TexAQSII, GoMACCS, and SHARP campaigns and TexAQS 2000 have remained consistent. Houston's industrial complex contributes to the formation of organic-rich aerosols at levels above that typical of urban areas and have been associated with emissions of hydrocarbons with high SOA-forming potential, such as aromatics.

Understanding particulate matter composition and concentrations is of concern not only due to direct human health impacts and visibility impacts, but also because chemical reactions at aerosol surfaces influence ozone formation, and these reactions depend on particle surface area (particle size) and particle composition. A variety of studies have been conducted to better characterize particulate matter size, composition and concentrations in Texas. TexAQS 2000 coincided with Gulf Coast Aerosol Research and Characterization Program (GC-ARCH) or the Houston Supersite which had the aim of improving the understanding of the concentrations, spatial and temporal variability, composition, and sources of fine particulate matter in southeastern Texas (Allen, 2005). A number of findings emerged from these studies. Daily average fine particulate matter concentrations ($PM_{2.5}$) were remarkably consistent spatially and seasonally in southeast Texas, ranging between 10 and 15 $\mu g/m^3$. However, extreme values of $PM_{2.5}$ mass concentrations showed more variability with a number of instances when localized, high concentrations were observed. Sulfate, ammonium, organic carbon (OC), and elemental carbon (EC) were the major constituents of $PM_{2.5}$ in southeast Texas, and relative concentrations of these components were, on average, also spatially homogeneous. Sulfate accounted for approximately 40% and OC for approximately 25% of the fine particulate mass. OC to EC ratios in southeast Texas were generally well above the value assumed for primary emissions, suggesting that much of the OC may be due to secondary organic aerosol (SOA) formation. Primary sources of $PM_{2.5}$ were associated with mobile sources, cooking, burning, dust, and industrial sources. Sources of secondary $PM_{2.5}$ precursors associated with inorganic sulfate and ammonium were transported from the interior continental United States, SO_2 from electricity generation, and livestock and domestic activities, respectively, and those associated with secondary organic aerosol included industrial point sources, mobile sources, area/non-road sources, and biogenic sources (notably in forested areas north and southwest of Houston urban core). Particle size distributions were not spatially homogeneous; industrial sites have higher concentrations of ultrafine particles than more residential sites, even on a seasonal basis.

Since the 2000 study, other studies have sought to further the characterization of particulate matter in southeastern Texas and/or to examine differences over time. Yu and Cowin (2009) found that the averages and ranges of OC, EC, and total carbon (TC) during SHARP were comparable to observations in the early 2000s (Allen, 2004; 2005). The average OC to EC ratio of Yu and Cowin (2009) was 6.9, indicating that secondary organic aerosols were a component in the carbonaceous aerosols observed in Houston; OC generally peaked concurrently with an ozone event (defined as concentrations > 75 ppb). Average EC was fairly low during SHARP similar to the findings of Allen (2004). Five types of particles were observed including 1) sulfate (primary and secondary); 2) mineral dust; 3) soot; 4) sea salt; and 5) mixed sulfate and sea salt, which varied in composition, size, shape, morphology, and mixing state.

Bahreini et al. (2009) measured organic aerosol (OA) in urban plumes from Houston and Dallas/Fort Worth as well as in industrial plumes in the Houston area during TexAQS II. Consistent with the TexAQS-2000 study, observations showed a greater amount of aerosol mass downwind of the industrial centers compared to urban area. Bahreini et al. (2009) found that observed ratios of the enhancement above background in OA, ΔOA, to the enhancement above background in carbon monoxide (CO), ΔCO, downwind of urban centers of Houston and Dallas/Fort Worth were within a factor of two of the same values in plumes from urban areas in the northeastern United States by de Gouw (2008) indicating similar concentrations of precursors and chemical processes. In Houston Ship Channel plumes, ΔOA/ΔCO exceeded that in the urban areas by factors ranging from 1.5 to 7. Initial carbon mixing ratios of aromatics in the urban plumes were approximately a factor of two *lower* than those in the Houston Ship Channel plumes, which Bahreini et al. (2009) noted had at least twice the potential for SOA formation from these precursors under similar NO_x conditions.

Bates et al. (2008) examined aerosol sources and transformation processes in the Houston-Galveston-Gulf of Mexico region, aboard the NOAA R/V Ronald H. Brown during TexAQS II/GoMACCS 2006. Aerosol measured in the Gulf of Mexico during onshore flow was highly impacted by Saharan dust and possibly ship emissions (acidic sulfate and nitrate). Mean and median mass concentrations of the total submicrometer and supermicrometer aerosol were higher than expected for marine atmospheres. As the background aerosol moved onshore, local urban and industrial sources added an organic rich submicrometer component (66% particulate organic matter, 20% sulfate, 14% elemental carbon) but no significant supermicrometer aerosol. Bates et al. (2008) found that these air masses, with minimal processing of urban emissions contained the highest $SO_2/(SO_2 + SO_4^{=})$ ratios and the highest hydrocarbon-like organic aerosol (i.e., non-oxygenated) to total organic aerosol ratios. In contrast, during periods of offshore flow, the aerosol was more processed and much richer in oxygenated organic aerosol.

7. The overnight transport of plumes from urban, petrochemical, and coal-fired power plants can potentially affect the air quality in regions several hundred kilometers downwind the next day.

Atmospheric chemical processes and transport that occur at night can influence next day ozone and fine particulate matter formation on urban and regional scales. Studies during TexAQS II and more recently have sought to further the understanding of nighttime plume chemistry and transport and the impacts of emissions sources and controls.

Two such studies utilized nighttime flights of the NOAA WP-3D aircraft during TexAQS II to investigate nocturnal VOC oxidation by NO_3. Brown et al. (2011) conducted a regional analysis to quantify loss rates and budgets for both NO_3 and highly reactive VOC downwind of Houston industrial, urban, and rural areas. Net NO_3 radical productions rates were large (1–2 ppbv h−1) within NO_x-containing plumes of industrial origin, but generally smaller in rural plumes and plumes that originated from urban Houston and were transported downwind. NO_3 was lost primarily to reaction with VOCs, with the sum of anthropogenic VOCs (30–54%) and isoprene (10–50%) as the largest contribution; alkenes, and to a lesser extent, aromatics, were the most significant anthropogenic VOC contribution. NO_3 was 3 to 5 times more important than O_3 as a nighttime oxidant of VOCs for the flights in the Houston area. Yarwood et al. (2012b) analyzed nighttime vertical profiles during missed approaches, takeoffs and landings at airfields in and around the Houston urban area. Nocturnal boundary layer depths varied between 100 – 400 m, with overlying residual layer depths of 0.8 – 1.5 km. Ozone was never titrated to zero by surface level NO_x emissions during these aircraft measurements, and nighttime oxidative and heterogeneous chemistry was active. Findings regarding nocturnal VOC oxidation and nitrate radical production were consistent with those reported by Brown et al. (2011). Both studies found nighttime NO_x loss through N_2O_5 heterogeneous uptake to be modest, but subject to uncertainty due to the uptake coefficient for N_2O_5. In previous analyses of the P-3 flights, Brown et al. (2009) determined reactive uptake coefficients for N_2O_5, $\gamma(N_2O_5)$, were generally in the range $0.5–6 \times 10^{-3}$ and were substantially smaller than current parameterizations used for atmospheric modeling; N_2O_5 uptake represented a significant, but not dominant, fraction of the NO_3 loss budget (Brown et al., 2011). Brown et al. (2011) found that loss of NO_3 to nighttime reactions with peroxy radicals was small, but also subject to uncertainty due to the lack of peroxy radical measurements.

Zaveri et al. (2010) examined the transport and chemical processing of a photochemically aged plume that contained a mixture of urban and petrochemical industrial emissions located north of Houston metropolitan area under southerly flow conditions across the state on July 26, 2005 using measurements from a Twin Otter aircraft. Enhanced levels of olefins and acetaldehyde of petrochemical industrial origin were observed in this plume at sunset and 8 hours later. A constrained plume modeling analysis indicated that small amounts of NO_x (<1 ppbv) were present in the photochemically aged plume at sunset and were converted to nitric acid, organic nitrates, and peroxy acyl nitrates via reactions of NO_3 radicals with olefins and aldehydes and subsequent radical chemistry at night. Predicted NO_3 and N_2O_5 mixing ratios were small, indicating fast loss of NO_3 due to its reactions with VOCs. The N_2O_5 heterogeneous uptake coefficient was likely on the order of 0.001 for Houston urban/industrial aerosol, but direct measurements of NO_3, N_2O_5, and HNO_3 were not made.

