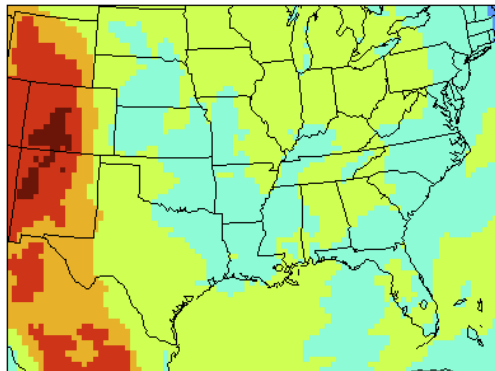


State of the Science of Air Quality in Texas:

Scientific Findings from the Air Quality Research Program (AQRP)

Report for the period 2010-2015

February 15, 2016



Prepared by:
David Allen, Elena McDonald-Buller, and Gary McGaughey
University of Texas at Austin

With input from:
Members of the Air Quality Division
Texas Commission on Environmental Quality

Air Quality Research Program Independent Technical Advisory Committee

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, and continuing through the 2012-2013 and 2014-2015 biennia, the Texas Commission on Environmental Quality (TCEQ) contracted with the University of Texas at Austin to administer the AQRP. During this period, the AQRP funded more than 50 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, and to summarize key findings from 2010-2015 AQRP projects.

The contributions of the AQRP program to the scientific understanding of air quality in Texas is grouped into major sections on emissions (Section 2.2), tropospheric chemistry (Section 2.3), and atmospheric physical processes (Section 2.4). Most of the research of the AQRP program has been focused on improving the understanding of emissions, chemistry and atmospheric physical processes that lead to ozone formation and accumulation. This is because ozone is the air pollutant for which the State has the greatest number of regions that do not meet National Ambient Air Quality Standards (NAAQS). With the recent tightening of the NAAQS for fine particulate matter, however, some regions in Texas are approaching non-attainment for fine particulate matter NAAQS; a number of AQRP projects have been funded to specifically address particulate matter. These projects are summarized in Section 2.5.

On the topic of emissions, AQRP projects over the past 6 years have focused on reducing uncertainties in emissions from industrial flaring, industrial sources of highly reactive volatile organic compounds (HRVOCs; ethene, propene, butenes and 1,3-butadiene), aldehyde emissions, fires, and biogenic volatile organic compounds. On the topic of tropospheric chemistry, AQRP projects have improved understanding of and models for the atmospheric chemistry of HRVOCs, biogenic hydrocarbons, and the cycling of nitrogen oxides in the atmosphere. On the topic of atmospheric physical processes, AQRP projects have improved models of physical pollutant loss mechanisms, and have made improvements in cloud characterizations, cloud processes, and models of wind fields. Further, multiple studies have examined how inter-state and global transport of pollutants impacts air quality in Texas. On the topic of fine particulate matter, AQRP projects have provided information regarding the chemical make-up of atmospheric particles in Texas and how atmospheric particles influence the cycling of gas phase air pollutants. Finally, multiple AQRP projects on the topics of emissions, tropospheric chemistry, atmospheric physical processes and particulate matter have been coordinated around large air quality field studies, in which many teams of investigators make measurements simultaneously. This coordination has provided scientific insights that are greater than would have been possible for projects performed in isolation.

CONTENTS

Executive Summary	2
1. Overview of Air Quality Research in Texas.....	4
1.1 Issues.....	4
1.2 Field measurement campaigns.....	8
2. State of the Science: Emissions, Chemistry, and Meteorology and Transport/Modeling.....	18
2.1 Overview and methods for developing state of the science findings	18
2.2 Ozone precursor emissions	19
2.3 Tropospheric chemistry	38
2.4 Atmospheric physical processes and long-range transport of pollutants.....	60
2.5 Particulate matter	75
3. Summary of Projects and Publications from the Air Quality Research Program (AQRP, 2010-2015).....	80

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, several of the state’s largest urban areas exceed the National Ambient Air Quality Standard (NAAQS) for ozone, and concentrations of particulate matter and 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 substantial improvements in air quality have been made in Texas. Over the period from 2000 to 2013, average design values of ozone concentrations* at regulatory monitors decreased by 24% in Texas, double the national average rate (Figure 1.1.1; TCEQ, 2015a). The Houston metropolitan area went from, in 1999, having the highest number of days exceeding the NAAQS for ozone of any U.S. city and one of the highest ozone design values, to, in 2014, having no monitors that had a fourth highest maximum daily 8-hour average ozone concentration greater than 85 ppb (the 1997 level of the NAAQS). Similar ozone reductions have occurred in other Texas cities, as shown in Figure 1.1.2).

*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.

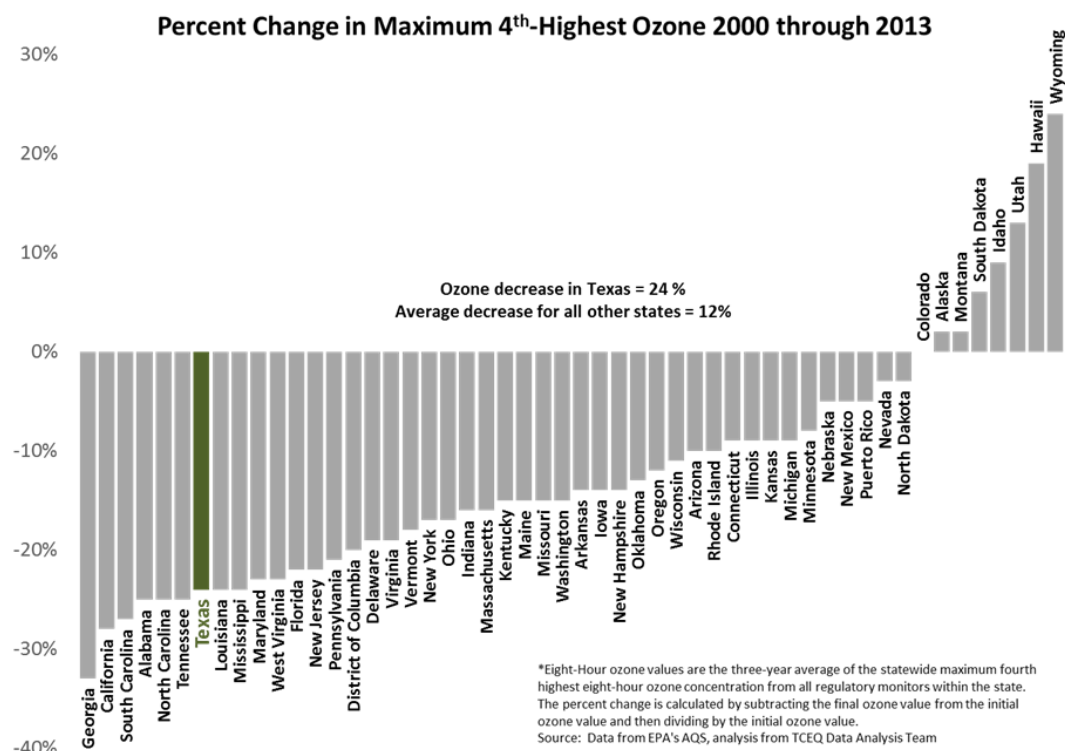


Figure 1.1.1 Comparison of ozone reductions in Texas to other States, 2000-2013.
Source: TCEQ (<http://www.tceq.texas.gov/airquality/airsuccess/air-success-criteria>)

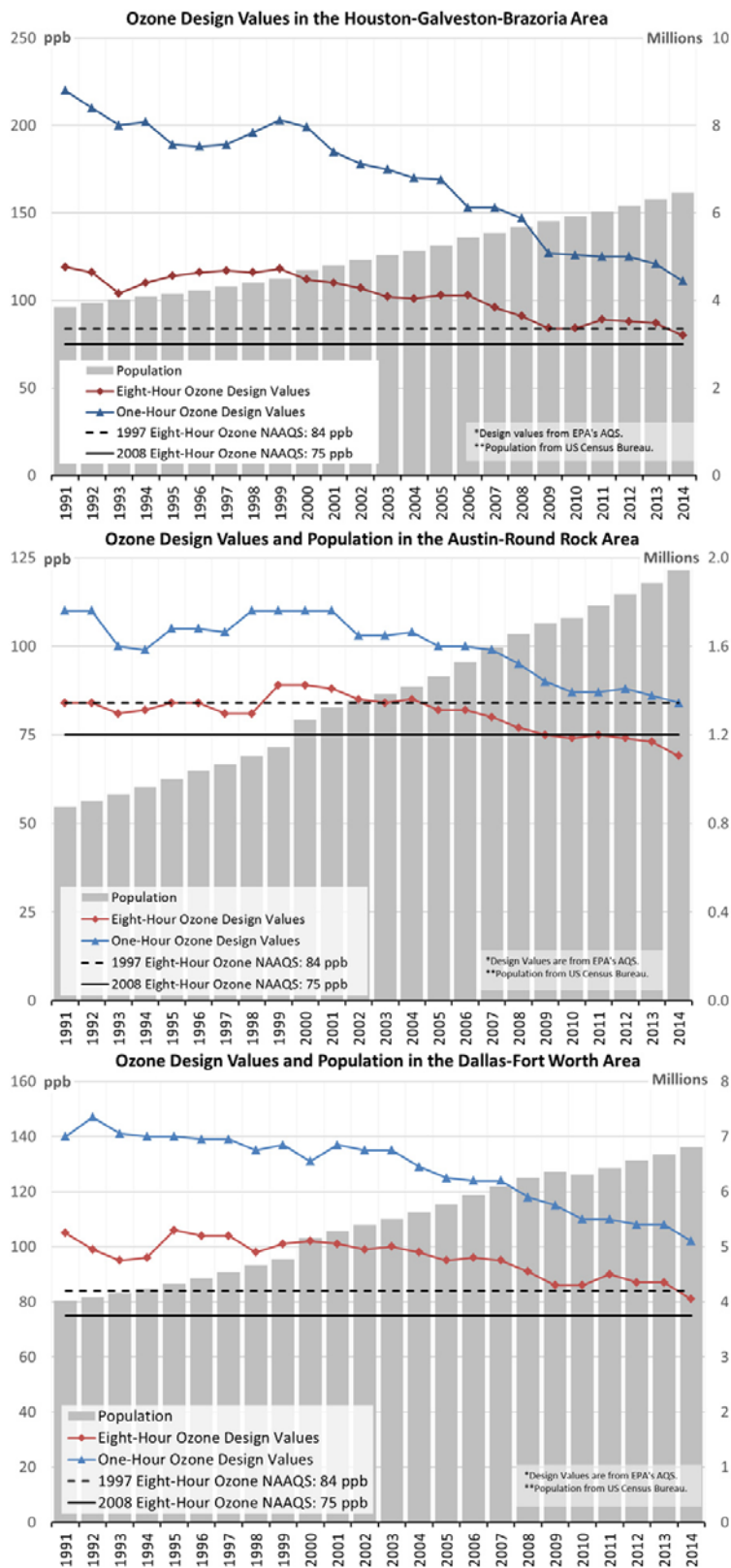


Figure 1.1.2. Trends in population and ozone design values in Texas cities over the past 25 years (TCEQ, 2015b); in all Texas cities, ozone design values have either decreased or remained constant, despite increases in population; two ozone design values are shown: design values based on eight hour averages of ozone concentrations, which are the design values used in the most recent NAAQS, and design values based on one hour averages of ozone concentrations, which were the design values used in standards prior to 1997; in 1997, EPA revoked the 1-hour ozone standard (0.12 ppm, not to be exceeded more than once per year) in all areas, although some areas have continued obligations under that standard.

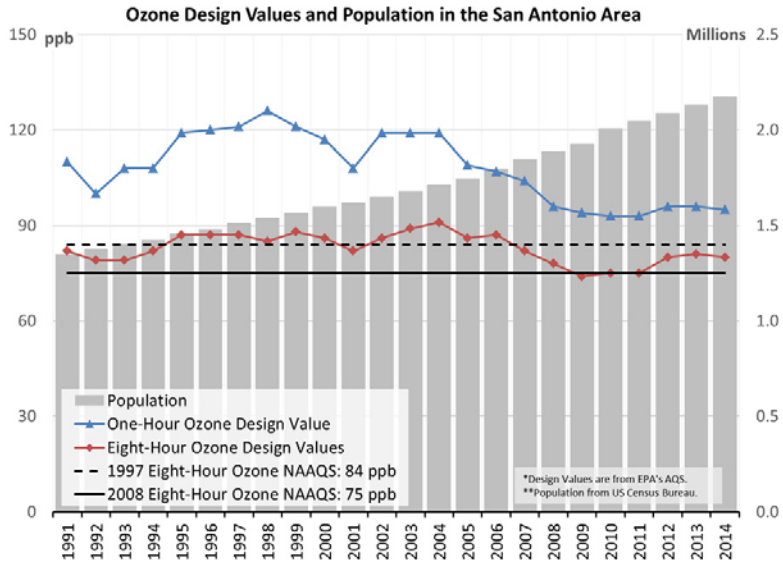


Figure 1.1.2 (continued). Trends in population and ozone design values in Texas cities over the past 25 years (TCEQ, 2015b); in all Texas cities, ozone design values have either decreased or remained constant, despite increases in population; two ozone design values are shown: design values based on eight hour averages of ozone concentrations, which are the design values used in the most recent NAAQS, and design values based on one hour averages of ozone concentrations, which were the design values used in standards prior to 1997; in 1997, EPA revoked the 1-hour ozone standard (0.12 ppm, not to be exceeded more than once per year) in all areas, although some areas have continued obligations under that standard.

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 of Texas has had in reducing ozone concentrations is its investments in air quality research. These investments have helped to identify focused strategies for emission reductions, designed to be most effective for conditions in Texas.

While progress in air quality over the past decade has been impressive, challenges remain. The Dallas-Fort Worth, Houston-Galveston-Brazoria area and the San Antonio region still do not meet the NAAQS for ozone, established in 2008. In addition, the U.S. Environmental Protection Agency (EPA) has recently (October 2015) lowered the NAAQS for ozone, potentially changing the attainment status for multiple regions in Texas. 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 many parts of Texas (McDonald-Buller et al., 2011; Berlin, et al., 2013). 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. 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 has changed emissions associated with electricity generation and chemical manufacturing. Again, identifying effective and efficient approaches to reducing emissions, as energy development continues, will require new scientific information.

These are just a few of the examples of the types of challenges Texas will face in continuing 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; Allen et al., 2012). Findings from recent work, particularly work funded by the Texas Air Quality Research Program (AQRP), are summarized.

References

- 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
- Allen, D., McDonald-Buller, E., McGaughey, G. et al., State of the Science of Air Quality in Texas: Scientific Findings from the Air Quality Research Program (AQRP) and Recommendations for Future Research (2012).
- Berlin, S.R., Langford, A.O., Estes, M., Dong, M., Parrish, D.D., Magnitude, decadal changes and impact of regional background ozone transported into the greater Houston, Texas area, *Environ. Sci. Technol.*, 47(24), 13985-13992, doi:10.1021/es4037644 (2013).
- 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).
- Texas Commission on Environmental Quality (TCEQ, 2015a), Air Quality Successes, available at: <http://www.tceq.texas.gov/airquality/airsuccess/air-success-criteria>
- Texas Commission on Environmental Quality (TCEQ, 2015b), Air Quality Successes, available at: <http://www.tceq.state.tx.us/airquality/airsuccess/airSuccessMetro>

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.

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, and 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,

Box 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 Shale oil and gas production region field measurements
- DISCOVER-AQ 2013

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, although recently measurements have been initiated in the Eagle Ford production region, south of San Antonio. These measurements are continuing and analysis of data from the campaigns is on-going.

In 2013, a field campaign, titled DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality), was conducted under the leadership of the National Aeronautics and Space Administration (NASA). DISCOVER-AQ used southeast Texas as a test bed for the use of satellite measurements in characterizing air quality. Sub-orbital (aircraft and ground station) measurements were conducted in concert with satellite measurements to assess the limits of current and the needs for future satellite measurement capabilities. Augmentations of the measurements, funded by TCEQ and the AQRP, leveraged the extensive investments made by NASA, and provided additional insights into the factors that control air quality in southeast Texas.