In addition to plumes that originate from urban and industrial areas, plumes from coal-fired power plants, which are frequently located in relatively rural areas, are also subject to nocturnal transport and chemical processing that may affect air quality downwind. Federal regulations, such as the recent Cross-State Air Pollution Rule (CSAPR), have aimed to reduce emissions of NO_x and SO_2 from power plants that contribute to ozone and fine particulate matter formation. Recently, Yarwood et al (2012b) analyzed the nighttime NOAA WP-3D aircraft intercepts, described above, of the plumes from two different Texas power plants, Oklaunion near Wichita Falls and W. A. Parish near Houston. The plants have different NO_x emissions due to their control technologies. In 2006, the Oklaunion plant had low NO_x burner technology, but not selective catalytic reduction (SCR). In contrast, the W. A. Parish plant coal-fired units had both technologies, resulting in lower NO_x emissions. Yarwood et al. (2012b) found that these differences in NO_x emissions led to differences in the titration of ambient ozone. The plume from Oklaunion had full titration of ozone through 74 km/2.4 hours of downwind transport that suppressed nighttime oxidation of NO_2 to higher oxides of nitrogen across the majority of the plume. The plume from W.A. Parrish did not have sufficient NO_x to titrate background ozone, which led to rapid nighttime oxidation of NO_2 during downwind transport. Empirical plume modeling suggested that NO_x controls may not only reduce emissions directly, but may also lead to an additional overnight NO_x loss of up to 73% for the sample conditions. Ambient ozone concentrations coincident with the Parrish plume, on the night that the measurements were collected were relatively high, which likely added to the production of NO_3 and the additional overnight NO_x loss. The results implied that power plant NOx emissions controls may have larger than expected impacts on next-day downwind ozone production following nighttime transport.

The findings from the study of Yarwood et al. (2012b) resulted in improvements to the Plume-in-Grid (PiG) formulation in CAMx Version 5.40, released in October 2011. These modifications will likely improve, although not completely, replicate the measured nighttime plume spread, which was minimal. PiG puff growth rates were modified to ignore growth contributions from horizontal and vertical shear during stable/nighttime conditions. Shear effects remain during neutral/unstable/daytime conditions. Minimum limits on vertical diffusivity, turbulent flux moments, and nighttime planetary boundary layer (PBL) depths were reduced. With these improvements, PiG puff behavior will change potentially significantly at night and above the boundary layer, usually leading to longer lifetimes.

References

Acker, K., A. Febo, S. Trick, C. Perrino, P. Bruno, P. Wiesen, D. Moller, W. Wieprecht, W., R. Auel, M. Giusto, A. Geyer, U. Platt, I. Allegrini, Nitrous acid in the urban area of Rome, Atmospheric Environment, 40 (2006a), 3123–3133, doi:10.1016/j.atmosenv.2006.01.028.

Acker, K., D. Moller, W. Wieprecht, F. Meixner, B. Bohn, S. Gilge, C. Plass-Dulmer, H. Berresheim, Strong daytime production of OH from HNO2 at a rural mountain site, Geophysical Research Letters 33 (2006b), L02809, doi:10.1029/2005GL024643.

Allen, D. T. State of the Science of Air Quality in Eastern Texas: Major Scientific Findings and Recommendations, files.harc.edu/Projects/AirQuality/Projects/H030.2004/H30FinalReport.pdf, 2004.

Allen D., Gulf Coast Aerosol Research and Characterization Program (Houston Supersite). Center for Energy and Environmental Resources, The University of Texas at Austin, Cooperative Agreement Number R-82806201 between the Environmental Protection Agency and The University of Texas at Austin, April 2005.

Bahreini, R. B. Ervens, A.M. Middlebrook, C. Warneke, J.A. de Gouw, P.F. DeCarlo, J.L. Brioude, A. Fried, J.S. Holloway, J. Peischl, D. Richter, J. Walega, P. Weibring, A.G. Wollny, F.C. Fehsenfeld, Organic aerosol formation in urban and industrial plumes near Houston and Dallas, Texas. Journal of Geophysical Research 114 (2009), doi:10.1029/2008JD011493.

Bates, T.S., P.K. Quinn, D. Coffman, K. Schulz, D.S. Covert, J.E. Johnson, E.J. Williams, B.M. Lerner, W.M. Angevine, S.C. Tucker, W.A. Brewer, A. Stohl, Boundary layer aerosol chemistry during TexAQS/GoMACCS 2006: Insights into aerosol sources and transformation processes. Journal of Geophysical Research 113 (2008), doi:10.1029/2008JD010023.

Behnke, W., C. George, V. Scheer, C. Zetzsch, Production and decay of ClNO2 from the reaction of gaseous N2O5 and NaCl solution: Bulk and aerosol experiments. Journal of Geophysical Research 102 (1997), doi:1029/96JD03057.

Bejan, I., Y.A.E. Aal, I. Barnes, T. Benter, B. Bohn, P. Wiesen, J. Kleffmann, The photolysis of ortho-nitrophenols: A new gas phase source of HONO. Physical Chemistry Chemical Physics 17 (2006), doi:10.1039/B516590C.

Berkowitz, C.M., C.W. Spicer, P.V. Doskey, Hydrocarbon observations and ozone production rates in western Houston during the Texas 2000 Air Quality Study. Atmospheric Environment 39 (2004), doi:j.atmosenv.2004.12.007.

Brown, S.S., W.P. Dube, H. Fuchs, T.B. Ryerson, A.G. Wollny, C.A. Brock, R. Bahreini, A.M. Middlebrook, J.A. Neuman, E. Atlas, J.M. Roberts, H.D. Osthoff, M. Trainer, F.C. Fehsenfeld, A.R. Ravishankara, Reactive uptake coefficients for N2O5 determined from aircraft measurements during the Second Texas Air Quality Study: Comparison to current model parameterizations. Journal of Geophysical Research 114 (2009), doi:10.1029/2008JD011679.

Brown S.S., W.P. Dube, J. Peischl, T.B. Ryerson, E. Atlas, C. Warneke, J.A. de Gouw, S. te Lintel Hekkert, C.A. Brock, F. Flocke, M. Trainer, D.D. Parrish, F.C. Feshenfeld, A.R. Ravishankara, Budgets for nocturnal VOC oxidation by nitrate radicals aloft during the 2006 Texas Air Quality Study. Journal of Geophysical Research 116 (2011), doi:10.1029/2011JD016544.

Carter, W.P.L., J. H. Seinfeld, Winter ozone formation and VOC incremental reactivities in the Upper Green River Basin of Wyoming. Atmospheric Environment 50 (2012), doi:10.1016/j.atmosenv.2011.12.025.

Chen, S., X. Ren, J. Mao, Z. Chen, W.H. Brune, B. Lefer, B. Rappenglück, J. Flynn, J. Olson, J.H. Crawford, A comparison of chemical mechanisms based on TRAMP-2006 field data, Atmospheric Environment (2009), doi: 10.1016/j.atmosenv.2009.05.027

Cowling, E.B., C. Furiness, B. Dimitriades, D. Parrish, M. Estes, et al., Final rapid science synthesis report: 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, TCEQ Contract Number 582-4-65614, 2007.

Czader, B., Rappenglück, B., Byun, D.W., Kim, S., Ngan, F.: Simulations of nitrous acid for the Houston metropolitan area and comparison with data from the Texas Air Quality Study 2006. International Conference on Atmospheric Chemical Mechanisms, 8-10 December 2010, Davis, California.

Daum, P.H., L.I. Kleinman, S.R. Springston, L.J. Nunnermacker, Y.-N. Lee, J. Weinstein-Lloyd, J. Zheng, C.M. Berkowitz, A comparative study of O_3 formation in the Houston urban and industrial plumes during the 2000 Texas Air Quality Study. Journal of Geophysical Research 108 (2003), doi:10.1029/2003JD003552.

de Gouw, J.A., C.A. Brock, E.L. Atlas, T.S. Bates, F.C. Fehsenfeld, P.D. Goldan, J.S. Holloway, W.C. Kuster, B.M. Lerner, B.M. Matthew, A.M. Middlebrook, T.B. Onasch, R.E. Peltier, P.K. Quinn, C.J. Senff, A. Stohl, A.P. Sullivan, M. Trainer, C. Warneke, R.J. Weber, E.J. Williams, Sources of particulate matter in the northeastern United States in summer: 1. Direct emissions and secondary formation of organic matter in urban plumes. Journal of Geophysical Research 113 (2008), doi:10.1029/2007JD009243.

Eom, I-Y., Q. Li, J. Li, P.K. Dasgupta, Robust hybrid flow analyzer for formaldehyde. Environmental Science & Technology 42 (2008), doi:10.1021/es071472h.

Feldman, M.S., T. Howard, E. McDonald-Buller, G. Mullins, D.T. Allen, A. Hansel, A. Wisthaler, Applications of satellite remote sensing data for estimating biogenic emissions in southeastern Texas. Atmospheric Environment 44 (2010), doi:10.1016/j.atmosenv.2009.11.048.

Finlayson-Pitts, B.J., M.J. Ezell, J.N. Pitts Jr., Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and $ClONO_2$. Nature 337 (1989), doi:10.1038/337241a0.

Finlayson-Pitts, B., L. Wingen, A. Sumner, D. Syomin, K. Ramazan. The heterogeneous hydrolysis of NO_2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism, Physical Chemistry Chemical Physics, 5 (2003), 223–242, doi:10.1039/b208564j.

Gilman, J.B., W.C. Kuster, P.D. Goldan, S.C. Herndon, M.S. Zahniser, S.C. Tucker, W. A. Brewer, B.M. Lerner, E.J. Williams, R.A. Harley, F.C. Fehsenfeld, C. Warneke, J.A. de Gouw, Measurements of volatile organic compounds during the 2006 TexAQS/GoMACCS campaign: Industrial influences, regional characteristics, and diurnal dependencies of the OH reactivity. Journal of Geophysical Research 114 (2009), doi:10.1029/2008JD011525.

Kercher, J.P., T.P. Riedel, J.A. Thornton, Chlorine activation by N_2O_5: Simultaneous, in situ detection of ClNO2 and N2O5 by chemical ionization mass spectrometry. Atmospheric Measurement Techniques 2 (2009).

Kleinman, L.I., P.H. Daum, Y.-N. Lee, L.J. Nunnermacker, S.R. Springston, J. Weinstein-Lloyd, F. Rudolph, A comparative study of ozone production in five U.S. metropolitan areas. Journal of Geophysical Research 110 (2005), doi:10.1029/2004JD005096.

Knipping, E.M., D. Dabdub, Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone. Environmental Science & Technology 37 (2003), doi:1021/es025793z.

Koo, B., G. Yarwood, An assessment of nitryl chloride formation chemistry and its importance in ozone non-attainment areas in Texas. TCEQ Grant No. 582-10-94300, January 2012.

Lefer, B., B. Rappenglück, The TexAQS-II radical and aerosol measurement project (TRAMP). Atmospheric Environment 44 (2010a), doi:10.1016/j.atmosenv.2010.03.011.

Lefer, B.L., W.H. Brune, D.R. Collins, J.E. Dibb, R.J. Griffin, S.C. Herndon, L.G. Huey, B.T. Jobson, W.T. Luke, J. Mellqvist, G.A. Morris, G.H. Mount, S.W. North, E.P. Olaguer, B. Rappenglück, X. Ren, J. Stutz, X. Yu, R. Zhang, Overview and Major Findings of the Study of Houston Atmospheric Radical Precursors (SHARP) Campaign. American Geophysical Union, Fall Meeting 2010b, abstract #A34C-05.

Lefer, B., J. Stutz, X. Ren, W. Brune, J. Dibb, Study of Houston Atmospheric Radical Precursors (SHARP) data analysis. Air Quality Research Program, TCEQ Grant No. 582-10-94300, November 2011.

Li, G., R. Zhang, J. Fan, X. Tie, Impacts of biogenic emissions on photochemical ozone production in Houston, Texas. Journal of Geophysical Research 112 (2007), doi:10.1029/2006JD007924.

Mao, J., X. Ren, S. Chen, W.H. Brune, Z. Chen, M. Martinez, H. Harder, B. Lefer, B., Rappenglück, J. Flynn, M. Leuchner, Atmospheric Oxidation Capacity in the Summer of Houston 2006: Comparison with Summer Measurements in Other Metropolitan Studies, Atmospheric Environment (2009), doi: 10.1016/j.atmosenv.2009.01.013

Neuman, J.A., J.B. Nowak, W. Zheng, F. Flocke, T.B. Ryerson, M. Trainer, J.S. Holloway, D.D. Parrish, G.J. Frost, J. Peischl, E.L. Atlas, R. Bahreini, A.G. Wollny, F.C. Fehsenfeld, Relationship between photochemical ozone production and NO_x oxidation in Houston, Texas. Journal of Geophysical Research 114, (2009), doi:10.1029/2008JD01688.

Olaguer, E.P., B. Rappenglück, B. Lefer, J. Stutz, J. Dibb, R. Griffin, W.H. Brune, M. Shauck, M. Buhr, H. Jeffries, W. Vizuete, J.P. Pinto, Deciphering the role of radical precursors during the Second Texas Air Quality Study, Journal of the Air &Waste Management Association 59 (2009a), doi:10.3155/1047-3289.59.11.1258.

Olaguer, E.P., D. Byun, B. Lefer, B. Rappenglück, J. Nielsen-Gammon, H. Jeffries, W. Vizuete, N. Gillani, E. Snyder, J. de Gouw, J. Melqvist, E. McDonald-Buller, D. Sullivan, C. Berkowitz, R. McNider, G. Morris, The 2009 TERC Science Synthesis. Texas Environmental Research Consortium (TERC), Houston Advanced Research Consortium (HARC), Project H-108, 2009b.

Olaguer, E.P., Beyond SHARP-- Primary Formaldehyde from Oil and Gas Exploration and Production in the Gulf of Mexico Region, American Geophysical Union, Fall Meeting 2010, abstract #A31B-0042, 2010.

Osthoff, H.D., J.M. Roberts, A.R. Ravishankara, E.J. Williams, B.M. Lerner, R. Sommariva, T.S. Bates' D. Coffman, P.K. Quinn, J.E. Dibb, H. Stark, J.B. Burkholder, R.K. Talukdar, J. Meagher, F.C. Fehsenfeld, S.S. Brown, High levels of nitryl chloride in the polluted subtropical marine boundary layer. Nature Geoscience 1 (2008), doi:10.1038/ngeo177.

Parrish, D.D., D.T. Allen, T.X. Bates, M. Estes, F.C. Fehsenfeld, G. Feingold, R. Ferrare, R.M. Hardesty, J.F. Meagher, J.W. Nielsen-Gammon, R.B. Pierce, T.B. Ryerson, J.H. Seinfeld, E.J. Williams, Overview of the Second Texas Air Quality Study (TexAQS II) and the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS). Journal of Geophysical Research 114 (2009), doi:10.1029/2009JD011842.

Parrish, D.D., T.B. Ryerson, J. Mellqvist, J. Johansson, A. Fried, D. Richter, J.G. Walega, R.A. Washenfelder, J.A. de Gouw, J. Peischl, K.C. Aikin, S.A. McKeen, G.J. Frost, F.C. Fehsenfeld, S.C. Herndon, Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region. Atmospheric Chemistry and Physics 12 (2012), doi:10.5194/acp-12-3273-2012.

Popescu, S., Expansion of Texas Land Use/Land Cover through Class Crosswalking and LiDAR Parameterization of Arboreal Vegetation, http://www.tceq.texas.gov/airquality/airmod/project/pj_report_ei.html, 2010.

Ryerson, T.B., M. Trainer, W.M. Angevine, C.A. Brock, R.W. Dissly, F. C. Fehsenfeld, G.J. Frost, P.D. Goldan, J.S. Holloway, G. Hubler, R.O. Jakoubek, W.C. Kuster, J.A. Neuman, D.K. Nicks, Jr., D.D. Parrish, J.M. Roberts, D.T. Sueper, Effect of petrochemical industrial emissions of reactive alkenes and NOx on tropospheric ozone formation in Houston, Texas. Journal of Geophysical Research 108 (2003), doi:10.1029/2002JD003070.

Seinfeld J.H., S.N. Pandis, Atmospheric chemistry and physics: From air pollution to climate change, 1st edition, J. Wiley, New York, 1998.

Simon. H. Y. Kimura, G. McGaughey, D.T. Allen, S.S. Brown, H.D. Osthoff, J.M. Roberts, D. Byun, D. Lee, Modeling the impact of CINO2 on ozone formation in the Houston area. Journal of Geophysical Research 114 (2009), doi:10.1029/2008JD010732.

Sommariva, R., S.S. Brown, J.M. Roberts, D.M. Brookes, A.E. Parker, P.S. Monks, T.S. Bates, D. Bon, J.A. de Gouw, G.J. Frost, J.B. Gilman, P.D. Goldan, S.C. Herndon, W.C. Kuster, B.M. Lerner, H.D. Osthoff, S.C. Tucker, C. Warneke, E.J. Williams, M.S. Zahniser, Ozone production in remote oceanic and industrial areas derived from ship based measurements of peroxy radicals during TexAQS 2006. Atmospheric Chemistry and Physics 11 (2011), doi:10.5194/acp-11-2471-2011.

Song, J. W. Vizuete, S. Chang, D. Allen, Y. Kimura, S. Kemball-Cook, G. Yarwood, M-A. Kioumourtzoglou, E. Atlas, A. Hansel, A. Wisthaler, E. McDonald-Buller, Comparisons of modeled and observed isoprene concentrations in southeast Texas. Atmospheric Environment 42 (2008), doi:10.1016/j.atmosenv.2007.11.016.

Stemmler, K. M. Ammann, C. Donders, J. Kleffmann, C. George, Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid. Nature 440 (2006), doi:10.1038/nature04603.

Stutz, J. O. Pikelnaya, G. Mount, E. Spinei, S. Herndon, E. Wood, O. Oluwole, W. Vizuette, E. Causo, Quantification of hydrocarbon NOx and SO2 emissions from petrochemical facilities in Houston: Interpretation of the 2009 FLAIR dataset, Quality Research Program, TCEQ Grant No. 582-10-94300, November 2011.

Tanaka, P.L., D.D. Riemer, S. Chang, G. Yarwood, E.C. McDonald-Buller, E.C. Apel, J.J. Orlando, P.J. Silva, J.L. Jimenez, M.R. Canagaratna, J.D. Neece, C.B. Mullins, D.T. Allen, Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas. Atmospheric Environment 37 (2003), doi:10.1016/S1352-2310(02)01007-5.