These field programs are described in more detail in Sections 1.2.1-1.2.7.

References:

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* 51, 12559-12568, 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* 51, 12569-12576, DOI: 10.1021/ie202675f (2012).

The DISCOVER-AQ program is described at the NASA web site: <http://discover-aq.larc.nasa.gov/> and in a feature article in the Air and Waste Management Association’s EM (Environmental Manager) magazine (September, 2014).

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 (NOAA), Brookhaven National Laboratory, Pacific Northwest National Laboratory, and the EPA, 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 HRVOCs 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 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.

References:

- 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/txaqsarchive/accelerated.htm>
- Web sites describing TexAQS and its principal findings have been maintained by the University of Texas, www.utexas.edu/research/ceer/txaqs www.utexas.edu/research/ceer/txaqsarchive

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 and particulate matter concentrations averaged over a day or year). 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 concentrations in eastern Texas, which represent the minimum ozone concentration that is likely achievable through only local controls, were found to approach or exceed 75 ppbv for an 8-hour average, which was the level of the NAAQS through 2015 (see Parrish et al., 2009, cited below).

A second set of major findings were associated with concentrations of 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 TCEQ 2010 Flare Study)

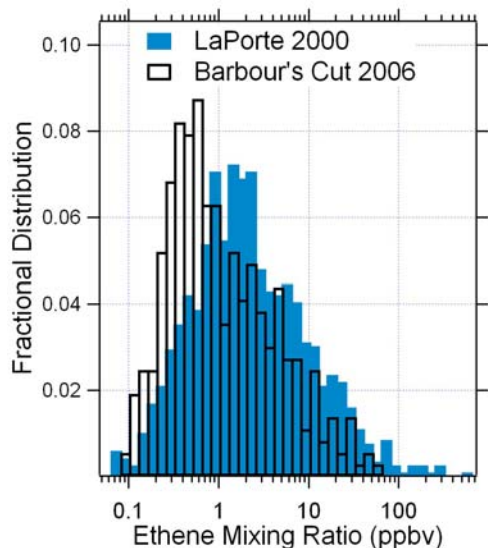


Figure 1.2.2. Comparison of ethene concentrations made at similar locations in the Houston Ship Channel region in 2000 (LaPorte) and 2006 (Barbour's Cut). A significant decrease in average and extreme ethene concentrations was observed.

Reference:

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)

The chemistry of atmospheric radicals, especially the hydroxyl radical (OH) and hydroperoxyl radical (HO₂), together called HO_x, 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 HO_x 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 (NO_x) and volatile organic compounds (VOCs). Both measurements and modeling were performed and reconciling model predictions and observations was a major focus of study.

Among the HONO formation mechanisms that were considered were gas-phase photolysis of nitrophenols, heterogeneous conversion of NO₂ on fresh and aged soot particles and soil surfaces, photolysis of surface adsorbed nitric acid, and heterogeneous conversion of HNO₃ on the surface of primary organic aerosol. HO_x production during the SHARP campaign at the Moody Tower measurement site in Houston was dominated by the photolysis of HONO in the early morning and by photolysis of O₃ in the midday; at night, OH production occurred mainly via O₃ 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 O₃ photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O₃ 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 NO₂ on the ground surfaces in Houston. Although daytime mechanisms for HONO formation have been a subject of exploration, it is evident that uncertainty remains.

References:

- Ren, X., van Duin, D., Cazorla, M., Chen, S., Mao, J., Zhang, L., Brune, W.H., Flynn, J.H., Grossberg, N., Lefer, B.L., Rappenglück, B., Wong, K.M., Tsai, C., Stutz, J., Dibb, J.E., Jobson, B.T., Luke, W.T., Kelley, P., Atmospheric oxidation chemistry and ozone production: Results from SHARP 2009 in Houston, Texas, *JGR Atmospheres* 118, 5770-5780 doi:10.1002/jgrd.50342 (2013).
- Olague, E.P., Kolb, C.E., Lefer, B., Rappenglück, B., Zhang, R., Pinto, J.P., Overview of the SHARP campaign: Motivation, design and major outcomes, *JGR Atmospheres*, Introduction to a Special Collection: doi:10.1002/2013JD019730 (2014).
- Couzo, E., Lefer, B., Stutz, J., Yarwood, G., Karamchandani, P., Henderson, B., Vizuete, W., Impacts of heterogeneous HONO formation on radical sources and ozone chemistry in Houston, Texas, *Atmospheric Environment*, 112, 344-355 (2015).
- 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 of formaldehyde. Also consistent with results from controlled flare studies, combustion efficiencies were found to vary from 0% (unlit) to 70% (over-assisted) to 99.9% (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/SO₂ 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 SO₂. Analysis of the emission inventory in Texas City, as well as triangulation and wind field analysis revealed that the most likely sources of HCHO were a Fluid Catalytic Cracking Unit (FCCU) regeneration unit and desulfurization processes (Olague et al., 2013).

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 some sites.

References:

- 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.
- Olague, E.P., Herndon, S.C., Buzcu-Guven, B., Kolb, C.E., Brown, M.J., Cuclis, A.E., Attribution of primary formaldehyde and sulfur dioxide at Texas City during SHARP/formaldehyde and olefins from large industrial releases (FLAIR) using an adjoint chemistry transport model, *JGR Atmospheres* 118, 11,317-11,326 doi:10.1002/jgrd.50794 (2013).
- Pikelnaya, O., Flynn, J.H., Tsai, C., Stutz, J., Imaging DOAS detection of primary formaldehyde and sulfur dioxide emissions from petrochemical flares, *JGR Atmospheres* 118, 8716-8728 doi:10.1002/jgrd.50643 (2013).

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

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.

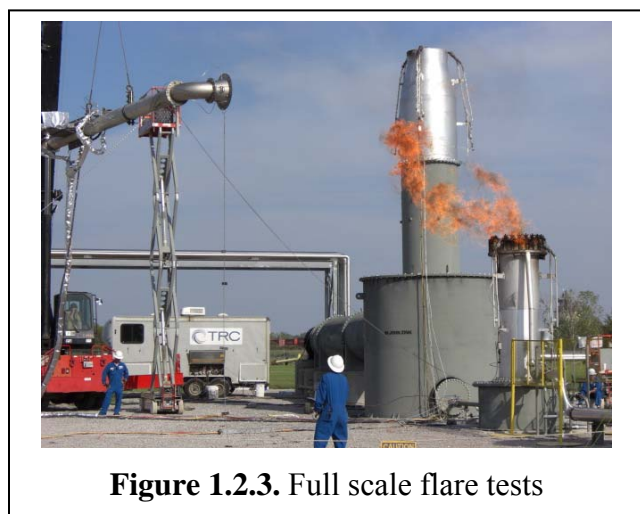


Figure 1.2.3. Full scale flare tests

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; Al-Fadhli et al., 2012).

References:

- 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.* 51, 12559-12568, 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.* 51, 12569-12576, 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*, 51, 12663-12673, DOI: 10.1021/ie201400z (2012).

1.2.6 Shale oil and gas production region 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 decade. 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 has changed emissions associated with electricity generation.

A series of field campaigns have been undertaken since 2010, primarily to characterize direct emissions of volatile organic compounds and air toxics in the shale gas and oil production regions. The majority of these measurements have been made in the Barnett Shale natural gas production region near Fort Worth, although recently measurements have been initiated in the Eagle Ford production region, south of San Antonio. With funding provided by the TCEQ and other sources, instantaneous, hourly and daily measurements of concentrations of a variety of air pollutants have been made. 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.

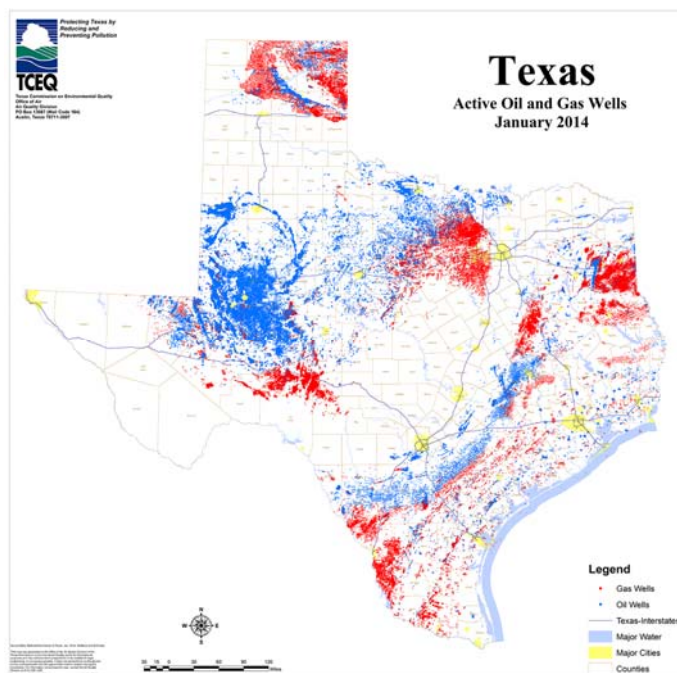


Figure 1.2.4. Locations of oil wells (blue) and gas wells (red) in Texas (2014).

http://www.tceq.state.tx.us/assets/public/implementation/barnett_shale/bs_images/txOilGasWells.png

While the results from some of these measurement studies have been summarized in the scientific literature (see references below) many analyses are on-going. Results should help to clarify the role of direct and indirect emission changes, associated with renewed oil and gas production activities, on ozone formation. For example, a series of studies (Eastern Research Group, 2011; Allen et al., 2013, 2015a,b) of emissions on and near natural gas production sites have indicated that emissions of hydrocarbons from a relatively small fraction of sites and

sources dominate total emissions. If these high emitting sources are accounted for in emission inventories, then emission estimates are generally consistent with ambient measurements (Zavala et al., 2014).

Using these emission inventories, air quality modeling has indicated that the impact of oil and gas production emissions on ozone formation is location dependent. In regions such as the Barnett Shale, changes in ozone formation in the Barnett Shale due to switching electricity generation from coal fired power plants to natural gas fired power plants is much larger than the additional ozone formation due to oil and gas production emissions in the Barnett Shale (Pacsi et al., 2013). In contrast, in regions such as the Eagle Ford Shale, NO_x emissions from oil and gas operations, in concert with reactive biogenic hydrocarbon emissions, lead to increases in ozone concentrations that are 1 ppb or more in nearby urban areas on some days. While there are also regions of decreased ozone concentrations due to switching electricity generation from coal fired power plants to natural gas fired power plants, these decreases occur in different regions than the increases associated with emissions from oil and gas production in the Eagle Ford (Pacsi et al., 2015).

References:

- Allen, D.T., Torres, V.M., Thomas, J., Sullivan, D., Harrison, M., Hendler, A., Herndon, S.C., Kolb, C.E., Fraser, M., Hill, A.D., Lamb, B.K., Miskimins, J., Sawyer, R.F., and Seinfeld, J.H. Measurements of Methane Emissions at Natural Gas Production Sites in the United States, *Proceedings of the National Academy of Sciences*, 110, 17768-17773, doi: 10.1073/pnas.1304880110 (2013).
- Allen, D.T., Pacsi, A., Sullivan, D., Zavala-Araiza, D., Harrison, M., Keen, K., Fraser, M., Hill, A.D., Sawyer, R.F., and Seinfeld, J.H. Methane Emissions from Process Equipment at Natural Gas Production Sites in the United States: Pneumatic Controllers, *Environmental Science & Technology*, 49 (1), 633–640, doi:10.1021/es5040156 (2015a).
- Allen, D.T., Sullivan, D., Zavala-Araiza, D., Pacsi, A., Harrison, M., Keen, K., Fraser, M., Hill, A.D., Lamb, B.K., Sawyer, R.F., and Seinfeld, J.H. Methane Emissions from Process Equipment at Natural Gas Production Sites in the United States: Liquid Unloadings, *Environmental Science & Technology*, 49 (1), 641–648, doi:10.1021/es504016r (2015b).
- 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 Barnett Shale field campaign are available at: <http://aqrp.ceer.utexas.edu/projects.cfm>
- Pacsi, A.P., Kimura, Y., McGaughey, G., McDonald-Buller, E.C., and Allen, D.T., Regional ozone impacts of increased natural gas use in the Texas power sector and development in the Eagle Ford shale, *Environmental Science & Technology*, 49, 3966-3973, doi: 10.1021/es5055012 (2015).
- Pacsi, A.P., Alhajeri, N.S., Zavala-Araiza, D., Webster, M.D. and Allen, D.T., Regional Air Quality Impacts of Increased Natural Gas Production and Use in Texas, *Environmental Science & Technology*, 47, 3521-3527, doi: 10.1021/es3044714 (2013)
- Zavala-Araiza, D., Sullivan, D.W., and Allen, D.T. Atmospheric hydrocarbon emissions and concentrations in the Barnett Shale natural gas production region, *Environmental Science & Technology*, 48, 5314-5321 doi: 10.1021/es405770h (2014).

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.” (From NASA DISCOVER-AQ web site: <http://discover-aq.larc.nasa.gov/science.php>)

The DISCOVER-AQ campaign employed NASA aircraft to make a series of flights, with scientific instruments on board to measure gaseous and particulate pollution. Flights began in the Baltimore-Washington, D.C. area in 2011 and continued with flights in Houston in 2013. The State of Texas, through the TCEQ and the Air Quality Research Program, worked with NASA to develop sampling strategies for the 2013 field measurement campaign in Houston. The flight paths for DISCOVER-AQ in Houston are shown in Figure 1.2.5. The field campaign involved coordinating ground measurements and instrumented aircraft flights with satellite overpasses.

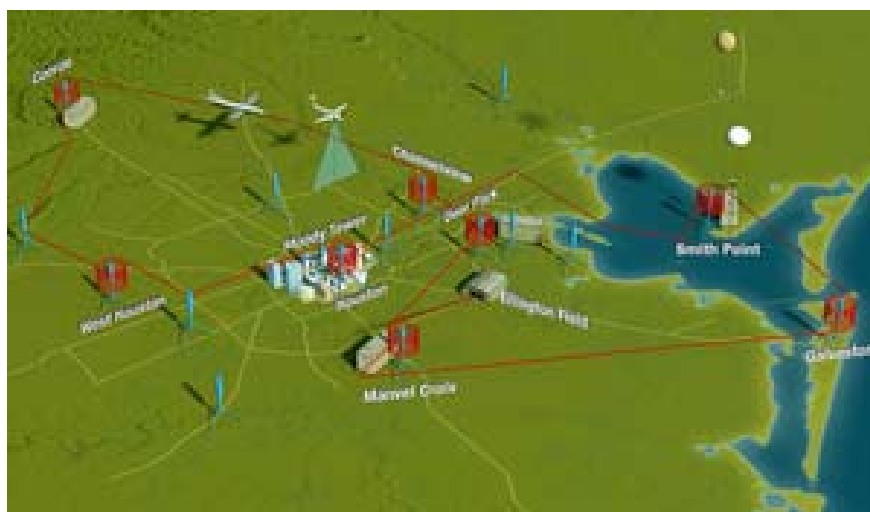


Figure 1.2.5. Flight track for NASA DISCOVER-AQ aircraft during the 2013 field campaign; the same flight track was flown on multiple days and included aircraft spirals that provided data on vertical distributions of air pollutants at eight fixed locations, shown on the map.

Reference:

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

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 NAAQS 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 San Antonio and the Dallas-Fort Worth area. Better understanding of how flare operating practices influence emissions can guide emission reduction strategies. The purpose of this document is to summarize the current state of scientific understanding on key issues addressed by the AQRP 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 identifies and, to the extent possible, 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 at Austin). The report was then revised based on reviews by both the TCEQ and the AQRP's Independent Technical Advisory Committee.

The findings are divided into 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 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 industrial flares, fires, biogenics, HRVOCs, emissions associated with oil and natural gas production, and emissions characterized by satellite measurements. Other categories of emissions (e.g., mobile sources, 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 (e.g., Allen and Durrenberger, 2003).