Thornton, J.A., J.P. Kercher, T.P. Riedel, N.L. Wagner, J. Cozic, J.S. Holloway, W.P. Dube, G.M. Wolfe, P.K., Quinn, A.M. Middlebrook, B. Alexander, S.S. Brown, A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. Nature 464 (2010), doi10.1038/nature08905.

Wameke, C., J.A. de Gouw, L.Del Negro, J. Brioude, S. McKeen, H. Stark, W.C. Kuster, P.D. Goldan, M. Trainer, F.C. Fehsenfeld, C. Wiedinmyer, A.B. Guenther, A. Hansel, A. Wisthaler, E. Atlas, J.S. Holloway, T.B. Ryerson, J. Peischl, L.G. Huey, A.T.C. Hanks, Biogenic emission measurement and inventories determination of biogenic emissions in the eastern United States and Texas and comparison with biogenic emission inventories. Journal of Geophysical Research 115 (2010), doi:10.1029/2009JD012445.

Wiedinmyer, C., A. Guenther, M. Estes, I.W. Strange, G. Yarwood, D.T. Allen, A land use database and examples of biogenic isoprene emission estimates for the state of Texas, USA. Atmospheric Environment 35 (2001), doi:10.1016/S1352-2310(01)00429-0.

Wong, K., Oh, H.-J., Lefer, B., Rappenglück, B., and Stutz, J.: Vertical profiles of nitrous acid in the nocturnal urban atmosphere of Houston, TX, Atmospheric Chemistry and Physics, 11, (2011), 3595–3609, doi:10.5194/acp-11-3595-2011.

Wong, K.W., C. Tsai, B. Lefer, C. Haman, N. Grossberg, W.H. Brune, X. Ren, W. Luke, J. Stutz, Daytime HONO vertical gradients during SHARP 2009 in Houston, TX. Atmospheric Chemistry and Physics 12 (2012), doi:10.5194/acp-12-635-2012.

Yarwood, G., G. Heo, W.P.L. Carter, G.Z. Whitten, Environmental chamber experiments to evaluate NOx sinks and recycling in atmospheric chemical mechanisms. Air Quality Research Program, TCEQ Grant No. 582-10-94300, February 17, 2012a.

Yarwood, G., P. Karamchandani, C. Emery, S-Y. Chen, S.S. Brown, D.D. Parrish, NOx reactions and transport in nighttime plumes and impact on next-day ozone. Air Quality Research Program, TCEQ Grant No. 582-10-94300, January 31, 2012b.

Yu, X-Y., J. Cowin, N. Laulainen, M. Iedema, B. Lefer, D. Anderson, D. Pernia, J. Flynn Radical initiated secondary aerosol formation (RISAF) – Particle measurements during SHARP. Houston Advanced Research Consortium (HARC), Project H-105, 2009.

Zaveri, R.A., P.B. Voss, C.M. Berkowitz, E. Fortner, J. Zheng, R. Xhang, R.J. Valente, R.L. Tanner, D. Holcomb, T.P. Hartley, L. Baran, Overnight atmospheric transport and chemical processing of photochemically aged Houston urban and petrochemical industrial plume, Journal of Geophysical Research 115 (2010), doi:10.1029/2009JD013495.

Zhang, R., J. Zheng, A. Zhalizov, S. North, D. Collins, Surface-induced Oxidation of Organics in the Troposphere (SOOT). Houston Advanced Research Center (HARC), H-101, November 20, 2009.

Zhou, X., G. Huang, K. Civerolo, U. Roychowdhury, K. Demerjian, Summertime observations of HONO, HCHO, and O3 at the summit of Whiteface Mountain, New York, Journal of Geophysical Research.-Atmospheres. 112 (2007), D08311, doi:10.1029/2006JD007256.

Zhou, X., N. Zhang, M. TerAvest, D. Tang, J. Hou, S. Bertman, M. Alaghmand, P. Shepson,, M. Carroll, S. Griffith, S. Dusanter, P. Stevens, Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, Nature Geoscience, 4 440–443, doi:10.1038/NGEO1164, 2011.

Ziemba, L.D., J.E. Dibb, R.J. Griffin, C.H. Anderson, S.I. Whitlow, B.L. Lefer, B. Rappenglück, J. Flynn, Heterogeneous conversion of nitric acid to nitrous acid on the surface of primary organic aerosol in an urban atmosphere. Atmospheric Environment 44 (2010), doi:10.1016/j.atmosenv.2008.12.024.

2.4 Meteorology

1. Regionally high ozone episodes in Texas most commonly occur during synoptic (i.e., large-scale) weather patterns that are consistent with the long-range transport of elevated background concentrations of ozone and/or its precursors into Texas.

Nielsen-Gammon (2005) showed that background ozone concentrations have a strong seasonality with peaks during the spring and late summer/early fall. This strong seasonality is associated with the frequency of occurrence, strength, and location of anticyclones that impact Texas weather. Cluster analyses of synoptic weather conditions showed that a center or ridge of high pressure in the lower troposphere is commonly located to the west or north of Houston during high ozone episodes (Rappenglück et al. (2008); Ngan and Byun (2011)). These weather patterns are associated with long-range northerly or easterly transport of continental air, which is often characterized by elevated ozone and/or its precursors, into Texas (e.g., Olaguer et al., 2009; McGaughey et al., 2010). These large-scale high pressure systems are sometimes associated with fair weather and light wind speeds that enhance the amount of locally-formed ozone as well. High ozone days during September most often occur in a postfrontal environment (Tobin and Nielsen-Gammon, 2010), which can increase background ozone in Houston from 30 ppbv to 60-70 ppbv (Rappenglück et al. (2008)). Ozone contributions associated with regional as well as local (e.g., sea breeze, nocturnal low-level jets, urban) circulation features must be correctly simulated in air quality models to accurately predict the magnitude and spatial extent of high ozone concentrations (Olaguer et al., 2009).

2. Mesoscale (i.e., local-scale) atmospheric circulation features play an important role during high ozone episodes in Texas.

The evolution and development of the sea breeze plays a dominant role in high ozone episodes along the Texas coast. Based on findings from TexAQS I, the worst ozone exceedances in HGB were associated with local stagnation associated with reversals of the wind direction along the sea-breeze front (Nielsen-Gammon et al., 2005; Banta et al., 2005; Darby, 2005). Analysis of TexAQS II data found the sea breeze reversal combines with the larger-scale circulation to form a wind pattern known as the coastal oscillation (Olaguer et al., 2009) and the interaction of the mesoscale sea-breeze circulation and synoptic-scale flows determine where ozone and its precursors are accumulated or diluted. A second complex coastal circulation is the nocturnal sea-breeze low level jet, which typically forms a few hundred meters above the surface. Ship-based Doppler measurements during TexAQS II found that strong jets were associated with low ozone concentrations the following afternoon in Houston while weaker jets during periods of northerly or easterly large-scale flow were associated with higher next-day ozone concentrations (Tucker et al., 2010). Observations at an instrumented tower in Moody, Texas found evidence of inland nighttime jets that only occasionally brought high ozone concentrations into the area during the summer but were associated with high ozone pulses more frequently during other seasons (Andrews et al., 2010; Oltmans et al., 2010). A third important local circulation feature associated with high ozone concentrations in Texas are stagnation zones along stationary fronts. Data collected in the vicinity of DFW during TexAQS I/II found that local pollution accumulated in zones of light winds and subsidence along the frontal trough (McNider, et al., 2009). The local circulation features in these “dead zones” may also be associated with re-entrainment of aged pollution aloft that may have originated from distant sources (Olaguer et al., 2009).

3. The evolution and development of the nighttime and daytime planetary boundary layer (PBL) influences the diurnal variability in surface ozone concentrations.

The PBL height effectively establishes a cap to near-surface vertical atmospheric mixing and defines the volume of air into which emissions from surface sources are well-mixed compared to the overlying free troposphere. A number of studies have demonstrated that afternoon mixing heights on high ozone days in Texas tend to be relatively high (Cowling et al., 2007; Rappenglück et al., 2008; Nielsen-Gammon, 2008) suggesting that the impact of concurrent meteorological conditions (such as light wind speeds) offset the diluting effect of increased near-surface dilution volume. In addition, the afternoon vertical growth of the PBL may mix to the surface relatively high concentrations of ozone and/or its precursor compounds aloft that were transported into Texas from other continental areas (Olaguer et al., 2009; Schade et al., 2011). Although rapid growth of the morning PBL causes dilution of freshly-emitted precursors and also alters chemical pathways (Olaguer et al., 2009), near-surface pollutants from the previous day trapped above the nocturnal boundary layer have been shown to explain 60-70% of the variability in afternoon mixed layer ozone concentrations (Morris, et al., 2010). The PBL in coastal areas is especially spatially and temporally complex, impacted by differences associated with both land and marine environments (e.g., Banta et al., 2005; Darby, 2005). Emissions that flow offshore into the shallow near-surface layer can result in very high ozone concentrations that return inland with little initial dilution (Banta et al., 2005).

4. Observations and results from TexAQS I/II have guided modeling and sensitivity studies designed to improve the performance of meteorological modeling applications in Texas.

The accurate simulation of the temporal and spatial evolution of important atmospheric features such as the boundary layer and sea breeze circulations require that vertical mixing and land surface processes be properly represented in meteorological models. Numerous studies have evaluated treatments of vertical diffusion and convective mixing in support of Texas air quality modeling applications in recent years (Emery et al., 2009; Hu et al., 2010a; ENVIRON, 2011) and have indicated that model performance is sensitive to the choice of PBL scheme. One of the most successful efforts to reduce uncertainties in the simulation of daytime lower-tropospheric winds and PBL heights is the assimilation of radar wind profiler data (e.g., Nielsen-Gammon et al., 2007; Zhang et al., 2007; Stuart et al., 2007) that remains essential for good meteorological modeling performance (TCEQ, 2011). Using a TexAQS II episode and a technique known as the Ensemble Kalman Filter, better agreement was obtained between observations and predictions of near-surface temperatures and wind profiles suggesting that additional experiments were warranted (Hu et al., 2010b).

Land-surface modeling (LSM), which fully simulates the energy exchange between the land/water surface and atmosphere, presents challenges in Texas areas. Studies by Misenis and Zhang (2010) using WRF/Chem found that meteorological predictions showed stronger sensitivity to the choice of LSM than to PBL schemes. Results also indicated that using more physically-complex model configurations (such as 2-way nesting or reduced horizontal grid spacing) did not necessarily provide more accurate results. Cheng et al. (2008) modified the LSM and PBL schemes in MM5 to utilize the Texas Forest Service land use and land cover dataset. Improvements in boundary layer mixing conditions and local wind patterns in the Houston Ship Channel demonstrated the importance of high resolution observational datasets to model performance. Using a single-layer urban canopy model (UCM), Lee et al. (2011) found that more realistic prediction of sensible and latent heat fluxes was associated with improved replication of diurnal profiles of temperature and PBL height over the Houston area. Although wind field performance was not substantially different between UCM, LSM, and modified LSM simulations, the results suggested that more accurate representation of the surface and explicit parameterization of physical processes is necessary for improvements in atmospheric modeling over urban areas.

5. The greatest differences in observed and predicted ozone concentrations in SIP modeling tend to occur when clouds are under-predicted (TCEQ DFW SIP, 2011).

Photochemistry is strongly influenced by clouds, which can both attenuate and enhance the actinic flux of ultraviolet (UV) radiation (e.g., Emery et al., 2010). Accurate simulation of cloud cover is necessary to simulate photolysis rates, and ozone predictions are very sensitive to photolysis rates (Byun et al., 2007; TCEQ, 2011). In addition, clouds impact the rate and depth of vertical mixing in the lower troposphere (e.g., Langford et al., 2010) as well as the chemical composition of the atmosphere (e.g., Flynn et al., 2010). The vertical depth and spatial/temporal distribution of clouds are some of the most difficult meteorological phenomena to accurately simulate (Pour-Biazar et al., 2007; Emery et al., 2010). Spurious thunderstorms and clouds are also common in air quality modeling (Olaguer et al., 2009), suggesting the need for flexibility in the selection of modeling parameterizations (TCEQ, 2011).

Pour-Biazar et al. (2007) used GOES satellite data to correct the photolysis rates in CMAQ for a TexAQS I episode. The results demonstrated that clouds increased the lifetime of ozone precursors leading to increased ozone production and improvements in model performance. A study by ENVIRON (2010) found that surface ozone predictions in CAMx were more responsive to the placement of sub-grid clouds than how photolysis rates were applied (TCEQ, 2011). Efforts by Pour-Biazar et al. (2011) to develop a GOES cloud assimilation technique in WRF relied on adjustments to the modeled vertical velocities to force better agreement between predicted and satellite-observed cloudiness. Although the study showed improvements of 7-10% in cloud prediction, additional work is needed.

References

Andrews, A., S. Oltmans, L. Patrick, Evaluating the low-level jet and ozone transport in central Texas: Phase 2 – influence of other constituents on ozone. Prepared for the Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-08-86246-FY10-08, 2010.

Banta, R.M., C.J. Senff, J. Nielsen-Gammon, L.S. Darby, T.B. Ryerson, R.J. Alvarez, S.P. Sandberg, E.J. Williams, M. Trainer. A bad air day in Houston. Bulletin of the American Meteorological Society 86 (2005), 10.1175/BAMS-86-5-657.

Byun, D.W., S.-T. Kim, S-B Kim, Evaluation of air quality models for the simulation of a high ozone episode in the Houston metropolitan area. Atmospheric Environment 41 (2007), doi:10.1016/j.atmosenv.2006.08.038.

Cheng, F.Y., D. W. Byun, Application of high resolution land use and land cover data for atmospheric modeling in the Houston-Galveston metropolitan area, part I: Meteorological simulation results. Atmospheric Environment 42 (2008), doi:10.1016/j.atmosenv.2008.02.059.

Cowling, E.B., C. Furiness, B. Dimitriades, D. Parrish, M. Estes, et al., Final rapid science synthesis report: 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, TCEQ Contract Number 582-4-65614, 2007.

Darby, L.S., Cluster analysis of surface winds in Houston, Texas, and the impact of wind patterns on ozone. Journal of Applied Meteorology and Climatology 44 (2005), doi:10.1175/JAM2320.1.

Emery,C., J. Johnson, P. Piyachaturawat, G. Yarwood, MM5 meteorological modeling of Texas for June 2006. Prepared for the Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-07-83986-FY08-02, 2009.

Emery, C., J. Jung, J. Johnson, G. Yarwood, Improving cloud impacts on photolysis using an on-line radiation model in CAMx. The 9th Annual CAMS Conference, Chapel Hill, NC, October 2010.

ENVIRON, Improving the characterization of clouds and their impact on photolysis rates within the CAMx photochemical grid model, Final report to the Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-07-84005-FY09, 2009.

ENVIRON, Dallas-Fort Worth modeling support: Improving the representation of vertical mixing processes in CAMx. Prepared for Doug Boyer, Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-11-10365-FY11-02, 2011.

Flynn, J., B. Lefer, B. Rappenglück, M. Leuchner, R. Perna, J. Dibb, L. Ziemba, C. Anderson, J. Stutz, W. Brune, X. Ren, J. Mao, W. Luke, J. Olson, G. Chen, J. Crawford, Impact of clouds and aerosols on ozone production in Southeast Texas. Atmospheric Environment 44 (2010), doi:10.106/j.atmosenv.2009.09.005.

Hu. X-M., J.W. Nielsen-Gammon, F. Zhang, Evaluation of three planetary boundary layer schemes in the WRF model. Journal of Applied Meteorology and Climatology 49 (2010a), doi:10.1175/2010JAMC2432.1

Hu. X-M., F. Zhang, J.W. Nielsen-Gammon, Ensemble-based simultaneous state and parameter estimation for treatment of mesoscale model error: A real-data study. Geophysical Research Letters 38 (2010b), doi:10.1029/2010GL043017.

Langford, A.O., S.C. Tucker, C.J. Senff, R.M. Banta, W.A. Brewer, R.J. Alvarez II, R.M. Hardesty, B.M. Lerner, E.J. Williams, Convective venting and surface ozone in Houston during TexAQS 2006. Journal of Geophysical Research 115 (2010), doi:10.1029/2009JD013301.

Lee, S.-H., S.-W. Kim, W.M. Angevine, L. Bianco, S.A. McKeen, C.J. Senff, M. Trainer, S.C. Tucker, R.J. Zamora, Evaluation of urban surface parameterizations in the WRF model using measurements during the Texas Air Quality Study 2006 field campaign, Atmospheric Chemistry and Physics 11 (2011), doi:10.5194/acp-11-2127-2011.

McGaughey, G., C. Durrenberger, D.T. Allen, E.C. McDonald-Buller, Conceptual model for ozone for the Austin area. Prepared for Capital Area Council of Governments (CAPCOG) and Texas Commission on Environmental Quality (TCEQ) by The University of Texas at Austin, 2010.

McNider, R., A Pour-Biazar, M. Shauck, S. Alvarez, M. Buhr, Stationary front experiment comparison of flight and model data. Houston Advanced Research Consortium (HARC), Project H-109, 2009.

Misensis, C., Y. Zhang, An examination of sensitivity of WRF/Chem predictions to physical parameterizations, horizontal grid spacing, and nesting options. Atmospheric Research 97 (2010), doi:10.1016/j.atmosres.2010.04.005.

Morris, G. A., B. Ford, B. Rappenglück, A.M. Thompson, A. Mefferd, F. Ngan, B. Lefer, An evaluation of the interaction of morning residual layer and afternoon mixed layer ozone in Houston using ozonesonde data. Atmospheric Environment 44 (2010) doi:10.1016/j.atmosenv.2009.06.057.