References:

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>

2.2.2 Emissions source characterization and inventory assessment from AQRP projects 2010-2015

Industrial flares

Studies performed during TexAQS 2000 indicated that high temporal variability in emissions from industrial sources in southeastern Texas could lead to rapid ozone formation, in particular when emissions were composed of HRVOCs (Murphy and Allen, 2005; Nam et al., 2006; Webster et al., 2007; Nam et al., 2008; Kleinman et al., 2003; Allen et al., 2004; Vizuete et al., 2008; Olaguer et al., 2009; Henderson et al., 2010). These findings motivated the collection of hourly emissions data from 141 industrial locations in the region during TexAQS II, which later were incorporated into a 2006 Special Inventory (TCEQ, 2008). Emissions from industrial flares constituted 45% of all VOC and 77% of all HRVOC emissions in the 2006 Special Inventory. The temporal patterns of emissions from industrial flaring operations were found to consist of multiple components, including nearly constant, routinely variable, or episodic (Nam et al., 2006; Webster et al., 2007; Pavlovic et al., 2009; Pavlovic et al., 2012a). Air quality modeling based on the 2006 Special Inventory suggested that the temporal variability of emissions from flaring operations could lead to additional ozone formation both locally and over large spatial scales (Pavlovic et al., 2010; Pavlovic et al., 2012b). Collectively, these studies indicated the importance of understanding and reducing emissions from flaring events in order to contribute to improvements in air quality in the region.

Industrial flares are safety devices designed to combust large emergency releases of hydrocarbons. However, emergency events are rare, and most flare operations occur at flow rates much lower than the maximum flare capacity. A key assumption had been that flares operating over the range of requirements stated in Title 40 Code of Federal Regulations (CFR) §60.18 achieve the assumed hydrocarbon destruction and removal efficiency (DRE) of 98-99 percent at varying vent gas flow rate turndown, assist ratios, and vent gas heat content. The TCEQ 2010 Flare Study (Tracking #2010-04) and AQRP Project 14-009 (Task 1; Allen and Torres, 2011) were designed to explore flare DRE performance. Field tests were conducted at the John Zink Company, LLC flare test facility in Tulsa, Oklahoma, to measure flare emissions and to collect process and operational data in a semi-controlled environment to determine the relationship between flare design, operation, vent gas lower heating value (LHV) and flow rate, destruction and removal efficiency (DRE), and combustion efficiency (CE). The tests indicated that at low flow rates, and with low heating value gases, standard emission estimation methods understated emissions if excess steam or air-assist was used. The most efficient industrial flare operation, as measured by the DRE and combustion efficiency (CE), was achieved at or near the incipient smoke point (Allen and Torres, 2011; Torres et al., 2012a; Torres et al., 2012b). Minimum levels of steam or air assist that complied with the flare manufacturer's recommendations should be used when possible. Air quality modeling of theoretical scenarios associated with low flaring destruction efficiencies showed that the majority of the ozone formation associated with low destruction efficiency flares was due to the unburned gases sent to the flare, rather than products of incomplete combustion (e.g., formaldehyde) (Al-Fadhli et al., 2011; Herndon et al., 2012). Field observations during the Formaldehyde and Olefin from Large Industrial Sources (FLAIR) campaign in Houston and Texas City in 2009 supported these findings (Parrish et al., 2012; AQRP Project 10-045, Stutz et al., 2011). The projects supported the development of remote sensing technologies, such as Passive and Active Fourier Transform Infrared (PFTIR, AFTIR)

Spectroscopy (Allen and Torres, 2011), and modeling techniques (e.g. AQRP Project 10-009 (Task 2), Rawlings et al., 2011; AQRP Project 10-022, Chen et al., 2011; Singh et al., 2012; Lou et al., 2012) that offered approaches for improving the detection, monitoring, and evaluation of flare operational conditions. Notably, the projects led to the development of a supplemental online flare operations training for plant personnel who monitor elevated, industrial-scale chemical and petrochemical flares (<https://sfot.ceer.utexas.edu>).

Most recently, on April 20, 2015, EPA revised AP-42 emission factors for refinery and chemical plant flaring operations as a result of a consent decree with environmental groups (http://www.epa.gov/ttn/chief/consentdecree/index_consent_decree.html). Revised emission factors for VOCs from affected flaring operations are substantially higher than previous emissions estimates.

Wildland fires and open burning

Wildland fires and open burning can be substantial sources of ozone precursors and particulate matter. The influence of fire events on air quality in Texas has been well documented by observational and modeling studies (e.g., Junquera et al., 2005; Morris et al., 2006; McMillan et al., 2010; Villanueva-Fierro et al., 2009; Kembell-Cook et al., 2014). The Fire INventory from NCAR (FINN) is a global fire emissions model that estimates daily emissions of trace gases and particles from open biomass burning. FINN is widely used in global and regional modeling studies (Wiedinmyer et al., 2011). FINN v.1 was released in 2010 and updated in 2011. FINN v.1.5 was released in 2014. AQRP Project 12-018 (McDonald-Buller et al., 2013) evaluated the sensitivity of FINN v.1 emissions estimates to the variability in input parameters and investigated the effects on modeled air quality using the Comprehensive Air Quality Model with Extensions (CAMx). Sensitivity studies used different input data sources for land cover, emission factors, fire detection, burned area, and fuel loading in FINN. The project found that variability in fire emissions is season- and region- dependent in the United States, and differences in emissions estimates due to varying input data resources could exceed a factor of two. The use of the different estimates of fire emissions had substantial impacts on predictions of ozone and fine particulate matter concentrations in Texas and other regions of the United States.

AQRP Project 14-011 (McDonald-Buller et al., 2015) conducted targeted improvements to the FINN model to benefit the global and regional air quality management and research communities, with a special focus on needs for Texas. A new algorithm for estimating area burned from satellite-derived fire detections was developed and incorporated into FINN to address a known under-prediction bias for area burned. Improvements in the area burned estimation were accompanied by better spatial resolution in the characterization of land cover, new fuel loading data with greater spatial resolution for the United States, and incorporation of new satellite-based estimates of barren land and vegetative cover. Crop-specific emission factors and fuel loadings were added to FINN as an option for users that have a land cover data resource that distinguishes major crop types typically found in the United States. These modifications have formed the basis of the next generation of the FINN model, FINN v.2. Annual emissions estimates were generated for 2012 to support TCEQ air quality modeling efforts. An approach was also developed for partitioning NO_x emissions estimates from FINN into aged NO_z forms (i.e., nitrogen dioxide [NO₂], nitric acid [HNO₃], peroxyacetyl nitrate [PAN], C₃ and higher peroxyacetyl nitrates, and organic nitrates) to account for rapid NO_x oxidation in fire plumes.

In addition, the project examined the sensitivity of FINN v.2 emissions estimates and predictions of regional air quality to land cover characterization. The MODIS Land Cover Type (LCT) product has been used as the default resource for land cover characterization in FINN, but new global, U.S. national, and Texas regional products are now available alternatives. These include the United Nations Global Land Cover (GLC-SHARE) and European Space Agency (ESA) Climate Change Initiative global data products, the U.S. Forest Service Fuel Characteristic Classification System (FCCS), the U.S. Department of Agriculture National Agricultural Statistical Service Cropland Data Layer (CDL), and a Texas (TCEQ) regional land cover product developed by Popescu et al. (2011). Differences between simulations highlighted the complex sensitivity of emissions estimates from the FINN model to various land cover inputs and associated fuel loadings and emission factors. At this time, McDonald-Buller et al. (2015) recommended use of the following combination of land cover products in FINN to support Texas air quality modeling activities: the Texas regional land cover product with the Cropland Data Layer, the U.S. Forest Service FCCS in the continental U.S., and the MODIS LCT product elsewhere. This combination provides the greatest spatial resolution and specificity in land cover and fuel loadings for the Texas regional domain and continental U.S. However, it is important to recognize the range of FINN emissions estimates that can be obtained with different land cover products and the strong need for *in situ* evaluation of fuel loadings.

Biogenic hydrocarbons

Biogenic volatile organic compounds (BVOCs), in particular isoprene (2-methyl-1, 3-butadiene, C₅H₈) and monoterpenes (a class of terpenes composed of two isoprene units), have been widely recognized for their key roles in atmospheric chemistry and climate, including contributions as precursors for tropospheric ozone (Atkinson, 2000) and secondary organic aerosol (SOA) formation (Tsingaridis and Kanakidou, 2003; Claeys et al., 2004). Globally, isoprene and monoterpenes have been estimated to comprise 70% and 11%, respectively, of total annual BVOCs emitted from vegetation (Sindelarova et al., 2014). Average Texas statewide VOC emissions reported in the EPA 2011 National Emission Inventory (Version 1) were ranked first within the continental United States at approximately 11,650 and 4,600 tons per day for biogenic and anthropogenic emissions, respectively.

Emissions of biogenic VOCs exhibit strong diurnal variability with temperature and sunlight and spatial gradients due to differences in land use and land cover. For example, observations made by Gilman et al. (2009) aboard the NOAA R/V Brown during TexAQS II/GoMACCS, indicated that BVOCs accounted for up to 20% of the VOC reactivity during the afternoon in the Houston-Galveston-Brazoria area. In sensitivity studies using a regional chemical transport model during the TexAQS 2000 time period, Li et al. (2007) found changes in ozone concentrations of ± 5 to 25 ppb over the Houston urban area and ± 5 to 10 ppb over the Houston Ship Channel in response to changes in isoprene emissions locally or from regions to the north of Houston. Characterization of land use and land cover has been an on-going priority of research in Texas since the late 1990s (e.g., Wiedinmyer et al., 2001; Feldman et al., 2010; Popescu et al., 2011). Land cover in Texas is highly diverse, varying from dense forest in East Texas to grasses and croplands towards the central regions. Huang et al. (2015a) found that misclassification between trees and grasses/crops has the potential to lead to large differences in biogenic emission estimates and maximum daily 8-hour ozone concentrations.

The TCEQ has relied on the Global Biosphere Emissions and Interactions System (GloBEIS3.1; <http://www.globeis.com/>) for estimating biogenic emissions for a number of years but has recently transitioned to the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2012). AQRP projects have provided information about the uncertainties, sensitivities, and potential improvements to MEGAN under varying climatic conditions. These projects have evaluated current soil moisture representations using simulated and observational soil moisture datasets and explored the sensitivity of isoprene emission estimates to alternative representations of soil moisture (AQRP Project 14-008, McGaughey et al., 2015); evaluated the default drought parameterization scheme in MEGAN through comparisons with isoprene field measurements and investigated the use of different emission factor fields in MEGAN (AQRP Project 14-030, Ying et al., 2015); developed quantitative estimates of isoprene and monoterpene emissions with updated land cover and emission factor inputs using airborne measurements (AQRP Project 14-016, Yarwood et al., 2015) and generated a satellite-derived Photosynthetically Active Radiation (PAR) product, which is a requisite parameter for biogenic emissions models (AQRP Project 14-017, Pour Biazar et al., 2015).

Through the AQRP projects, essential inputs to the MEGAN model, including leaf area index, plant functional type characterization, and emission factors, have been updated based on available recent ground survey, remote sensing, and land surface model data products, and aircraft measurements during the DISCOVER-AQ campaign. MEGAN predictions of isoprene and monoterpene emissions have demonstrated a persistent high bias compared with aircraft flux data, suggesting large uncertainties still exist with the input data (e.g. Warneke et al., 2010). Predictions from air quality models such as CAMx and the Community Multi-scale Air Quality Modeling System (CMAQ) that have used MEGAN for biogenic emissions estimates in Texas have generally demonstrated a high bias in isoprene and ozone concentrations relative to aircraft and/or ground observations (Kota et al., 2015). Other studies over different global regions have evaluated MEGAN estimates of isoprene emissions using ground and aloft observations (e.g., Müller et al., 2008; Langford et al., 2010; Geng et al., 2011) aircraft measurements (e.g. Song et al., 2008; Warneke et al., 2010; Carlton et al., 2011), and satellite derived formaldehyde data (e.g. Palmer et al., 2006; Millet et al., 2008; Müller et al., 2008). MEGAN isoprene estimates have exhibited both high and low biases relative to observational data.

Biases in MEGAN estimates have been attributed to uncertainties in default emission factors (e.g. Langford et al., 2010; Ferreira et al., 2010), land cover data (e.g., Geng et al., 2011), spatial and temporal resolution of climate data (Pugh et al., 2013; Ashworth et al., 2010), and simulation of solar radiation and temperatures by the Weather Research and Forecast (WRF) model associated with the underestimation of aerosols and clouds, among other factors. AQRP projects have aimed at improving MEGAN estimates and understanding the implications on photochemical model predictions. Ying et al. (2015), for example, indicated that the use of emission factor fields from BEIS v3.61 and its input data (BELD4) could significantly improve MEGAN's capabilities in reproducing the observed isoprene concentrations at locations in Texas. Pour Biazar et al. (2015) found that use of satellite-derived PAR in MEGAN resulted in lower isoprene emissions estimates (by 15%~29%) relative to PAR fields derived from WRF over Texas climate regions during August and September of 2013. Sensitivity studies by Yarwood et al. (2015) examined the effects of altering the chemical mechanism, dry deposition

velocities for biogenic trace gases, and emission factors in the photochemical model CAMx on concentrations of a subset of species (isoprene, isoprene products, sum of monoterpenes, ozone, OH); the results indicated the need for further verification of emission factors, reconciliation of substantial differences between leaf-, tower-, aircraft-, and satellite-based emission estimates, use of assimilation approaches (satellite and/or in-situ observations) for improving solar radiation and temperature inputs to MEGAN, and application of current land cover data.

Extreme climate events such as severe drought are a recurring phenomenon in Texas and have the potential to affect regional air quality through stresses to biogenic systems. Despite previous leaf- and ecosystem-level studies, the impact of drought on biogenic emissions (primarily isoprene) remains somewhat controversial. Limited ecosystem-level studies have shown stimulated isoprene emissions under drought conditions (Pressely et al., 2006) as well as short-term increases followed by long-term decreases (Potosnak et al., 2014). MEGAN estimates of biogenic emissions are influenced by competing effects of model input parameters (i.e. reductions in leaf area index and soil moisture may lead to negative impacts on isoprene emissions while elevated temperatures may enhance emissions during drought; Huang et al., 2015b) and also uncertainties in input data. The parameterization of water stress on plants during drought in MEGAN is based on soil moisture and wilting point; predicted isoprene emissions have been shown to be highly sensitive to the specific soil moisture database employed (AQRP Project 14-008, McGaughey et al., 2015). Observations of soil moisture in much of eastern Texas are sparse, although NASA's Soil Moisture Active Passive (SMAP) satellite mission and the Texas Soil Observation Network (TxSON) should result in new data resources in the future.

Emissions of Highly Reactive Volatile Organic Compounds (HRVOCs)

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 $29\% \pm 20\%$ 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., $\text{C}_2\text{H}_4/\text{NO}_x$ and $\text{C}_3\text{H}_6/\text{NO}_x$) over the same time period indicated decreases of $30\% \pm 30\%$; 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, measurements during TexAQS 2000 and TexAQS II indicate that the best emission inventories significantly underestimate industrial VOC emissions in Houston (e.g., Ryerson et al., 2003; De Gouw et al., 2009; Parrish et al., 2009; Mellqvist et al., 2010; Washenfelder et al., 2010; Kim et al., 2011). For example, Washenfelder et al. (2010) had found that measured ratios of $\text{C}_2\text{H}_4/\text{NO}_x$ and $\text{C}_3\text{H}_6/\text{NO}_x$ exceeded emission inventory values by factors of 1.4-20 and 1-24, respectively.