Ngan, F., D. Byun, Classification of weather patterns and associated trajectories of high-ozone episodes in the Houston-Galveston-Brazoria area during the 2005/06 TexAQS-II. Journal of Applied Meteorology and Climatology 50 (2011), 485-499.

Nielsen-Gammon, J.W., J. Tobin, A. McNeel, G. Li, A conceptual model for eight-hour ozone exceedances in Houston, Texas Part I: Background ozone levels in eastern Texas. Houston Advanced Research Consortium (HARC), Project H-12, 2005.

Nielsen-Gammon, J.W., J. Tobin, A. McNeel, A conceptual model for eight-hour ozone exceedances in Houston, Texas Part II: Eight-hour ozone exceedances in the Houston-Galveston metropolitan areas. Houston Advanced Research Consortium (HARC), Project H-12, 2005.

Nielsen-Gammon, J.W., R.T. McNider, W.M. Angevine, A.B. White, K. Knupp, Mesoscale model performance with assimilation of wind profiler data: Sensitivity to assimilation parameters and network configuration, Journal of Geophysical Research-Atmospheres 112 (2007), doi:10.1029/2006jd007633.

Nielsen-Gammon, J.W., Analysis of TexAQS II meteorological data. Prepared for the Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-5-64593-FY07-20, 2008.

Olaguer, E.P., D. Byun, B. Lefer, B. Rappenglück, J. Nielsen-Gammon, H. Jeffries, W. Vizuete, N. Gillani, E. Snyder, J. de Gouw, J. Melqvist, E. McDonald-Buller, D. Sullivan, C. Berkowitz, R. McNider, G. Morris, The 2009 TERC science synthesis. Texas Environmental Research Consortium (TERC), Houston Advanced Research Consortium (HARC), Project H-108, 2009.

Oltmans, S., A. Andrews, L. Patrick, Influence of transport by the nocturnal jet on ozone levels in Central Texas. Prepared for the Texas Commission on Environmental Quality (TCEQ), TCEQ Contract Number 582-08-86246-FY10-05, 2010.

Pour-Biazar, A., R.T. McNider, S.J. Roselle, R. Suggs, G. Jedlovec, D.W. Byun, S. Kim, C.J. Lin, T.C. Ho, S. Haines, B. Dornblaser, R. Cameron, Correcting photolysis rates on the basis of satellite observed clouds. Journal of Geophysical Research 112 (2007), doi:10.1029/2006JD007422.

Pour-Biazar, A., K. Doty, Y-H Park, R.T. McNider, Cloud assimilation into the Weather and Research and Forecast (WRF) model. Submitted to Thomas C. Ho, Lamar University, Prepared for Bright Dornblaser, Texas Commission on Environmental Quality (TCEQ), 2011.

Rappenglück, B., R. Perna, S. Zhong, G. A. Morris, An analysis of the vertical structure of the atmosphere and the upper-level meteorology and their impact on surface ozone levels in Houston, Texas. Journal of Geophysical Research 113 (2008), doi:10.1029/2007JD009745.

Schade, G.W., S. Khan, C. Park, I. Boedeker, Rural Southeast Texas air quality measurements during the 2006 Texas Air Quality Study. Journal of the Air & Waste Management Association 61, (2011), doi:10.1080/10473289.2001.608621.

Stuart, A.L., A.Aksoy, F. Zhang, J.W. Nielsen-Gammon, Ensemble-based data assimilation and targeted observation of a chemical tracer in a sea breeze model. Atmospheric Environment 41 (2007), doi:10.1016/j.atmosenv.2006.11.046.

TCEQ, Revisions to the State of Texas air quality implementation plan for the control of ozone air pollution, Dallas-Fort Worth eight-hour ozone nonattainment area, Project Number 2010-022-SIP-NR. Available: http://m.tceq.texas.gov/airquality/sip/dfw_revisions.html, December 7, 2011.

Tobin, J., J.W. Nielsen-Gammon, Modeling ozone as a function of meteorological conditions in the Houston non-attainment region: Identifying meaningful meteorological controls and estimating trend in meteorologically adjusted ozone. Houston Advanced Research Consortium (HARC), Project H-107, 2010.

Tucker, S.C., R.M. Banta, A.O. Langford, C.J. Senff, W.A. Brewer, E.J. Williams, B.M. Lerner, H.D. Osthoff, R.M. Hardesty, Relationships of coastal nocturnal boundary layer winds and turbulence to Houston ozone concentrations during TexAQS 2006. Journal of Geophysical Research 115 (2010), 10.1029/2009JD013169.

Zhang, F., N. Bei, J.W. Nielsen-Gammon, L. Guohui, R. Zhang, A. Stuart, A. Aksoy, Impacts of meteorological uncertainties on ozone pollution predictability estimated throughout meteorological and photochemical ensemble forecasts, Journal of Geophysical Research 112 (2007), doi:10.1029/2006JD007429.

2.5 Transport of Ozone and Its Precursors/Modeling

1. The long-range transport of ozone is an important contributor during periods of high ozone concentrations throughout the eastern half of Texas.

Using a subset of monitoring stations surrounding the metropolitan area, Nielsen-Gammon (2005) found that background ozone concentrations in Houston have a double peak, with high levels in the spring and late summer/early fall, and estimated that the background and local contributions during summer were roughly equal. For Dallas, Tobin and Nielsen-Gammon (2010) found that average background contributions during summer were greater than the average local contributions. Kemball-Cook et al. (2009) noted that ozone transported into Houston and Dallas was 55-60 ppb on many study days during the TexAQS I and II programs. Using ozonesonde data, Rappenglück et al. (2008) estimated that background ozone levels in Houston ranged from 30 ppbv during maritime (e.g., southerly) flow to 60-70 ppb during continental (e.g., northerly or easterly) flow. Langford et al. (2009) found that nearly 84% of the variance in daily maximum 8-hour ozone concentrations among 30 monitors in Houston was attributed to changes in the regional background due to long-range transport. Regional transport may play an even larger role during high ozone episodes in other areas of Texas. For example, McGaughey et al. (2010) estimated that background ozone in Austin accounted for approximately 85% of the maximum monitored levels. Schade et al. (2011) showed that elevated ozone coincided with northerly flow following the passage of cold fronts through College Station and background ozone concentrations were estimated to be as high as 80 ppb.

Aircraft studies are generally consistent with the background ozone results based on ground monitoring data. Kemball-Cook et al. (2009) found that background ozone into Houston contributed, on average, 50% and 66% of the total ozone on 8-hour exceedance days during 2000 and 2006, respectively. In DFW, background ozone accounted for up to 72% of the maximum downwind ozone concentration. Based on data obtained by Alvarez et al. (2011) on five sampling days in the DFW area during summer 2011, background ozone varied between 40% and 66%. The use of satellite data to investigate long-range transport has been demonstrated by studies such as McMillan, et al. (2010). Retrievals of tropospheric CO from NASA's Atmospheric InfraRed Sounder (AIRS) tracked smoke from fires in the Pacific Northwest to Houston and additional analyses suggested these smoke emissions contributed to increases in observed Houston ozone concentrations.

Numerous modeling and source apportionment techniques have been used to estimate the contributions of Texas ozone from specific source regions. Pierce et al. (2009) quantified the contributions of background ozone production in Houston and Dallas by combining modeling and satellite observations. The majority of high ozone events occurred during periods of elevated background ozone production owing to NOy enhancements from emissions in the Southern Great Lakes for Houston and from within Chicago and Houston for Dallas. Average ozone production in excess of 15 ppbv/day could occur during continental-scale transport. Kim et al. (2009) using CAMQ and HDDM found that long-range east-northeasterly winds favored interstate transport into Dallas during two 2005 episode periods. The CAMx and HDDM modeling indicated that NOx emissions in neighboring states (e.g., Oklahoma, Arkansas, Louisiana, and Mississippi) contributed approximately 10 ppb, on average, while VOC emissions from upwind states had a negligible impact. Using CAMx and APCA, Kemball-Cook et al. (2009) found similar results in terms of the frequently identified upwind states. Zhang and Ying (2011) found that local emissions had the largest contribution to Houston ozone but that ozone from upwind sources could account for 20-50% of the overall average daytime ozone concentration in HGB and BPA. Southeastern states were important upwind source regions, and even northeastern states could have 20-25 ppb contributions during favorable transport conditions.

2. The amount of ozone transport between Texas metropolitan areas can be significant on some days.

The results of photochemical modeling studies have supported the importance of intrastate transport between Texas areas. Zhang and Ying (2011) used an episode from 2000 to investigate source attribution of ozone concentrations in HGB/BPA. They showed that contributions from other counties in Texas accounted for 7-36% of HGB/BPA predicted ozone. Zero-out studies that quantified the impact of Houston emissions on other Texas areas found that transported Houston ozone could increase predicted concentrations in Austin or DFW by 10-20 ppbv (Dionisio, 2010). DFW SIP modeling (TCEQ, 2011) results for six representative high ozone days demonstrated that non-DFW Texas emissions contributed approximately 18%, on average, to simulated ozone concentrations at the Denton monitor, with daily contributions ranging between 4 ppb and 26 ppb. Kim et al. (2009) found that interstate and within-Texas contributions dominated the ozone concentrations accounting for about half of the ozone at the DFW-area Kaufman monitor. The intra-state (local and other Texas areas) contribution from NOx emissions sources could exceed 15 ppbv.

High ozone episodes in Texas are often characterized by large-scale flow patterns with northerly or easterly winds in the lower troposphere that are associated with high background concentrations of ozone and/or its precursors into Texas (e.g., Olaguer et al., 2009; Tobin and Nielsen-Gammon, 2010). Similarly, large-scale flow patterns are sometimes conducive to the transport of the Houston urban plume into adjacent Texas areas as well. Senff et al. (2010) used data collected on six flights in the Houston area to investigate the impact of the Houston urban plume on east Texas ozone concentrations. The study found that daily ozone exported from the Houston area raised regional background ozone by about 10 ppbv over a 40,000 km^2 geographic area. The potential importance of Houston transport to downwind areas was supported by an observational study by Schade et al. (2011). On five study days in College Station, Texas, during August 2006, background ozone increases of 20 – 50 ppbv during periods of southeasterly winds were attributed to the Houston urban plume. In general, back-trajectories nearer to the center of Houston were associated with the largest enhancements in ozone concentrations.

References

Alvarez, S.L., G.P. Roberts, G. Zanin, M.E. Shauck, B. Rappenglück, Airborne measurements to investigate ozone production and transport in the Dallas Forth Worth (DFW) area during the 201 ozone season. Air Quality Research Program, TCEQ Grant No. 582-10-94300, November 2011.

Dionisio, M, The characterization of regional transport. Ph.D. Dissertation, The University of Texas at Austin, May 2010.

Kemball-Cook, S., D.D. Parrish, T.B. Ryerson, U. Nopmongcol, J. Johnson, E. Tai, and G. Yarwood, Contributions of regional transport and local sources to ozone exceedances in Houston and Dallas: Comparison of results from a photochemical grid model to aircraft and surface measurements, Journal of Geophysical Research 114 (2009), doi:10.1029/2008JD010248.

Kim, S., D.W. Byun, and D. Cohan, Contributions of inter- and intra-state emissions to ozone over Dallas-Fort Worth, Texas. Civil Engineering and Environmental Systems 26 (2009), doi:10.1080/10286600802005364.

Langford, A.O., C.J. Senff, R.M. Banta, R.M. Hardesty, R.J. Alvarez II, S.P. Sandberg, L.S. Darby, Regional and local background ozone in Houston during Texas Air Quality Study 2006. Journal of Geophysical Research 114 (2009), doi:10.1029/2008JD011687.

McGaughey, G., C. Durrenberger, D.T. Allen, E.C. McDonald-Buller, Conceptual model for ozone for the Austin area. Prepared for Capital Area Council of Governments (CAPCOG) and Texas Commission on Environmental Quality (TCEQ) by The University of Texas at Austin, 2010.

McMillan, W.W., R.B. Pierce, L.C. Sparling, G. Osterman, K. McCann, M.L. Fischer, B. Rappenglück, R. Newsom, D. Turner, C. Kittaka, K. Evans, S. Biraud, B. Lefer, A. Andrews, S. Oltmans, An observational and modeling strategy to investigate the impact of remote sources on local air quality: A Houston, Texas, case study from the Second Texas Air Quality Study (TexAQS II). Journal of Geophysical Research 115 (2010), doi:10.1029/2009JD011973.

Nielsen-Gammon, J.W., J. Tobin, A. McNeel, G. Li, A conceptual model for eight-hour ozone exceedances in Houston, Texas Part I: Background ozone levels in eastern Texas. Houston Advanced Research Consortium (HARC), Project H-12, 2005.

Osterman, G. and C. Boxe, 2011. Improving the characterization of pollution transported into Texas using OMI and TES satellite and *in situ* data and HYSPLIT back trajectory analyses. TCEQ Report, 83 pp.

Pierce, R. B., J. Al-Saadi, C. Kittaka, T. Schaack, A. Lenzen, K. Bowman, J. Szykman, A. Soja, T. Ryerson, A.M. Thompson, P. Bhartia, G.A. Morris. Impacts of background ozone production on Houston and Dallas, Texas, air quality during the Second Texas Air Quality Study field mission. Journal of Geophysical Research, 114 (2009), doi:10.1029/2008JD011337.

Pierce, R.B., J. Al-Saadi, C. Kittaka, T. Schnaack, A. Lenzen, K. Bowman, J. Szykman, A. Soja, T. Ryerson, A.M. Thompson, P. Bhartia, G.A. Morris, Impacts of background ozone production on Houston and Dallas, Texas, air quality during the Second Texas Air Quality Study field mission. Journal of Geophysical Research 114 (2009), doi:10.1029/2008JD011337.

Rappenglück, B., R. Perna, S. Zhong, G. A. Morris, An analysis of the vertical structure of the atmosphere and the upper-level meteorology and their impact on surface ozone levels in Houston, Texas. Journal of Geophysical Research 113 (2008), doi:10.1029/2007JD009745.

Schade, G.W., S. Khan, C. Park, I. Boedeker, Rural Southeast Texas air quality measurements during the 2006 Texas Air Quality Study. Journal of the Air & Waste Management Association 61, (2011), doi:10.1080/10473289.2001.608621.

Senff, C.J., R.J. Alvarez II, R.M. Hardesty, R.M. Banta, A.O. Langford, Airborne lidar measurements of ozone flux downwind of Houston and Dallas. Journal of Geophysical Research 115 (2010), doi:10.1029/2009Jd013689.

Tobin, J., J.W. Nielsen-Gammon, Modeling ozone as a function of meteorological conditions in the Houston non-attainment region: Identifying meaningful meteorological controls and estimating trend in meteorologically adjusted ozone. Houston Advanced Research Consortium (HARC), Project H-107, 2010.

Zhang H., Q. Ying, Contributions of local and regional sources of NOx to ozone concentrations in Southeast Texas. Atmospheric Environment 45 (2011), doi:10.1016/j.atmosenv.2011.02.047.

3. Findings from the Air Quality Research Program (AQRP, 2010-2012)

Fourteen research projects, one field study support project and one synthesis project were funded by the AQRP during the 2010-2012 biennium. The 14 research projects are listed, by category, in Table 3-1. Full project reports are available at the AQRP web site (http://aqrp.ceer.utexas.edu/reports.cfm). Key findings from the research projects, organized into the topical areas of emissions, chemistry, and transport/modeling are summarized below.

Table 3-1. AQRP Research Projects 2010-2012

Project Number	Title
Dallas-Fort Worth Area Studies	
10-024	Surface Measurements and One-Dimensional Modeling Related to Ozone Formation in the Suburban Dallas-Fort Worth Area
10-034	Dallas Measurements of Ozone Production
10-044	Airborne Measurements to Investigate Ozone Production and Transport in the Dallas/Fort Worth (DFW) Area During the 2011 Ozone Season
Houston Area Studies	
10-032	SHARP Data Analysis: Radical Budget and Ozone Production
10-045	Quantification of Hydrocarbon, NOx and SO2 Emissions from Petrochemical Facilities in Houston: Interpretation of the 2009 FLAIR Dataset
Flares and Emission Inventories	
10-006	Quantification of Industrial Emissions of VOCs, NO2 and SO2 by SOF and Mobile DOAS
10-009	Additional Flare Test Days for TCEQ Comprehensive Flare Study
10-022	Development of Speciated Industrial Flare Emission Inventories for Air Quality Modeling in Texas
Modeling and Atmospheric Chemistry	
10-008	Factors Influencing Ozone-Precursor Response in Texas Attainment Modeling
10-015	An Assessment of Nitryl Chloride Formation Chemistry and its Importance in Ozone Non-Attainment Areas in Texas
10-020	NOx Reactions and Transport in Nighttime Plumes and Impact on Next-Day Ozone
10-021	Dry Deposition of Ozone to Built Environment Surfaces
10-029	Wind Modeling Improvements with the Ensemble Kalman Filter
10-042	Environmental Chamber Experiments to Evaluate NOx Sinks and Recycling in Atmospheric Chemical Mechanisms

Emissions:

Despite improvements in inventory estimates over the past decade, significant discrepancies are still observed between annual average reported emissions and instantaneous emission estimates inferred from observed concentrations. Some of these discrepancies can be resolved through refinement of the temporal resolution of emissions; other discrepancies may be due to missing or under-estimated sources.

The AQRP projects related to industrial flaring have provided information about both temporal variability and potential underestimation of emissions. The studies of flares under controlled operating conditions demonstrated that at low flow rates, and with low heating value gases, standard emission estimation methods may understate emissions if excess steam or air-assist is used. Subsequent air quality modeling demonstrated that these emissions, coupled with the temporal variability in the emissions, can lead to additional ozone formation both locally and over large spatial scales. Field observations in the FLAIR project support these findings. Specifically:

- Field tests in a semi-controlled environment indicate that the most efficient industrial flare operation, as measured by the destruction and removal efficiency and combustion efficiency, are achieved at or near the incipient smoke point. Minimum levels of steam or air assist that comply with the flare manufacturer's recommendations should be used when possible.