During 2009 (SHARP, Lefer, 2009), 2011 (AQRP Project 10-006, Johansson et al., 2013) and 2013 (DISCOVER-AQ, AQRP Project 13-005, Johansson et al., 2013; AQRP Project 14-007, Johansson et al., 2015), atmospheric VOC gas columns downwind of specific local source regions in the Houston area have been repeatedly investigated using a combination of mobile Differential Optical Absorption Spectroscopy (DOAS) and Solar Occultation Flux (SOF). Johansson et al. (2014) reported that although alkane emissions between 2006 and 2011 were

generally stable, emissions of ethene and propene have declined. For example, measurements downwind of the Houston Ship Channel indicated ethene and propene emissions during 2006 of 1511 kg h⁻¹ and 878 kg h⁻¹, respectively, compared to approximately 600 kg h⁻¹ for both species during both 2009 and 2011. In the most recent analysis of limited mobile DOAS sampling performed in Houston during DISCOVER-AQ (2013), Johansson et al. (2015) found additional decreases in alkene concentrations; for example, Houston Ship Channel emissions for ethene and propene were estimated at 475 kg h⁻¹ and 394 kg h⁻¹, respectively. However, the authors noted that measured VOC emissions were 5-15 times higher than those based on year-specific emission inventories, while for SO₂ and NO₂ the ratios were typically 0.5–2 (Johansson et al., 2014). The results of Johansson et al. (2014) were generally consistent with those from previous studies for Houston that have suggested an under representation of alkenes within emissions inventories of up to an order of magnitude (e.g., the findings of Mellqvist et al. (2010), which were based only on SOF measurements collected during 2006, as well as Air Quality Project 10-045 (Stutz et al., 2011) which estimated ethene and propene emissions using inverse modeling and in-situ observations collected during 2009).

Barnett Shale 2011 field campaign

The Barnett Shale is an oil and gas production region located largely to the west of the Dallas area that saw rapid expansion and economic growth between 2005 and 2010. An AQRP-sponsored field campaign conducted in 2011 sought to better understand the effects of Barnett Shale activity on air quality in the region. Aircraft measurements collected by AQRP Project 10-044 (Alvarez et al., 2011) 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 Dallas-Fort Worth and Barnett Shale emissions that would alter the VOC/NO_x 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, such as immediately downwind of a large compressor station in the Eagle Mountain Lake area.

Fourier Transform InfraRed Spectroscopy (FTIR) and canister sampling analysis performed by AQRP Project 10-006 (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); however, high ethene concentrations have not been observed in other contemporary studies (e.g., Sullivan, 2010; TITAN, 2010; Zielinska et al., 2011). The largest oil and gas sources of methane and other hydrocarbon emissions near Fort Worth were gas treatment facilities combined with large compressor stations. Flashing emissions on one occasion from a condensate tank were estimated at 140 kg/h for methane and 10 kg/h for ethane (among other species).

Deployment of the Measurement of Ozone Production Sensor (MOPS) during August – October 2011 at the Meacham site near Dallas-Fort Worth by AQRP Project 10-034 (Lefer and Brune, 2011) showed that ozone production on sunny days peaked at 40-60 ppbv/h during mid-morning, suggesting that Meacham may be an ozone source region. 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. Findings from AQRP Project 10-024 (Griffin et al., 2011) suggested that the air masses transported to Eagle Mountain Lake were aged and originated over

the Dallas-Fort Worth metropolitan area; the impact of local sources were detected only intermittently. Aircraft measurements collected by Alvarez et al., (2011) within the photochemically aged plume downwind of Dallas-Fort Worth showed modest concentrations of NO, NO₂, and reactive alkenes and indicated enhancements in maximum ozone concentrations by factors ranging from 1.5-2.5 relative to upwind concentrations.

Satellite observations of NO₂ column densities

Nitrogen oxides are precursors to both ozone and fine particulate matter. Over the past decade, anthropogenic NO_x emissions have declined substantially due, largely, to reductions from mobile and stationary point sources (e.g., <http://www.epa.gov/ttnchie1/trends/>); between 2005 and 2014, NO_x emissions reported to EPA's National Emission Inventory (NEI) indicated that U.S. anthropogenic emissions have declined by approximately 39%. Emissions from point sources, such as electric generating units, are commonly measured directly using continuous emission monitors (CEMs); however, other spatially distributed NO_x sources and the sparseness of ground-level monitoring present challenges in tracking the spatial and temporal variations in emissions.

Satellite NO₂ column observations provide an effective proxy to infer NO_x emissions from surface-based sources (e.g., Boersma et al., 2008a; Lamsal et al., 2011, 2015; Streets et al., 2013; Tang et al., 2013; Vinken et al., 2014, among many others) and are widely used to estimate trends (e.g., Boersma et al., 2008b; Russell et al., 2012; Zhou et al., 2012; Schneider et al., 2015, among many others). In a study focused on eastern Texas, McDonald-Buller et al. (2012) found that NO₂ column densities were highest over urban areas and highway corridors and had decreases between 2005 and 2010 in reasonable agreement with changes in ground-based observations. A comparison of trends between satellite observations and results from photochemical modeling indicated largest differences in rural regions suggesting possible underestimation of emissions associated with oil and gas activities. More recent studies have also demonstrated declines in NO₂ column densities during the past decade within various eastern Texas metropolitan areas (e.g., Choi and Souri, 2015; Lamsal et al., 2015; Tong et al., 2015). Lamsal et al. (2015) estimated that atmospheric NO₂ concentrations over Dallas and Houston decreased by 35-40% between 2005 and 2013 and noted the importance of accounting for seasonal and interannual variability in the vertical concentration profiles required by standard satellite retrieval algorithms. Further analyses using a high-resolution chemical transport model suggested that emissions reductions were greater during 2005-2010 compared to 2010-2013.

Although uncertainties remain (e.g., refer to review by Streets et al., 2013), NO₂ column retrievals are widely used to constrain emissions inventories for global and regional modeling (e.g., Boersma et al., 2008a; Kim et al., 2009; Lin et al., 2010; Tang et al., 2013; 2015; Vinken et al., 2014). In studies for Texas, Tang et al. (2013, 2015) found that a regionally-based inversion approach to adjust NO_x emissions deteriorated model performance (as evaluated by comparison to ground-based measurements) while an emission sector-based methodology showed some improvement. AQR Project 13-TN2 (Kim et al., 2013) developed techniques and software that can be used to more efficiently process and integrate geo-spatial datasets with air quality modeling predictions; for example, urban emission features can be refined by downscaling and re-gridding relatively coarse resolution GOME-2 column NO₂ observations using fine-scale photochemical model (CMAQ) predictions. AQR Project 14-014 (Choi and Li, 2015) used a

sector-based inversion methodology and NO₂ columns derived from Ozone Monitoring Instrument (OMI) observations to downwardly adjust an NEI inventory with a known high bias. Additional treatment of the OMI dataset included adjustments for cloud fraction, solar angle, and, importantly, removal of the a priori “first-guess” influences in the vertical concentration profiles. The adjustments to the inventory, which reduced emissions from anthropogenic sectors and increased emissions associated with biogenic activity, showed improved agreement with available surface and aircraft observations. However, a recent study by Kembball-Cook et al. (2015) noted large differences in top-down emissions using two different operational products derived from the same satellite dataset suggesting high sensitivity to the specific dataset employed.

2.2.3 References

AQRP Projects:

AQRP Project 10-006: Johansson J., J. Mellqvist, J. Samuelsson, B. Offerle, B. Rappenglück, D. Anderson, B. Lefer, S. Alvarez, and J. Flynn, (2011), Quantification of industrial emissions of VOCs, NO₂ and SO₂ by SOF and mobile DOAS, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-009 (Task1): Allen, D.T., and V.M. Torres, (2011), TCEQ Flare Study, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-009 (Task2): Rawlings, B.C., O.A. Ezekoye, and T.F. Edgar, (2011), Additional test days for TCEQ 2010 flare study, modeling of flare performance using multivariate image analysis and computational fluid dynamics, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-022: Chen, D., Lou, H., Li, K., Martin, C., and X.C. Li, (2011), Development of speciated industrial flare emission inventories for air quality modeling in Texas, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-024: Griffin, R., J. Dibb, B. Lefer, and A. Steiner, (2011), Surface measurements and one-dimensional modeling related to ozone formation in the suburban Dallas-Fort Worth area, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-034: Lefer B., and W. Brune (2011), Dallas measurement of ozone production sensor (MOPS), Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-044: Alvarez, S., G.P. Roberts, G. Zanin, M.E. Shauck, and B. Rappenglueck, (2011), Airborne measurements to investigate ozone production and transport in the Dallas-Fort Worth (DFW) area during the 2011 ozone season, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-045: Stutz, J., O. Pikelnaya, G. Mount, E. Spinei, S. Herndon, E. Wood, O. Oluwole, W. Vizuette, and E. Causo, (2011), Quantification of hydrocarbon, NO_x, and SO₂ emissions from petrochemical facilities in Houston: Interpretation of the 2009 FLAIR dataset, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 12-018: McDonald-Buller, E., Y. Kimura, C. Wiedinmyer, and C. Emery, (2013), The effects of uncertainties in fire emission estimates on predictions of Texas air quality, Prepared for the Texas Air Quality Research Project, <http://aqrp.ceer.utexas.edu/>

AQRP Project 13-005: Johansson, J., J. Mellqvist, J. Samuelsson, B. Offerle, P. Andersson, B. Lefer, J. Flynn, and S. Zhuoyan, (2013), Quantification of industrial emissions of VOCs, NO₂ and SO₂ by SOF and Mobile DOAS during DISCOVER-AQ, Prepared for the Texas Air Quality Research Program <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-007: Johansson J., J. Mellqvist, P. Andersson, B. Lefer, J. Flynn, and L. Judd, (2015), Analysis of VOC, NO₂, SO₂ and HCHO data from SOF, mobile DOAS, and MW-DOAS during DISCOVER-AQ, Prepared for the Texas Air Quality Research Program <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-008: McGaughey, G., Y. Kimura, L. Huang,, E. McDonald-Buller, Y. Sun, and R. Fu, (2015), Soil moisture characterization for biogenic emissions modeling in Texas, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-011: McDonald-Buller, E., Y. Kimura, C. Wiedinmyer, C. Emery, Z. Liu, and G. Yarwood, (2015), Targeted Improvements in the Fire INventory from NCAR (FINN) model for Texas air quality planning, Prepared for the Texas Air Quality Research Project, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-014: Choi, Y. and X. Li, (2015), Constraining NO_x emissions using satellite NO₂ column measurements over the southeast Texas, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-016: Yarwood, G., A. Guenther, J. de Gouw, and D. Parrish, (2015), Improved land cover and emission factor inputs for estimating biogenic isoprene and monoterpene emissions for Texas air quality simulations, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-017: Pour Biazar, A., R.T. McNider, and D. Cohan, (2015), Incorporating space-borne observations to improve biogenic emission estimates in Texas, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-030: Ying, Q., G.W. Schade, J. Nielsen-Gammon, and H. Gao, (2015), Improving modeled biogenic isoprene emissions under drought conditions and evaluating their impact on ozone formation, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 12-TN2: Kim H.C., F. Ngan, P. Lee, and D. Tong, (2013), Development of an IDL-based geospatial data processing framework for meteorology and air quality modeling, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

Other:

Al-Fadhli, F.M., Y. Kimura, E. McDonald-Buller, and D. Allen, (2011), 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. Vizuite, T. Edgar, H. Jeffries, B. Kim, M. Webster, and M. Symons, (2004), 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., and V.M. Torres, (2011), TCEQ Flare Study Project, Final Report. Available: <http://www.tceq.texas.gov/assets/public/implementation/air/rules/Flare/TCEQ2010FlareStudyDraftFinalReport.pdf>, August 2011.

Ashworth, K., O. Wild, and C.N. Hewitt, (2010), Sensitivity of isoprene emissions estimated using MEGAN to the time resolution of input climate data. *Atmospheric Chemistry and Physics*, 10(3), 1193-1201.

Atkinson, R. (2000), Atmospheric chemistry of VOCs and NO_x, *Atmospheric Environment*, 34(12), 2063-2101.

Boersma, K.F., D.J. Jacob, E.J. Bucsela, A.E. Perring, R. Dirksen, R.J. van der A, R.M. Yantosca, R.J. Park, M.O. Wenig, T.H. Bertram, and R.C. Cohen, (2008a), Validation of OMI tropospheric NO₂ observations during INTEX-B and application to constrain NO_x emissions over the eastern United States and Mexico, *Atmospheric Environment*, 42, 4480-4497.

Boersma, K.F., D.J. Jacob, H.J. Eskes, R.W. Pinder, I. Wang, J., and R.J. van der A, (2008b), Intercomparison of SCIAMACHY and OMI tropospheric NO₂ columns: observing the diurnal evolution of chemistry and emissions from space, *Journal of Geophysical Research*, 113 <http://dx.doi.org/10.1029/2007JD008816>.

Carlton, A.G., and K.R. Baker, (2011), Photochemical modeling of the Ozark isoprene volcano: MEGAN, BEIS, and their impacts on air quality predictions. *Environmental Science & Technology*, 45(10), 4438-4445.

Claeys, M., B. Graham, G. Vas,, W. Wang, R. Vermeylen, V. Pashynska, J. Cafmeyer, P. Guyon, M.O. Andreae, P. Artaxo, and W. Maenhaut, (2004), Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, 303(5661), 1173-1176.

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, and X. Zhu, (2009), Airborne measurements of ethene from industrial sources using Laser Photo-Acoustic Spectroscopy. *Environmental Science & Technology*, 43, 2437–2442.

Feldman, M.S., T. Howard, T., E. McDonald-Buller, G. Mullins, D.T. Allen, A. Hansel, and A. Wisthaler, (2010), Applications of satellite remote sensing data for estimating biogenic emissions in southeastern Texas, *Atmospheric Environment*, 44(7), 917-929.

Ferreira, J., C.E. Reeves, J.G. Murphy, L. Garcia-Carreras, D.J. Parker, and D.E. Oram, (2010), Isoprene emissions modelling for West Africa: MEGAN model evaluation and sensitivity analysis, *Atmospheric Chemistry and Physics*, 10(17), 8453-8467.

Geng, F., X. Tie, A. Guenther, G. Li, J. Cao, and P. Harley, (2011), Effect of isoprene emissions from major forests on ozone formation in the city of Shanghai, China. *Atmospheric Chemistry and Physics*, 11(20), 10449-10459.

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, and J.A. de Gouw, (2009), 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: Atmospheres*, 114(D7).

Guenther, A. B., X. Jiang, C.L. Heald, T. Sakulyanontvittaya, T. Duhl, L.K. Emmons, and X. Wang, (2012), The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): An extended and updated framework for modeling biogenic emissions, *Geoscientific Model Development Discussions*, 5, 1503-1560.

Henderson, B.H., H.E. Jeffries, B.-U. Kim, and 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., D.D. Nelson, Jr., E.C. Wood, W.B. Knighton, C.E. Kolb, Z. Kodosh, V.M. Torres, and D.T. Allen, (2012), Application of the Carbon Balance Method to Flare Emissions Characteristics, *Industrial & Engineering Chemistry Research*, 51(39), 12577-12585, doi: 10.1021/ie202676b

Huang, L., E. McDonald-Buller, G. McGaughey, Y. Kimura, and D.T. Allen, (2015a), Comparison of regional and global land cover products and the implications for biogenic emissions modeling, *Journal of the Air & Waste Management Association*, doi: 10.1080/10962247.2015.1057302

Huang, L., G. McGaughey, E. McDonald-Buller, Y. Kimura, and D.T. Allen, (2015b), Quantifying regional, seasonal and interannual contributions of environmental factors on isoprene and monoterpene emissions estimates over eastern Texas, *Atmospheric Environment*, 106, 120-128.

Johansson, J.K.E., J. Mellqvist, J. Samuelsson, B. Offerle, B. Lefer, B. Rappenglück, J. Flynn, and G. Yarwood, (2014), Emission measurements of alkenes, alkanes, SO₂, and NO₂ from stationary sources in Southeast Texas over a 5 year period using SOF and mobile DOAS, *Journal of Geophysical Research Atmospheres*, 119, 1973–1991, doi:10.1002/2013JD020485.

Junquera, V., M.M. Russell, W. Vizuete, Y. Kimura, and D. Allen, (2005), Wildfires in Eastern Texas in August and September 2000: Emissions, aircraft measurements, and impact on photochemistry, *Atmospheric Environment*, 39(27), 4983-4996, 2005.

Kemball-Cook, S., T. Pavlovic, J. Johnson, L. Parker, D.J. Rasmussen, J. Zagonis, L. Ma, and G. Yarwood., (2014), Analysis of wildfire impacts on high ozone days in Houston, Beaumont, and Dallas-Fort Worth during 2012 and 2013, Final report for WO582-11-10365-FY14-19, prepared for the Texas Commission on Environmental Quality, Austin, TX, by ENVIRON International Corporation, Novato, CA (July 2014).

Kemball-Cook, S., G. Yarwood, J. Johnson, B. Dornblaser, and M. Estes, (2015), Evaluating NO_x emission inventories for regulatory air quality modeling using satellite and air quality model data, *Atmospheric Environment*, 117: 1-8, doi: 10.1016/j.atmosenv.2015.07.002.

Kim, S.W., A. Heckel, G.J. Frost, A. Richter, J. Gleason, J.P. Burrows, S. McKeen, E.Y. Hsie, C. Granier, and M. Trainer, (2009), NO₂ columns in the western United States observed from space and simulated by a regional chemistry model and their implications for NO_x emissions, *Journal of Geophysical Research*, 114, D11301. <http://dx.doi.org/10.1029/2008JD011343>.

Kim, S.-W., S.A. McKeen, G.J. Frost, S.-H. Lee, M. Trainer, A. Richter, W.M. Angevine, E. Atlas, L. Bianco, K.F. Boersma, J. Brioude, J.P. Burrows, J. de Gouw, A. Fried, J. Gleason, A. Hilboll, J. Mellqvist, J. Peischl, D. Richter, C. Rivera, T. Ryerson, S. te Lintel Hekkert, J. Walega, C. Warneke, P. Weibring, and E. Williams, (2011), Evaluations of NO_x and highly reactive VOC emission inventories in Texas and their implications for ozone plume simulations during the Texas Air Quality Study 2006, *Atmospheric Chemistry and Physics*, 11, 11361-11386, doi:10.5194/acp-11-11361-2011, 2011.

Kimura, Y., G. McGaughey, M. Feldman, D. T. Allen, and E. McDonald-Buller, (2012), Spatial and temporal variability in OMI NO₂ observations and NO_x emissions inventories in eastern Texas, *Air & Waste Management Association 104th Annual Conference & Exhibition*, San Antonio, TX, June 2012.

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

Kota, S., G. Schade, M. Estes, D. Boyer, Q. Ying, Evaluation of MEGAN predicted biogenic isoprene emissions at urban locations in Southeast Texas, *Atmospheric Environment*, 110, 54-64, doi: 10.1016/j.atmosenv.2015.03.027

Lamsal, L.N., B. Duncan, Y. Yoshida, N. Krotkov, K.E. Pickering, D. Streets, and Z. Lu, (2015), U.S. NO₂ trends (2005-2013): EPA Air Quality System (AQS) data versus improved observations from the Ozone Monitoring Instrument (OMI), *Atmospheric Environment*, 110, 130-143, doi:10.1016/j.atmosenv.2015.03.055.

Lamsal, L.N., R.V. Martin, A. Padmanabhan, A. van Donkelaar, Q. Zhang, C.E. Sioris, K. Chance, T.P. Kurosu, and M.J. Newchurch, (2011), Application of satellite observations for timely updates to global anthropogenic NO_x emission inventories, *Geophysical Research Letters*, 38, L05810. <http://dx.doi.org/10.1029/2010GL046476>.

Langford, B., P.K. Misztal, E. Nemitz, B. Davison, C. Helfter, T.A.M. Pugh, A.R. MacKenzie, S.F. Lim, and C.N. Hewitt, (2010), Fluxes and concentrations of volatile organic compounds from a South-East Asian tropical rainforest, *Atmospheric Chemistry and Physics*, 10(17), 8391-8412.

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, and R. Zhang, (2010), Overview and major findings of the Study of Houston Atmospheric Radical Precursors (SHARP) Campaign. American Geophysical Union, Fall Meeting 2010, abstract #A34C-05.

Li, G., R. Zhang, J. Fan, and X. Tie, (2007), Impacts of biogenic emissions on photochemical ozone production in Houston, Texas, *Journal of Geophysical Research Atmospheres*, 112(D10).

Lou, H., D. Chen, C. Martin, X. Li, K. Li, H. Vaid, K. Singh, and P. Gangadharan, (2012), Optimal reduction of the C1-C3 combustion mechanism for the simulation of flaring, *Industrial & Engineering Chemistry Research*, 51 (39), 12697-12705, October, 2012.

McMillan, W.W., R.B. Pierce, L.C. Sparling, G. Osterman, K. McCann, M.L. Fischer, B. Rappenglück, R. Newson, D. Turner, C. Kittaka, K. Evans, S. Biraud, B. Lefer, A. Andrews, and S. Oltmans, (2010), 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, D01301.

Mellqvist, J., J. Samuelsson, J.K.E. Johansson, C. Rivera, B. Lefer, S. Alvarez, and J. Jolly, (2010), Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method, *Journal of Geophysical Research*, 115, D00F17, doi:10.1029/2008JD011682.

Millet, D.B., D.J. Jacob, K.F. Boersma, T.M. Fu, T.P. Kurosu, K. Chance, C.L. Heald, and A. Guenther, (2008), Spatial distribution of isoprene emissions from North America derived from formaldehyde column measurements by the OMI satellite sensor, *Journal of Geophysical Research: Atmospheres*, 113(D2).

Morris, G.A., S. Hersey, A.M. Thompson, S. Pawson, J. E. Nielsen, P.R. Colarco, W.W. McMillan, A. Stohl, S. Turquety, J. Warner, B.J. Johnson, T. L. Kucsera, D. E. Larko, S.J.

- Oltmans, and J.C. Witte, (2006), Alaskan and Canadian forest fires exacerbate ozone pollution over Houston, Texas on 19 and 20 July 2004, *Journal of Geophysical Research*, 111, D24S03.
- Müller, J.F., T. Stavrou, S. Wallens, I.D. Smedt, M.V. Roozendaal, M.J. Potosnak, J. Rinne, B. Munger, A. Goldstein, and A.B. Guenther, (2008), Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model, *Atmospheric Chemistry and Physics*, 8(5), 1329-1341.
- Murphy, C.F., and D.T. Allen, (2005), Hydrocarbon emissions from industrial release events in the Houston-Galveston area and their impact on ozone formation, *Atmospheric Environment* 39 (2005), 3785-3798.
- Nam, J., Y. Kimura, W. Vizuete, C. Murphy, and D.T. Allen, (2006), Modeling the impact of emission events on ozone formation in Houston, Texas, *Atmospheric Environment* 40, 5329-5341.
- Nam, J., M. Webster, Y. Kimura, H. Jeffries, W. Vizuete, and D.T. Allen, (2008), Reductions in ozone concentrations due to controls on variability in industrial flare emissions in Houston, Texas, *Atmospheric Environment*, 42, 4198-4211.
- Nam, J., M. Webster, Y. Kimura, H. Jeffries, W. Vizuete, and D.T. Allen, (2008), Reductions in ozone concentrations due to controls on variability in industrial flare emissions in Houston, Texas, *Atmospheric Environment*, 42, 4198–4211.
- Olague, E. P., B. Rappenglück, B. Lefer, J. Stutz, J. Dibb, R. Griffin, W.H. Brune, M. Shauck, M. Buhr, H. Jeffries, W. Wiuete, and J.P. Pinto, (2009), Deciphering the role of radical precursors during the Second Texas Air Quality Study, *Journal of the Air & Waste Management Association* 59, 1258–1277.
- Palmer, P.I., D.S. Abbot, T.M. Fu, D.J. Jacob, K. Chance, T.P. Kurosu, A. Guenther, C. Wiedinmyer, J.C. Stanton, M.J. Pilling, S.N. Pressley, B. Lamb, and A.L. Sumner, (2006), Quantifying the seasonal and interannual variability of North American isoprene emissions using satellite observations of the formaldehyde column. *Journal of Geophysical Research Atmospheres*, 111(D12).
- 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, and E.J. Williams, (2009), 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.
- 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, and S.C. Herndon, (2012), Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region. *Atmospheric Chemistry and Physics*, 12, doi:10.5194/acp-12-3273-2012.

Pavlovic, R.T., E. McDonald-Buller, E., D.T. Allen, and G. Yarwood, (2009), 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, and D.T. Allen, (2010), 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, and E.C. McDonald-Buller, (2012a), Temporal variability in flaring emissions in the Houston-Galveston area, *Industrial & Engineering Chemistry Research*, 51, doi:10.1021/ie2013357.

Pavlovic, R.T., F.M. Al-Fadhli, Y. Kimura, D.T. Allen, E.C. McDonald-Buller, (2012b), Impacts of emission variability and flare combustion efficiency on ozone formation in the Houston-Galveston-Brazoria area, *Industrial & Engineering Chemistry Research*, 51, doi:10.1021/ie203052w.

Popescu, S. C., Stuke, J., Mutlu, M., Zhao, K., Sheridan, R., and N.W. Ku, (2011), Expansion of Texas land use/land cover through class crosswalking and lidar parameterization of arboreal vegetation secondary investigators, Retrieved June 8, 2015 from https://www.tceq.texas.gov/assets/public/implementation/air/am/contracts/reports/oth/5820564593FY0925-20110419-tamu-expansion_tx_lulc_arboreal_vegetation.pdf.

Potosnak, M. J., L. LeSturgeon, S.G. Pallardy, K.P. Hosman, L. Gu, T. Karl, C. Geron, and A.B. Guenther, (2014), Observed and modeled ecosystem isoprene fluxes from an oak-dominated temperate forest and the influence of drought stress, *Atmospheric Environment*, 84, 314-322.

Pressley, S., B. Lamb, H. Westberg, and C. Vogel, (2006), Relationships among canopy scale energy fluxes and isoprene flux derived from long-term, seasonal eddy covariance measurements over a hardwood forest, *Agricultural and Forest Meteorology*, 136(3), 188-202.

Pugh, T.A.M., K. Ashworth, O. Wild, and C.N. Hewitt, (2013), Effects of the spatial resolution of climate data on estimates of biogenic isoprene emissions, *Atmospheric Environment*, 70, 1-6.

Russell, A.R., L.C. Valin, and R.C. Cohen, (2012), Trends in OMI NO₂ observations over the United States: effects of emission control technology and the economic recession, *Atmospheric Chemistry and Physics*, 12, 12197-12209. <http://dx.doi.org/10.5194/acp-12-12197-2012>.

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, and D.T. Sueper, (2003), Effect of petrochemical

industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas, *Journal of Geophysical Research*, 108, doi:10.1029/2002JD003070.

Schneider, P., W.A. Lahoz, and R.J. van der A, (2015), Recent satellite-based trends of tropospheric nitrogen dioxide over large urban agglomerations worldwide. *Atmospheric Chemistry and Physics*, 15, 1205-1220. <http://dx.doi.org/10.5194/acp-15-1205-2015>.

Sindelarova, K., C. Granier, I. Bouarar, A. Guenther, S. Tilmes, T. Stavrou, J.-F. Muller, U. Kuhn, P. Stefani, and W. Knorr, (2014), Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years, *Atmospheric Chemistry and Physics*, 14(17), 9317-9341.

Singh, K., T. Dabade, H. Vaid, P. Gangadharan, D. Chen, H. Lou, X. Li, K. Li, and C. Martin, (2012), Computational fluid dynamics modeling of industrial flares operated in stand-by mode, *Industrial & Engineering Chemistry Research*, 51(39), 12611-12620.

Streets, D.G., G.R. Carmichael, B. de Foy, R.R. Dickerson, B.N. Duncan, D.P. Edwards, J.A. Haynes, D.K. Henze, M.R. Houyoux, D.J. Jacob, N.A. Krotkov, L.N. Lamsal, Y., Liu, Z. Lu, R.V. Martin, G.G. Pfister, R.W. Pinder, and K.J. Wecht, (2013), Emissions estimation from satellite retrievals: a review of current capability, *Atmospheric Environment*, 77, 1011-1042.

Song, J., W. Vizuete, S. Chang, D. Allen, Y. Kimura, S. Kemball-Cook, G. Yarwood, M.-A. Kioumourtzoglou, E. Atlas, A. Hansei, A. Wisthaler, and E. McDonald-Buller, (2008), Comparisons of modeled and observed isoprene concentrations in southeast Texas, *Atmospheric Environment*, 42(8), 1922-1940.

Sullivan, D. (2010), 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.

Tang, W., D. Cohan, L.N. Lamsal, X. Xiao, and W. Zhou, (2013), Inverse modeling of Texas NO_x emissions using space-based and ground-based NO₂ observations, *Atmospheric Chemistry and Physics*, 13, 11005-11018.

Tang, W., D. Cohan, A. Pour-Biazar, L.N. Lamsal, A. White, X. Xiao, W. Zhou, B.H. Henderson, and B.F. Lash, (2015), Influence of satellite-derived photolysis rates and NO_x emissions on Texas ozone modeling, *Atmospheric Chemistry and Physics*, 15, <http://dx.doi.org/10.5194/acpd-15-1601-2015>.

Texas Commission on Environmental Quality (TCEQ), TexAQS II emissions inventory files modeled for intensive period of August 15 through September 15, 2006, 2008 <ftp://ftp.tceq.state.tx.us/pub/OEPAA/TAD/Modeling/HGB8H2/ei/point/2006Aug15-Sept15/> (accessed Jan 2008).

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

Torres, V.M., X. Herndon, Z. Kodesh, and D.T. Allen, (2012a), Industrial flare performance at low flow conditions: Part 1. Study Overview, *Industrial & Engineering Chemistry Research*, 51 (39), 12559-12568, doi 10.1021/ie202674t.

Torres, V.M., S. Herndon, and D.T. Allen, (2012b), Industrial flare performance at low flow conditions: Part 2. Air and Steam assisted flares, *Industrial & Engineering Chemistry Research*, 51(39), 12569–12576, doi 10.1021/ie202675f.

Tsigaridis, K., and M. Kanakidou, (2003), Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis. *Atmospheric Chemistry and Physics*, 3(5), 1849-1869.

Villanueva-Fierro, I., C.J. Popp, R.W. Dixon, R.S. Martin, J.S. Gafney, N.A. Marley, and J.M. Harris, (2009), Ground-level chemical analysis of air transported from the 1998 Mexican-Central American fires to the Southwestern USA, *Revista Internacional de Contaminacion Ambiental*, 25(1), 23-32, 2009.

Vinken, G.C.M., K.F. Boersma, A. van Donkelaar, and L. Zhang, (2014), Constraints on ship NO_x emissions in Europe using GEOS-Chem and OMI satellite NO₂ observations. *Atmospheric Chemistry and Physics*, 14, 1353-1369. <http://dx.doi.org/10.5194/acp-14-1353-2014>.

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

Warneke, C., J.A. De Gouw, L. Del Negro, J. Brioude, S. McKeen, H. Stark, F. Fehsenfeld, C. Wiedinmyer, A. Guenther, and A.T. Hanks, (2010), 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 Atmospheres*, 115(D7), doi: 10.1029/2009JD012445.

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, and W. Zheng, (2010), Characterization of NO_x, SO₂, ethene, and propene from industrial emission sources in Houston, Texas, *Journal of Geophysical Research Atmospheres*, 115, D16311, doi:10.1029/2009jd013645.

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

Wiedinmyer, C., A. Guenther, M. Estes, I.W. Strange, G. Yarwood, and D.T. Allen, (2001), A land use database and examples of biogenic isoprene emission estimates for the state of Texas, USA, *Atmospheric Environment*, 35(36), 6465-6477.

Wiedinmyer, C., S.K. Akagi, R.J. Yokelson, L.K. Emmons, J.A. Al-Saadi, J.J. Orlando, and A.J. Soja, (2011), The Fire INventory from NCAR (FINN): A high resolution global model to estimate the emissions from open burning, *Geoscientific Model Development*, 4(3), 625-641.

Zhou, Y., D. Brunner, C. Hueglin, S. Henne, and J. Staehelin, (2012), Changes in OMI tropospheric NO₂ columns over Europe from 2004 to 2009 the influence of meteorological variability, *Atmospheric Environment*, 46, 482-495.