- Further development of remote sensing technologies, such as Passive and Active Fourier Transform Infrared Spectroscopy, and modeling techniques, such as Multivariate Image Analysis, may offer approaches for improving the detection, monitoring, and evaluation of flare operational conditions in the future.

A variety of additional studies have involved field measurements to resolve emission inventories. A particular focus has been on alkenes and aldehydes.

- Remote sensing measurements in the Houston Ship Channel and Texas City indicated that alkane and ethene emissions were similar in 2006, 2009, and 2011, while propene emissions decreased. Formaldehyde emissions in the Houston Ship Channel and Texas City were similar between 2009 and 2011, and many sources were associated with industries also emitting alkenes. In the Houston Ship Channel, Beaumont/Port Arthur, and Longview areas, comparison of the 2011 measurements with the 2009 TCEQ inventory showed primarily good agreement for NO_x and SO_2 but large discrepancies in VOC with observations at certain locations, such as Mont Belvieu, exceeding reported emissions by 400-1500% for alkanes, 300-1500% for ethene, and 170-800% for alkenes.

- The strength of industrial emissions sources of formaldehyde and olefins were assessed in Texas City and the Houston Ship Channel region during the 2009 FLAIR study. Consistent with previous studies, computed ethene, propene, benzene, and 1,3-butadiene emission rates significantly exceeded levels reported in emissions inventories (by more than 2 orders of magnitude in some cases). Ignited flares emitted formaldehyde at the tip at rates between 0.3-2.5 kg/h. Combustion efficiencies were found to vary from 0 (unlit) to 0.7 (steaming) to 0.999. A large source of primary formaldehyde emissions was identified in a Texas City refinery complex with a strength of 18 ± 5 kg/h, which may be associated with a FCCU regeneration unit.

Chemistry

Atmospheric chemistry in Texas has a number of unique features. The combinations of industrial and urban emissions, and forested and coastal environments lead certain chemical pathways to become more significant in Texas than in other regions. Specific findings arising from the AQRP program that address ozone and radical formation under Texas conditions include:

- Nitryl chloride can affect tropospheric oxidation capacity and ozone formation in coastal and inland regions. Representation of the chemistry of nitryl chloride formation in CAMx has been implemented and chlorine/chloride sources have been characterized for Texas emissions inventories.

- Volatile organic compounds can remove NO_x by forming NO_x sink compounds that reduce the availability of NO_x for ozone formation. These NO_x sink species may eventually react to return NO_x back to the atmosphere, known as NO_x recycling, potentially causing additional ozone production in NO_x-limited regions. Novel experimental data, describing the NO_x sinks for aromatics and isoprene and NO_x-recycling from photolysis of alkyl nitrates and nitrocresols, have been obtained and used to develop a revised version of the Carbon Bond mechanism (CB6) known as CB6r1.

- Calculated HO_x production during the SHARP campaign in Houston was dominated by the photolysis of HONO in the early morning and by photolysis of O_3 in the midday; at night, OH production occurred mainly via O_3 reactions with alkenes. On average, the daily HO_x production rate was 23.8 ppbv day^{-1} in the region, of which 31% was from O_3 photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O_3 reactions with alkenes.

- Recent measurements have indicated that daytime observed HONO mixing ratios are often far larger than the expected photostationary state with OH and NO in Houston and other locations throughout the world. Statistically significant vertical gradients of HONO throughout the day, with smaller mixing ratios aloft, have suggested that a likely source of daytime HONO could be photocatalytic conversion of NO_2 on the ground in Houston. Although daytime mechanisms for HONO formation have been a subject of exploration, it is evident that uncertainty remains and further studies are needed. As further progress is made, incorporation into air quality models will be important.

Transport/Modeling

One of the ways in which air quality models are improved is by collecting detailed field measurements that can be used to evaluate the performance of the air quality models. Previous field measurement campaigns in the state were primarily focused on southeast Texas. In 2010-2012, a field measurement program in the Dallas-Fort Worth area was funded by AQRP. The measurements led to a number of significant findings and future comparisons with modeling results are expected to lead to additional insights.

- Aircraft measurements downwind of the Dallas-Fort Worth area indicated enhancements in maximum ozone concentrations by factors ranging from 1.5-2.5 relative to upwind concentrations. Downwind concentrations of NO, NO_2, and reactive alkenes were modest indicating a photochemically aged air mass.

- Aircraft flights over portions of the Barnett Shale did not find enhancements in ozone concentrations clearly associated with oil and gas emissions, but persistent southerly winds (~10 mph) may not have favored mixing of urban DFW and Barnett Shale emissions that would change the VOC/NOx ratio towards a regime favoring ozone production. On some occasions, elevated concentrations of reactive alkenes (up to 10 ppbv) and formaldehyde (4-6 ppbv compared to background concentrations of 2-3 ppbv) were measured over the Barnett Shale, such as immediately downwind of a large compressor station in the Eagle Mountain Lake area.

- Preliminary results from deployment of the Measurement of Ozone Production Sensor (MOPS) during August – October 2011 at the Meacham site near Dallas-Fort Worth showed that ozone production on sunny days peaked at 40-60 ppbv/h in the mid-mornings, which suggested that Meacham may be an ozone source region. Preliminary ozone production rates at Eagle Mountain Lake were generally lower, with peak ozone productivities of 40 ppbv/h in the late mornings on only a few days.

- Preliminary analyses of surface measurements during May 30 – June 30, 2011 indicated that Eagle Mountain Lake was most often affected by aged and processed air from the Dallas-Fort Worth metropolitan area and intermittently by emissions from nearby oil and gas operations in the Barnett Shale.

- The largest sources of methane and other hydrocarbon species at oil and gas locations near Fort Worth were gas treatment facilities combined with large compressor stations. Emissions were an order of magnitude lower from smaller compressor stations and well pads; however, flashing emissions on one occasion from a condensate tank were estimated at 140 kg/h methane and 10 kg/h ethane (and other species) suggesting further study for this potentially important intermittent source.

In addition to the field measurement program, AQRP projects also included data analysis of previously conducted field programs. Among these were flights examining the long range transport, overnight, of urban, industrial and power plant plumes. Results from laboratory and field studies of pollutant loss mechanisms (dry deposition) were also incorporated into air quality models.

- Overnight transport of plumes from urban, petrochemical, and coal-fired power plant plumes can affect regional air quality the following day. Aircraft flights in the Houston area have shown NO_3 to be 3 to 5 times more important than O_3 as a nighttime oxidant of VOCs. Net NO_3 radical productions rates can be large (1–2 ppbv h^{-1}) within NO_x-containing plumes of industrial origin from Houston. Nighttime NO_x loss through N_2O_5 heterogeneous uptake is modest, but should be an area of continued study.

- Analysis of nighttime aircraft intercepts from two different Texas power plants resulted in improvements to the plume-in-grid formulation in CAMx version 5.40, released in October 2011. Plume-in-grid puff growth rates were modified to ignore growth contributions from horizontal and vertical shear during stable/nighttime conditions. Shear effects remain during neutral/unstable/daytime conditions. Minimum limits on vertical diffusivity, turbulent flux moments, and nighttime planetary boundary layer depths were reduced. With these improvements, plume-in-grid puff behavior will change potentially significantly at night and above the boundary layer, usually leading to longer lifetime.

- The heterogeneity of the urban environment is typically not represented in the dry deposition algorithms used for photochemical modeling. Refined characterization of the urban built environment on the dry deposition of ozone in Austin, Texas resulted in decreases in predicted daily maximum 8-hour average ozone concentrations of 0.2 to 1.3 ppb. The results were primarily attributed to deposition to urban vegetation and highlighted the importance of characterizing Texas urban landscapes undergoing rapid development.

4. Recommendations for AQRP Research, 2012-2013

A primary goal of the State of Texas Air Quality Research Program (AQRP) is to support scientific research related to Texas air quality, in the areas of emissions inventory development, atmospheric chemistry, meteorology and air quality modeling. As outlined in this State of the Science document, the research needs in these areas are significant and continuing. Because AQRP resources are limited, proposed research projects should focus on high priority, targeted areas.

For the 2012-2013 biennium, the targeted areas for AQRP research are:

- Analysis of data collected in the Dallas-Fort Worth (Barnett Shale) field campaign
- Analysis of flare operating regimes that provide both high combustion efficiency and minimal smoke formation
- Deployment of supplementary measurements in a large field measurement campaign planned by NASA for the summer of 2013
- Analysis of prior Texas field study data and modeling tools to investigate transformation of gas-phase pollutants to aerosol phase
- Investigation of how the temporal resolution of meso-scale meteorology and photochemical grid models must be altered for high spatial resolution modeling; investigation of mesoscale modeling of cloud formation and the effects of clouds upon ozone and PM chemistry;
- Analysis of radical chemistry in Texas cities, especially HONO formation, ozone removal and production by halogen chemistry, and atmospheric chemistry within industrial plumes.
- Analysis of the impact of global and regional transport of air pollutants on Texas