Zielinska, B., E. Fujita, and D. Campbell, (2010), 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

2.3.1 Overview

Atmospheric chemistry in Texas has a number of unique features. The combinations of industrial and urban emissions, and forested and coastal environments, cause certain chemical pathways to become more significant in Texas than in other regions. Specific findings arising from the AQRP program that address tropospheric chemistry under Texas conditions are summarized in this Section.

2.3.2 Tropospheric chemistry assessment from AQRP projects 2010-2015

NO_x sink and recycling reactions and gas-particle partitioning of organic nitrates

Reaction products arising from the oxidation of anthropogenic or biogenic volatile organic compounds can act to reduce the availability of NO_x for ozone formation by forming NO_x sink compounds, including organic nitrates and nitric acid. NO_x sink species may eventually react to return NO_x back to the atmosphere in a process known as NO_x recycling. Organic nitrates and their role as NO_x sink species, their participation in NO_x recycling reactions, and their gas-particle partitioning have been the subject of several coordinated studies involving experimental chamber measurements and photochemical modeling and have received increasing attention recently because of the implications for ozone and organic aerosol formation on local, regional, and global scales.

The chemistry of organic nitrates in the atmosphere has been reviewed in detail by Perring et al. (2013), AQRP Project 12-012 (Hildebrandt Ruiz and Yarwood, 2013), and elsewhere, and is summarized only briefly here. Organic nitrates (RONO₂) are primarily formed as products of the reaction of organic peroxy radical (RO₂) and nitric oxide (NO). RO₂ radicals arise from the oxidation of anthropogenic or biogenic volatile organic compounds (VOCs) by hydroxyl radical (OH), ozone (O₃), nitrate (NO₃) or photolysis. Although information for many compounds is not complete, the organic nitrate functionality and formation yields (α) depend upon the size and structure of the organic backbone (R) of the peroxy radical. For example, alkanes have higher reported yields than alkenes at an equivalent number of carbon atoms; yields generally increase with an increasing number of carbon atoms (Perring et al., 2013). Precursors to organic nitrates vary by location with anthropogenic and biogenic emission source regions (Perring et al., 2013). Larger RONO₂ molecules are semi-volatile and are expected to partition between the gas and particle phases. Gas-particle partitioning and hydrolysis of organic nitrates in the condensed phase influence their role as sources and sinks of NO_x. Once formed, organic nitrates can be transported, chemically processed, removed by deposition to vegetation and other surfaces, or partition into the aerosol phase, depending on their structure. Organic nitrates have sufficiently long atmospheric chemical lifetimes (hours to days) to be affected by regional or longer-range transport, such that they have the potential to influence NO_x budgets and air quality over extended spatial scales. For example, organic nitrates extend the range of downwind transport of NO_x and the potential for ozone formation on regional scales.

Recent advances have been made in understanding RONO₂ chemistry and gas-particle partitioning in ambient and laboratory studies (e.g., Rollins et al., 2010; Liu et al., 2012; Rollins et al., 2013; Rindelaub et al., 2015; Bean and Hildebrandt Ruiz, 2015; Lee et al., 2015) and early modifications to the chemical mechanisms have begun to represent these processes in CAMx and

other photochemical grid models. Environmental chamber experiments conducted as part of AQRP Project 10-042 (Yarwood et al., 2012) provided experimental evidence for NO_x production when organic nitrates degraded by OH reaction and photolysis and provided an initial foundation for modifications to the Carbon Bond mechanism in CAMx (CB6r1 mechanism). The CB6r2 mechanism was developed during AQRP Project 12-012 (Hildebrandt Ruiz and Yarwood, 2013) to improve the level of detail regarding the formation and fate of organic nitrates.

Influence of nitryl chloride chemistry on tropospheric oxidation capacity and ozone formation

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 (ClNO_2) and nitrate, which depends on, among other factors, particulate chloride (PCI) availability (Finlayson-Pitts et al., 1989; Behnke et al., 1997; Kercher et al., 2009; Osthoff et al., 2008; Thornton et al., 2010; Roberts et al., 2008). 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). Simpson et al. (2015) provide a comprehensive overview of the current understanding of the chemistry of nitryl halides in polluted regions. The presence of nitryl chloride has been characterized in the coastal environments of Houston during the 2006 TexAQS/Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS) (Osthoff et al., 2008) and the Los Angeles area during the 2010 CalNex campaign by Riedel et al. (2012) and Mielke et al. (2013), as well as for the inland regions of Boulder, Colorado (Thornton et al., 2010), Calgary, Alberta, Canada, (Mielke et al., 2011), southwestern Germany (Phillips et al., 2012), and the Uintah Basin of Utah (Edwards et al., 2013).

The influences of nitryl chloride production and chemistry on regional air quality and implications for air quality management have been examined using chemical transport models (e.g., Simon et al., 2009; Sarwar et al., 2012; Sarwar et al., 2014). Results of these studies have suggested increases in ozone due to ClNO_2 production are generally within 1-6 nmol/mol in the Northern Hemisphere with seasonal and spatial variations. AQRP Project 10-015 (Koo et al., 2012) developed an initial parameterized mechanism for ClNO_2 chemistry in CAMx, which has typically been used for regulatory air quality modeling in Texas. CAMx version 6.20 (v.6.20; http://www.camx.com/files/camxusersguide_v6-20.pdf) incorporates an extension of CB6r2 chemistry (CB6r2h) to address reactions involving ocean-borne halogen compounds. The CB6r2h includes updates to the chlorine (Cl) reaction mechanism of Koo et al. (2012) as well as reaction mechanisms for bromine and iodine (Yarwood et al., 2014).

Contribution of intermediate Volatile Organic Compounds (IVOCs) to secondary organic aerosol formation

Understanding the composition and sources of fine particulate matter ($\text{PM}_{2.5}$) in Houston is important to air quality planning as the region experiences concentrations close to the level of the NAAQS. Over half of fine particulate matter in the Houston region is composed of organic material including primary organic aerosol (POA), which is comprised of compounds that are emitted as particles and have not reacted in the atmosphere, and secondary organic aerosol (SOA), which is formed when gas-phase compounds undergo one or more chemical

transformations in the gas-phase, forming less volatile compounds that then partition between the gas- and particle-phases. These gas-phase precursors of SOA are classified (in decreasing order of vapor pressure/volatility) as volatile organic compounds (VOC), intermediate volatility organic compounds (IVOC) or semivolatile organic compounds (SVOC). Sources of organic aerosol (OA) in Houston include POA and SOA from urban anthropogenic activity, the petrochemical industry, and fires, as well as SOA from biogenic VOCs. The importance of organics in controlling fine PM mass in the Houston region has been recognized through ambient air quality data collection during field campaigns such as TexAQS 2000 and DISCOVER-AQ.

Recent studies have suggested the importance of intermediate volatile organic compounds as precursors of SOA (e.g., Ait-Helal, 2014; Yuan et al., 2013; Robinson et al., 2007). In a review of emissions inventories from the point source sector in Harris County, AQRP Project 14-024 (Hildebrandt Ruiz et al., 2015) identified butyl CARBITOL™ and methyl naphthalene as potential IVOCs, as well as compound mixtures associated with petrochemicals processing that could contain IVOCs. Hildebrandt Ruiz et al. (2015) found that of six IVOCs (n-pentadecane, 2,6,10-trimethyldodecane, 2-methylnaphthalene, butyl CARBITOL™, Texanol™, and mineral spirits) examined in laboratory chamber experiments, all but Texanol™ formed SOA.

A state of the science approach for modeling gas-aerosol partitioning and chemical aging of primary and secondary atmospheric organic aerosols based on the Volatility Basis Set (Donahue et al., 2006) has recently been added as an option in CAMx but has yet to be widely applied for air quality planning efforts in Texas. AQRP Project 14-024 used CAMx with the 1.5 dimensional volatility basis set (1.5-D VBS) to simulate organic aerosol formation in the Houston region during the 2013 DISCOVER-AQ campaign. The 1.5-D VBS scheme accounts for systematic variations in both volatility and oxidation state (O:C ratio) to model the magnitude and chemical aging of OA. Emissions of IVOCs from major combustion sources were added using IVOC fractions of total non-methane organic gas (NMOG) emissions estimated from environmental chamber studies. Analysis of ambient air quality data analysis during DISCOVER-AQ was used to guide model improvements; biases of modeled versus observed organic carbon and chemically aged oxygenated OA (OOA: anthropogenic and biogenic) were generally within 30% at Houston area sites.

Chemical pathways for secondary organic aerosol from isoprene

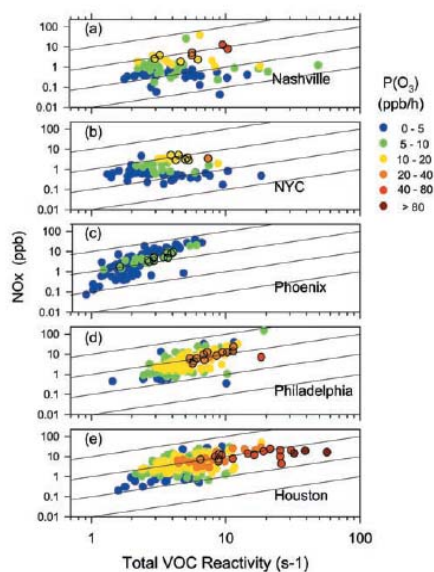
Within the last decade, it has been recognized that photochemical oxidation of isoprene leads to significant yields of gas-phase intermediates that contribute to SOA formation. The production of isoprene-derived SOA is enhanced by anthropogenic emissions, including NO_x and SO₂ typical of urban areas (Budisulistiorini et al., 2015; Surratt et al., 2006, Kroll et al., 2006). Recent studies have identified important reactive intermediates formed under low and high NO_x conditions (Surratt et al., 2006; Kroll et al., 2006) and the influence of varying aerosol acidity (Surratt et al., 2006; Surratt et al., 2010) and relative humidity (Carlton et al., 2009). Predictions of isoprene-derived SOA formation have required fundamental improvements in the gas and aerosol-phase chemical mechanisms in regional and global scale models and identified the need for evaluation of revised mechanisms against controlled chamber experiments (Chen et al., 2015; AQRP Project 14-003, Vizuete and Surratt, 2015); evaluation of model revisions against ambient measurements has indicated overall better performance in representing seasonal and spatial

patterns of biogenic SOA (Carlton et al., 2009; Karl et al., 2009; Baek et al., 2011; Ying et al., 2015; Li et al., 2015; Lin et al., 2013), although uncertainties remain.

Ozone production rates and efficiencies in the Houston Area

The proximity of NO_x and reactive VOC-rich plumes in Houston's extensive petrochemical complex lead to conditions that favor rapid ozone formation (e.g., Kleinman et al., 2002, 2005; Ryerson et al., 2003; Mao et al., 2010). During TexAQS 2000, ozone production rates and ozone production efficiencies (OPE) 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, comparisons 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.

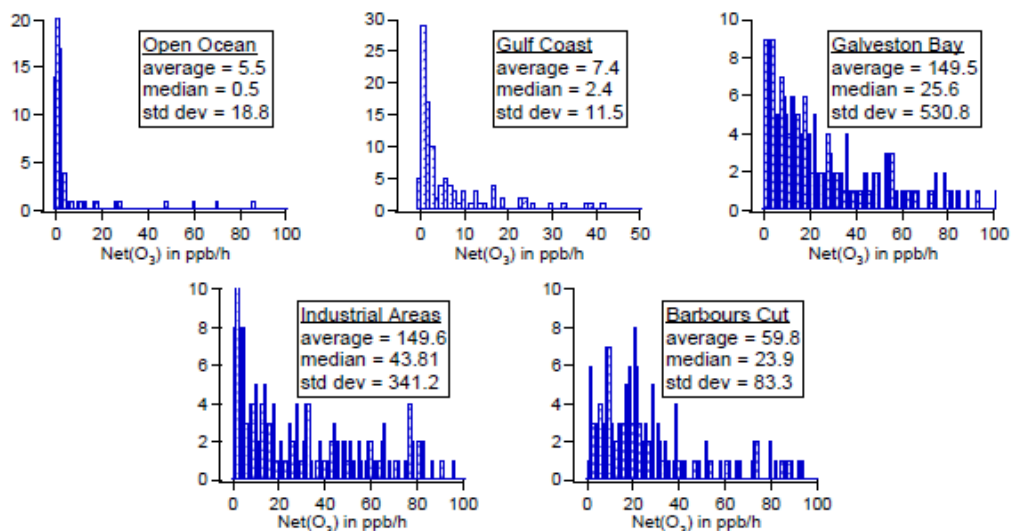
Figure 2.3.1. Ozone production rates for five U.S. cities in the style of an ozone isopleths diagram from Kleinman et al. (2005). Samples comprising the top 10% of the distribution in each city are outlined in bold.



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. More recently, AQR Project 13-024 (Ren et al., 2013) found OPEs of approximately 16 based on observations during the summer of 2013 at a Galveston monitoring location. Zhou et al. (2014) indicated that large OPEs (8–15) occurred in diluted industrial plumes transported over the isoprene-rich northern rural areas, while lower OPEs (5-7) are generally found in urban and industrial plumes transported southward. Using measurements collected aboard the NOAA P-3 during DISCOVER-AQ, AQR Project 14-020 (Ren, 2015) calculated an average OPE of approximately 8, which is greater than the value of 5.9 +/- 1.2 ppbv calculated for the TexAQS II (2006) period (Neuman et

al., 2009). Overall, these findings suggest that highly reactive air masses continue to be important in ozone formation in Houston, that the high reactivity is due to both anthropogenic and biogenic emissions, and that the locations of high ozone concentrations resulting from highly reactive emissions are variable, due to Houston's complex meteorology.

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.



AQRP Project 10-032 (Lefer et al., 2011) investigated ozone production sensitivity during three campaigns: TexAQS 2000 (late summer), TexAQS II Radical and Aerosol Measurement Program (TRAMP, fall 2006), and SHARP 2009 (spring), and found similar behavior across the campaigns, during which the early morning and late afternoon periods were most sensitive to VOC and NO_x, respectively. Lefer et al. (2011) noted that afternoon ozone sensitivity had a longer NO_x-sensitive period during SHARP 2009 compared to the results for 2000 and 2006 (e.g., Mao et al., 2010). Using measurements collected aboard the NOAA P-3 during DISCOVER-AQ and at eight surface sites where the P-3 conducted vertical spiral profiles, AQRP Project 14-020 (Ren, 2015) employed an observation-constrained box model based on the Carbon Bond mechanism, Version 5 (CB05), to investigate ozone production sensitivities. Across the surface sites, ozone formation ranged from VOC sensitive for the entire day at Deer Park to mostly NO_x sensitive at Smith Point and Conroe; Moody Tower and Channelview were either VOC sensitive or in the transition regime. Throughout the Houston area, overall ozone production tended to be VOC sensitive in the mornings with average rates of 20-30 ppbv hr⁻¹ and maximum rates of 30-50 ppbv h⁻¹; these relatively high rates suggested that VOC controls may be an effective way to control ozone in Houston. In the afternoon, average ozone production rates were 5-10- ppbv hr⁻¹ under mostly NO_x sensitive conditions but spatial variability existed.

Zhou et al. (2014) also noted that periods with the most rapid ozone formation were VOC-sensitive while slow ozone formation was NO_x-limited. Zhou et al. (2014) indicated that despite reductions in both NO_x and HRVOCs between 2000 and 2006 (e.g., Cowling et al., 2007;

Gilman et al., 2009; Washenfelder et al., 2010) that have reduced ozone production by 40-50% in Houston, OPEs were similar between the two periods consistent with results from previous studies (e.g., Cowling et al., 2007; Neuman et al., 2009). In an investigation of the impact of structural and parametric uncertainties on predicted ozone and precursor concentrations, AQRP Project 10-008 (Cohan et al., 2011) identified the importance of emission rates, reaction rate constants, and boundary conditions on predicted Dallas-Fort Worth area ozone concentrations during June 2006 under predominantly NO_x-limited conditions. Collectively, these results and those from other studies (e.g., Kleinman et al., 2005; Xiao et al., 2010; Sommariva et al., 2011) have indicated the importance of both HRVOC and NO_x controls to further reduce ozone concentrations in Texas.

β-Hydroxynitrates as unique markers for ozone enhancements in Houston industrial plumes

Quantifying the relative contributions of individual HRVOCs to ozone formation has remained challenging despite their long-recognized role in ozone formation in the Houston Ship Channel. β-hydroxynitrates (βHNs) are formed when HRVOCs react in the atmosphere in the presence of nitrogen oxides (NO_x). Using a combination of data analysis and reactive plume modeling, AQRP Project 14-026 (Yarwood et al., 2015) leveraged recent aircraft measurements of C₂-C₅ hydroxynitrates, made during the National Aeronautics and Space Administration (NASA) Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC⁴RS) campaign in the fall of 2013, as a novel initial approach to link observed enhancements of ozone and formaldehyde to reactions of specific HRVOCs and isoprene in Houston Ship Channel plumes.

Ozone enhancements in plume intercepts ranged from 4 to 54 ppb. The fraction of these enhancements directly attributable to HRVOC and isoprene emissions (as indicated by the O₃/βHN ratios) ranged from 6% to 24%. Isoprene contributed, on average, 35% (range of 9% to 56%) of the directly attributable ozone enhancement. Direct contributions of individual HRVOCs to the anthropogenic ozone enhancement were ranked on average as ethene (49%), propene (32%), butenes (13%), and butadiene (6%). Variability in these relative contributions reflected in part, differences in HRVOC reaction rates as plumes were photochemically processed downwind of release.

The modeled direct contributions of HRVOCs determined for one flight day using the SCICHEM Lagrangian puff model were generally consistent with the observational data. Direct formation of ozone from the HRVOC emissions in the Houston Ship Channel explained 12-25% of the plume ozone increments; the remaining ozone was formed indirectly by the interaction of Houston Ship Channel emissions with emissions of other species such as isoprene. The project found that representing Houston Ship Channel emissions by multiple, narrower source plumes accelerated plume chemistry and improved model performance. Plume chemistry was found to be sensitive to whether HRVOCs and NO_x were released together or segregated in separate plumes that interact as they disperse and overlap each other.

Mechanisms for HONO formation

Nitrous acid (HONO) is a precursor to the formation of hydroxyl radical (OH). Collectively known as HO_x, OH, and hydroperoxyl radical (HO₂) have important roles in the formation of ozone and fine particulate matter. Field campaigns, such as the TexAQS II, TRAMP, SHARP,

and FLAIR, have sought to improve the characterization of HONO and understanding of its influence on radical budgets, primarily in the Houston-Galveston-Brazoria airshed. Findings during these studies have been used to guide improvements in the formation pathways for HONO in CAMx (Couzo et al., 2014; Karamchandani et al., 2014).

Measurements during the SHARP campaign indicated that photolysis of HONO in the early morning is an important radical production source in Houston (AQR Project 12-028, Lefer et al., 2014; Karamchandani et al., 2014). Sources of HONO include production by homogeneous gas-phase reactions, direct emissions from combustion sources, or production by heterogeneous reactions on ground or aerosol surfaces (Karamchandani et al., 2014). 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 urban and rural locations throughout the world (e.g., Wong et al., 2012; Acker et al., 2006a; Acker et al., 2006b, Zhou et al., 2007; Carter and Seinfeld, 2012; Spartaro et al., 2013), including the Houston area (Olague et al., 2009; Wong et al., 2012). Moreover, the dominant HONO formation pathway in both the Carbon Bond and SAPRC chemical mechanisms commonly used in air quality models was the homogeneous gas-phase reaction of OH with NO, which was insufficient to replicate observed nocturnal and daytime HONO formation. Direct emissions of HONO could also not account for observed concentrations. Additional work is necessary to reconcile HONO measurements with observations.

Daytime formation mechanisms that account for enhanced HONO formation have been a focal point of studies over the past several years. Both gas-phase and heterogeneous mechanisms on aerosol surfaces have been investigated, including gas-phase photolysis of ortho-nitrophenols (Bejan et al., 2006), daytime reaction of photo-excited NO₂ with water vapor (Li et al., 2008), heterogeneous conversion of NO₂ on fresh and aged soot particles (Zhang et al., 2009; Lefer et al., 2010), humic acids and soil surfaces (Stemmler et al., 2006), photolysis of surface adsorbed nitric acid (Zhou et al., 2011), and heterogeneous conversion of HNO₃ on the surface of primary organic aerosol (Ziemba et al., 2010). In the Houston area during SHARP, Wong et al. (2012) and AQR Project 10-032 (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 gas-phase NO₂ on the ground. Karamchandani et al. (2014) have developed and implemented a surface model to CAMx that allows heterogeneous production of HONO through a representation of the surface as a reservoir of deposited species that can sorb or penetrate into soils and vegetation and undergo chemical processing and re-emission to ambient air. Couzo et al. (2014) found that heterogeneous HONO formation through this parameterization reduced the normalized mean error by 30% - 45% for modeled daytime and nighttime concentrations relative to SHARP measurements and had more significant effects than increases in direct HONO emissions.

Sources and concentrations of ambient formaldehyde

As described in detail by Seinfeld and Pandis (1998) and others (e.g., Parrish et al., 2012; Olague et al., 2014), formaldehyde originates from primary emissions sources (e.g., flares, industrial processes such as catalytic cracking, motor vehicles) as well as from secondary chemical production through the oxidation of biogenic and anthropogenic 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.

Measured formaldehyde concentrations in the Houston Ship Channel exceeded 50 ppb during TexAQS II (Eom et al., 2008) and 20 ppb during DISCOVER-AQ (AQRP Project 14-002, Fried and Loughner, 2015). During 2009 (SHARP; Lefer, 2009) and 2011 (AQRP Project 10-006, Johansson et al., 2013; AQRP Project 13-005, Johansson et al., 2015), atmospheric columns of HCHO associated with specific local source regions were repeatedly investigated using mobile Differential Optical Absorption Spectroscopy (DOAS) and Solar Occultation Flux (SOF). Emissions from two Texas City and two Mont Belvieu sources were estimated to range from 6 to 15 kg h⁻¹, compared to emissions of approximately 40 and 22 kg h⁻¹ from a Ship Channel source during 2009/2011 and 2013, respectively. AQRP Project 14-045 (Stutz et al., 2011) used comparable measurement technology during FLAIR to infer an emissions flux from a collection of Texas City industrial facilities on the order of 20 kg h⁻¹. Stutz et al., 2011 noted direct HCHO emissions from burning flares at rates that ranged from 0.3 to 2.5 kg h⁻¹ similar to results from other flare measurement studies (e.g., Pikelnaya et al., 2013).

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 (Rappengluck et al., 2010; Buzcu et al., 2011; Parrish et al., 2012; Olaguer, 2013; Olaguer et al., 2013; Zhang et al., 2013; Johansson et al., 2014). For example, using CO and SO₂ as primary markers for mobile and industrial source emissions, respectively, Rappenglück et al. (2010) calculated formaldehyde source contributions during TexAQS II at Moody Tower of 38.5% from primary vehicular emissions, 24.1% from secondary photochemistry, and 8.9% from industrial emissions. Analyzing the Moody Tower dataset but using Positive Matrix Factorization (PMF), Buzcu et al. (2011) attributed 23% of HCHO to primary emissions from motor vehicles, 24% from the oxidation of biogenic or industrial isoprene, 17% from other industrial emissions, and the remainder from OH driven secondary photochemistry. Using a plume chemistry model to investigate 13 individual HCHO events sampled in the Houston-Galveston-Brazoria area during 2009 and 2011, Johansson et al. (2014) found that primary emissions contributed 90%, on average, to measured concentrations and that only three cases had modeled contributions greater than 10% attributed to photochemical production.

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, they concluded 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 ($92 \pm 4\%$), with only $4 \pm 2\%$ directly emitted from these facilities. The authors noted there are cases where targeted reductions of primary formaldehyde emissions may be warranted, for example, Fried et al. (2015) indicated the importance of episodic spikes in emissions. Using a source apportionment technique within CMAQ, Zheng et al., (2013) attributed 20 to 30% of regional HCHO concentrations to primary emissions (biogenic, natural gas combustion, and vehicles) and 30 to 50% associated with secondary

formation (biogenic, industrial, and vehicles) with the remainder from upwind sources (30 to 50%).

Olague et al. (2014) indicated that discrepancies between primary and secondary attributions may be due, in part, to differences in the assumed relationship between tracer combustion species (e.g., CO) and primary emissions as well as in the spatial and temporal representation of the corresponding measurements. For example, Johansson et al. (2014) noted that the highest HCHO emission rate included in their study was approximately 120 kg h^{-1} ; on a regional scale, these emissions are small compared to HCHO formed from secondary production, which may be an order of magnitude higher. Nonetheless, there is recognition by air quality stakeholders that understanding formaldehyde sources is critical to defining effective ozone control strategies in the Houston area.

Representation of alkene chemistry in an atmospheric chemical mechanism

Using reliable atmospheric chemical mechanisms in regulatory air quality modeling is necessary to formulate effective and efficient emission control strategies for achieving ozone reductions. Seven alkenes (ethene, propene, 1,3-butadiene, 1-butene, isobutene, trans-2-butene, and cis-2-butene) associated with industrial emissions have been classified as HRVOCs (Texas Administrative Code, Title 30, Part 1, Chapter 115; TCEQ, 2012) and have been a focus of novel emissions reduction strategies in southeastern Texas due to their recognized impacts on ozone production. Condensed chemical mechanisms commonly used for air quality modeling in the U.S., including versions of the CB (Yarwood et al., 2005; Whitten et al., 2010; Yarwood et al., 2010) and Statewide Air Pollution Research Center (SAPRC) (Carter, 2000; Carter, 2010) mechanisms, have historically been designed to model ozone formation from typical urban ambient VOC mixtures, not under atmospheric conditions significantly influenced by highly variable HRVOC emissions. AQRP Project 12-006 (Heo and Carter, 2014) designed and conducted environmental chamber experiments to evaluate the representation of alkene chemistry for HRVOCs and non-HRVOCs in the SAPRC, and to a more limited extent the CB, chemical mechanisms. SAPRC mechanisms with varying levels of VOC lumping were implemented in CMAQ (Byun and Schere, 2006) to simulate a summer ozone episode during the TexAQS II.

Statistical analysis of peak and hourly ozone concentrations by Heo and Carter (2014) indicated that SAPRC-11D, the most detailed SAPRC mechanism ever applied in regional air quality simulations that used approximately 300 explicit VOC species, exhibited the best performance overall in southeastern Texas. However, its performance was not drastically better than SAPRC-11L, a condensed and fixed-parameter version of SAPRC-11D, suggesting that an intermediate explicit representation could yield benefits in performance as well as computational feasibility for routine air quality modeling applications. The project provided insights on the need for reliable emissions data as well as lumping methods for alkenes that could guide future chemical mechanism developments indicating, for example, that unbranched C_{3+} terminal alkenes shared similar ozone formation mechanisms but also have non-negligible differences, that unbranched internal alkenes share similar ozone formation chemistries, and that lumping branched terminal alkenes and branched internal alkenes with unbranched internal alkenes introduces significant inaccuracies. Explicitly modeling propene and 1,3-butadiene is potentially useful to improve the

accuracy of ozone predictions based on the spatial variability of their emissions in southeastern Texas.

Effects of emissions reductions on nighttime power plant plume chemistry and transport

Plumes from coal-fired power plants, which are frequently located in relatively rural areas, are subject to nocturnal transport and chemical processing that may affect air quality downwind. Coal-fired electric power plants have historically produced a large fraction of total U.S. NO_x emissions, but emissions from this sector have been declining during the last decade driven by federal regulations. AQRP Project 10-020 (Yarwood et al., 2012) and Brown et al. (2012) analyzed nighttime aircraft intercepts of plumes from two different Texas power plants (Oklaunion near Wichita Falls and W. A. Parish near Houston) with different control technologies to demonstrate the effect of NO_x emissions reductions on nighttime NO_x oxidation rates. 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. The spatial extents of nighttime-emitted plumes was found to be limited, and mixing of highly concentrated plume NO_x with ambient ozone was a determining factor for its nighttime oxidation. The plume from Oklaunion had full titration of ozone through 74 km/2.4 hours of downwind transport that suppressed nighttime oxidation of NO₂ 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 NO₂ during downwind transport. Plume modeling showed that NO_x controls not only reduced emissions directly but also led to an additional overnight NO_x loss of 36% to 44% on average. The maximum reduction for 12 h of transport in darkness was 73%. The results implied that power plant NO_x emissions controls may produce a larger than linear reduction in next-day, downwind ozone production following nighttime transport. The findings have been used to guide improvements in the Plume-in-Grid (PiG) formulation in CAMx.

Nighttime nitrate radical chemistry in the Houston urban boundary layer

Aircraft measurements during the second Texas air quality study provided unique insights on the nighttime chemistry and structure of the Houston urban boundary layer. AQRP Project 10-020 (Yarwood et al., 2012) found that nocturnal boundary layer depths vary between 100 – 400 m with overlying residual layer depths of 0.8 – 1.5 km. Nitrate radical had a strong influence on hydrocarbon oxidation (Stutz et al., 2009). Production rates for NO₃ ranged from 1-2 ppbv h⁻¹ (Brown et al., 2009; Brown et al., 2011; Brown and Stutz, 2012) with maximum values of 2.7 ppbv h⁻¹ (Yarwood et al., 2012) within NO_x plumes of industrial origin, but were generally smaller in rural plumes and plumes that originated from urban Houston and were transported downwind.

Nitrate radical was the dominant nighttime oxidant, with net oxidation rates 3 - 5 times faster than those due to ozone (Brown et al., 2011; Brown and Stutz, 2012). Net VOC oxidation rates due to NO₃ and O₃ varied between 0.1 - 1 ppbv hr⁻¹, (Yarwood et al., 2012) primarily associated with highly reactive alkenes, including isoprene, isobutene (2-methyl-1-propene) and 1,3-butadiene (Stutz et al., 2009; Brown et al., 2009; Brown et al., 2011; Brown and Stutz, 2012). Biogenic emissions were frequently observed at modest levels within the nocturnal boundary layer and underwent rapid oxidation (0.2 - 1 ppbv hr⁻¹), mainly by NO₃ (Yarwood et al., 2012; Brown et al., 2011). These NO₃-VOC reactions were more significant as a NO₃ loss pathway

than heterogeneous reactions of either NO₃ or N₂O₅ in the Houston urban boundary layer in contrast to other urban locations (Stutz et al., 2009).

Rate of sulfur dioxide to sulfate transformation in the Houston Ship Channel

In June of 2010, the EPA promulgated a more stringent primary NAAQS for sulfur dioxide (SO₂), requiring that the 99th percentile of 1-hour daily maximum concentrations averaged over 3 years not exceed 75 ppb. Fossil-fueled power plants and industrial facilities are the main sources of SO₂ emissions within the United States. The EPA recommends the use of the AERMOD steady-state Gaussian plume model (EPA, 2010) for near-source 1-hour SO₂ modeling assuming no chemical transformation of SO₂. Photochemical oxidants convert SO₂ to sulfate thereby reducing SO₂ concentrations. AERMOD does not treat photochemical oxidants and represents SO₂ transformation as a simple exponential decay process. This approach may not be appropriate for the reactive atmosphere of the Houston Ship Channel that may have more rapid SO₂ to sulfate conversion rates. Using NOAA P-3 aircraft measurements collected during the 2006 Texas Air Quality Study in the Houston Ship Channel area, AQRP Project 12-013 (Koo and Morris, 2013) determined a representative SO₂ transformation rate of 0.04 hr⁻¹ (half-life of 17 hours). This rate can be used with the AERMOD model to simulate 1-hour SO₂ concentrations and is higher than that reported for power plant plumes. Investigations to determine sulfur dioxide to sulfate conversion rates within the Houston Ship Channel region that can be used with AERMOD under a range of meteorological conditions should continue to be examined.

2.3.3 References

AQRP Projects:

AQRP Project 10-006: Johansson, J., J. Mellqvist, J. Samuelsson, B. Offerle, B. Rappenglück, D. Anderson, B. Lefer, S. Alvarez, and J. Flynn, (2011), Quantification of industrial emissions of VOCs, NO₂ and SO₂ by SOF and Mobile DOAS, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-008: Cohan, D., G. Yarwood, B. Koo, X. Xiao, and A. Digar, (2011), Factors influencing ozone-precursor response in Texas attainment modeling, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-015: Koo, B., G. Yarwood, and J. Roberts, (2012), An assessment of nitryl chloride formation chemistry and its importance in ozone non-attainment areas in Texas, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-020: Yarwood, G., P. Karamchandani, C. Emery, S.-Y. Chen, S.S. Brown, and D.D. Parrish, (2012), NO_x reactions and transport in nighttime plumes and impact on next-day ozone, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-032: Lefer, B., J. Stutz, X. Ren, W. Brune, and J. Dibb, (2011), Study of Houston Atmospheric Radical Precursors (SHARP) data analysis, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-042: Yarwood, G., G. Heo, W.P.L. Carter, and G.Z. Whitten, (2012), environmental chamber experiments to evaluate NO_x sinks and recycling in atmospheric

chemical mechanisms, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 10-045: Stutz, J., O. Pikelnaya, G. Mount, E. Spinei, S. Herndon, E. Wood, O. Oluwole, W. Vizuete, and E. Causo, (2011), Quantification of hydrocarbon, NO_x, and SO₂ emissions from petrochemical facilities in Houston: Interpretation of the 2009 FLAIR dataset, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 12-006: Heo, G., and W.P.L. Carter, (2014), Chamber experiments and CMAQ modeling to improve mechanisms to model ozone formation from HRVOCs, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 12-012: Hildebrandt Ruiz, L., and G. Yarwood, (2013), interactions between organic aerosol and NO_y: Influence on oxidant production, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 12-013: Koo, B., and R. Morris, (2013), Development of transformation fate of SO₂ to sulfate for the Houston Ship Channel using the TexAQs 2006 Field Study Data, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 12-028: Lefer, B., J. Stutz, W. Vizuete, E. Couzo, G. Yarwood, and P. Karamchandani, (2014), Implementation and evaluation of new HONO mechanisms in a 3-D chemical transport model for spring 2009 in Houston, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 13-005: Johansson, J., J. Mellqvist, J. Samuelsson, B. Offerle, P. Andersson, B. Lefer, J. Flynn, and S. Zhuoyan, (2013), Quantification of industrial emissions of VOCs, NO₂ and SO₂ by SOF and Mobile DOAS during DISCOVER-AQ, Prepared for the Texas Air Quality Research Program <http://aqrp.ceer.utexas.edu/>

AQRP Project 13-024: Ren, X., (2013), Surface measurement of trace gases in support of DISCOVER-AQ in Houston in summer 2013, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-002: Fried, A., and C. Loughner, Analysis of airborne formaldehyde data over Houston Texas acquired during the 2013 DISCOVER-AQ and SEAC4RS campaigns, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-003: Vizuete, W., and J.D. Surratt, (2015), Update and evaluation of model algorithms needed to predict particulate matter from isoprene, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-020: Ren, X., (2015), Analysis of ozone production and its sensitivity in Houston using the data collected during DISCOVER-AQ, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-024: Hildebrandt Ruiz, L., Y. Xu, G. Yarwood, and G. Heo, (2015), Interactions between organic aerosol and NO_y: Influence on oxidant production, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-026: Yarwood G., P. Karamchandani, L. Parker, D. Parrish, T. Ryerson (2015), Quantifying ozone production from light alkenes using novel measurements of hydroxynitrate reaction products in Houston during the NASA SEAC⁴RS Project, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>.

Other:

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

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

Ait-Helal, W., A. Borbon, S. Sauvage, J.A. de Gouw, A. Colomb, V. Gros, F. Freutel, M. Crippa, C. Afif, U. Baltensperger, M. Beekmann, J.-F. Doussin, R. Durand-Jolibois, I. Fronval, N. Grand, T. Leonardis, M. Lopez, V. Michoud, K. Miet, S. Perrier, A.S.H. Prévôt, J. Schneider, G. Siour, P. Zapf, and N. Locoge, (2010), Volatile and intermediate volatility organic compounds in suburban Paris: variability, origin and importance for SOA formation, *Atmospheric Chemistry and Physics*, 14, 10439–10464, 2014 www.atmos-chem-phys.net/14/10439/2014/ doi:10.5194/acp-14-10439-2014

Baek, J., Y. Hu, M. T. Odman, and A.G. Russell (2011), Modeling secondary organic aerosol in CMAQ using multigenerational oxidation of semi-volatile organic compounds, *Journal of Geophysical Research*, 116, D22204, doi:10.1029/2011JD015911.

Bean, J. and L. Hildebrandt Ruiz, (2015), Hydrolysis and gas-particle partitioning of organic nitrates formed in environmental chamber experiments from the photo-oxidation of α -pinene, in preparation, 2015.

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

Bejan, I., Y. Abd El Aal, I. Barnes, T. Benter, B. Bohn, P. Wiesen, and J. Kleffmann, (2006), The photolysis of ortho-nitrophenols: A new gas phase source of HONO, *Physical Chemistry Chemical Physics*, 8, 2028 - 2035, doi:10.1039/b516590c.

Berkowitz, C.M., C.W. Spicer, P.V. Doskey, (2004), Hydrocarbon observations and ozone production rates in western Houston during the Texas 2000 Air Quality Study. *Atmospheric Environment*, 39, 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, and A.R. Ravishankara, (2009), 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, doi:10.1029/2008JD011679.

Brown, S.S., W.P. Dube, P. Karamchandani, G. Yarwood, J. Peischl, T.B. Ryerson, J.A. Neuman, J.B. Nowak, J.S. Holloway, R.A. Washenfelder, C.A. Brock, G.J. Frost, M. Trainer, D.D. Parrish, F.C. Fehsenfeld, and A.R. Ravishankara, (2012), Effects of NO_x control and plume mixing on nighttime chemical processing of plumes from coal-fired power plants, *Journal of Geophysical Research*, 117, D07304, doi:10.1029/2011JD016954.

Brown, S.S., and J. Stutz, (2012), Nighttime radical observations and chemistry, *Chemical Society Reviews*, 7, 41(19): 6405-47. doi: 10.1039/c2cs35181a.

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. Fehsenfeld, and A.R. Ravishankara, (2011), Budgets for nocturnal VOC oxidation by nitrate radicals aloft during the 2006 Texas Air Quality Study. *Journal of Geophysical Research*, 116, doi:10.1029/2011JD016544.

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, and A.R. Ravishankara, (2009), 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, doi:10.1029/2008JD011679.

Budisulistiorini, S.H., X. Li, S.T. Bairai, J. Renfro, Y. Liu, Y.J. Liu, K.A. McKinney, S.T. Martin, V.F. McNeill, H.O.T. Pye, A. Nenes, M.E. Neff, E.A. Stone, S. Mueller, C. Knote, S.L. Shaw, Z. Zhang, A. Gold, and J.D. Surratt, (2015), Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee ground site, *Atmospheric Chemistry and Physics*, 15, 8871-8888, doi:10.5194/acp-15-8871-2015, 2015.

Byun, D., and K.L. Schere, (2006), Review of the governing equations, computational algorithms, and other components of the Models-3 community multiscale air quality (CMAQ) modeling system. *Applied Mechanics Reviews* 59, 51-77.

Carlton, A.G., C. Wiedinmyer, and J.H. Kroll, (2009), A review of Secondary Organic Aerosol (SOA) formation from isoprene, *Atmospheric Chemistry and Physics*, 9, 4987-5005, doi:10.5194/acp-9-4987-2009, 2009.

Carter, W.P.L., (2000), Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment. Report to the California Air Resources Board, Contracts 92-329 and 95-308. Available at <http://www.cert.ucr.edu/~carter/absts.htm#saprc99>.

Carter, W.P.L., (2010), Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales. Revised Final report to the California Air Resources Board Contract

No. 03-318. January 27. Available at www.cert.ucr.edu/~carter/SAPRC. See also Carter, W.P.L., 2010. Development of the SAPRC-07 chemical mechanism, *Atmospheric Environment* 44, 5324-5335.

Carter, W.P.L., (2010b). Development of the SAPRC-07 chemical mechanism. *Atmospheric Environment*, 44(40), 5324-5335.

Carter, W.P.L., and J. H. Seinfeld, (2012), Winter ozone formation and VOC incremental reactivities in the Upper Green River Basin of Wyoming, *Atmospheric Environment*, 20, April 2012, 255-266.

Claeys, M., B. Graham, G. Vas,, W. Wang, R. Vermeylen, V. Pashynska, J. Cafmeyer, P. Guyon, M.O. Andreae, P. Artaxo, and W.Maenhaut, (2004), Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, 303(5661), 1173-1176.

Chen, Y.Z., K.G. Sexton, R.E. Jerry, J.D. Surratt, and W. Vizuete, (2015), Assessment of SAPRC07 with updated isoprene chemistry against outdoor chamber experiments, *Atmospheric Environment*, 105, 109-120.

Couzo, E., B. Lefer, J. Stutz, G. Yarwood, P. Karamchandani, B. Henderson, and W. Vizuete, (2015), Impacts of heterogeneous HONO formation on radical sources and ozone chemistry in Houston, Texas, *Atmospheric Environment*, 112, 344-355.

Cowling, E.B., C. Furiness, B. Dimitriadis, D. Parrish, M. Estes et al., Final rapid science synthesis report: Findings from the Second Texas Air Quality Study (TexAQS II), (2007), A report to the Texas Commission on Environmental Quality by the TexAQS II Rapid Science Synthesis Team, TCEQ Contract Number 582-4-65614, 31 August 2007.

Daum, P.H., L.I. Kleinman, S.R. Springston, L.J. Nunnermacker, Y.-N. Lee, J. Weinstein-Lloyd, J. Zheng, and C.M. Berkowitz, (2003), A comparative study of O₃ formation in the Houston urban and industrial plumes during the 2000 Texas Air Quality Study, *Journal of Geophysical Research* 108, doi:10.1029/2003JD003552.

Donahue, N.M., A.L. Robinson, C.O. Stanier, and S.N. Pandis, (2006), Coupled partitioning, dilution, and chemical aging of semivolatile organics, *Environmental Science & Technology*, 40, 2635–43. doi:10.1021/es052297c.

Edwards, P.M., C. J. Young, K. Aikin, J. deGouw, W.P. Dubé, F. Geiger, J. Gilman, D. Helmig, J.S. Holloway, J. Kercher, B. Lerner, R. Martin, R. McLaren, D.D. Parrish, J. Peischl, J.M. Roberts, T.B. Ryerson, J. Thornton, C. Warneke, E.J. Williams, and S.S. Brown, (2013), Ozone photochemistry in an oil and natural gas extraction region during winter: Simulations of a snow-free season in the Uintah Basin, Utah, *Atmospheric Chemistry Physics*, 13, 8955-8971, 2013 www.atmos-chem-phys.net/13/8955/2013/doi:10.5194/acp-13-8955-2013

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

EPA, (2010), Applicability of Appendix W modeling guidance for the 1-hr SO₂ National Ambient Air Quality Standard, memorandum. August 23.
(http://www.epa.gov/ttn/scram/guidance/clarification/ClarificationMemo_AppendixW_Hourly-SO2-NAAQS_FINAL_08-23-2010.pdf)

Finlayson-Pitts, B.J., M.J. Ezell, J.N. and Pitts Jr., (1989), Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N₂O₅ and ClONO₂, *Nature*, 337, doi:10.1038/337241a0.

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, and J.A. de Gouw, (2009), 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, doi:10.1029/2008JD011525.

Guven, B.B., and E.P. Olaguer, (2011), Ambient formaldehyde source attribution in Houston during TexAQS II and TRAMP, *Atmospheric Environment*, 45(25), 4272–4280, doi:10.1016/j.atmosenv.2011.04.079.

Johansson, J., J. Mellqvist, J. Samuelsson, B. Offerle, J. Moldanova, B. Rappengluck, B. Lefer, and J. Flynn, (2014), Quantitative measurements and modeling of industrial formaldehyde emissions in the Greater Houston area during campaigns in 2009 and 2011, *Journal of Geophysical Research*, 119, 4303-22.

Karamachandani, P., C. Emery, G. Yarwood, B. Lefer, J. Stutz, E. Couzo, and W. Vizuete, (2015), Implementation and refinement of a surface model for heterogeneous HONO formation in a 3-D chemical transport model, *Atmospheric Environment*, 112, 356-368.

Karl, M., K. Tsigaridis, E. Vignati, and F. Dentener, (2009), Formation of secondary organic aerosol from isoprene oxidation over Europe. *Atmos. Chem. Phys.*, 9, 7003-7030, doi:10.5194/acp-9-7003-2009.

Kercher, J.P., T.P. Riedel, and J.A. Thornton, (2009), Chlorine activation by N₂O₅: Simultaneous, in situ detection of ClNO₂ and N₂O₅ by chemical ionization mass spectrometry, *Atmospheric Measurement Techniques*, 2, 193–204.

Kleinman, L. I., P. H. Daum, Y.-N. Lee, L. J. Nunnermacker, S. R. Springston, J. Weinstein-Lloyd, and J. Rudolph, (2002), Ozone production efficiency in an urban area, *Journal of Geophysical Research*, 107 (D23), 4733, doi:10.1029/2002JD002529.

Kleinman, L.I., P.H. Daum, Y.-N. Lee, L.J. Nunnermacker, S.R. Springston, J. Weinstein-Lloyd, and J. Rudolph, (2005), A comparative study of ozone production in five U.S. metropolitan areas, *Journal of Geophysical Research*, 110, D02301, doi:10.1029/2004JD005096.

Knipping, E.M., and D. Dabdub, (2003), Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone, *Environmental Science & Technology* 37, doi:10.21/es025793z.

Kroll, J. H., N.L. Ng, S.M. Murphy, R.C. Flagan, and J.H. Seinfeld, (2006), Secondary organic aerosol formation from isoprene photooxidation, *Environmental Science & Technology*, 40, 1869–1877.

Lee, L., P.J. Wooldridge, J. deGouw, S.S. Brown, T.S. Bates, P.K., Quinn, and R.C. Cohen, (2015), Particulate organic nitrates observed in an oil and natural gas production region during wintertime, *Atmospheric Chemistry and Physics*, 15, doi: 10.5194/acpd-15-10677-2015.

Lefer, B., (2009), Study of Houston Atmospheric Radical Precursors (SHARP), Rep. H100, Texas Environmental Research Consortium, Houston Advanced Research Center.

Lefer, B., B. Rappengluck, J. Flynn, and C. Haman, (2010), Photochemical and meteorological relationships during the Texas-II Radical and Aerosol Measurement Project (TRAMP). *Atmospheric Environment*, 44, 4005-4013, <http://dx.doi.org/10.1016/j.atmosenv.2010.03.011>.

Li, S, J. Matthews, and A. Sinha, (2008), Atmospheric hydroxyl radical production from electronically excited NO₂ and H₂O. *Science*, 319 (5870), 1657-1660, ISSN 0036-8075.

Li, J., M. Cleveland, L.D. Ziemba, R.J. Griffin, K.C. Barsanti, J.F. Pankow, and Q. Ying, (2015), Modeling regional secondary organic aerosol using the master chemical mechanism, *Atmospheric Environment* 102, 52- 61.

Lin Y., H. Zhang, H.O. Pye, Z. Zhang, W.J. Marth, S. Park, M. Arashiro, T. Cui, S.H. Budisulistiorini, K.G. Sexton, W. Vizuete, Y. Xie, D.J. Luecken, I.R. Piletic, E.O. Edney, L.J. Bartolotti, A. Gold, and J.D. Surratt, (2013), *Proceedings of the National Academy of Science*, 110(17), 6718-23, doi: 10.1073/pnas.1221150110. Epub 2013 Apr 3.

Liu, S., J.E. Shilling, C. Song, N. Hiranuma, R.A. Zaveri, and L.M. Russell, (2012), Hydrolysis of organonitrate functional groups in aerosol particles, *Aerosol Science Technology* 46, 1359–1369, doi:10.1080/02786826.2012.716175.

Mao, J., Ren, X., Chen, S., Brune, W.H., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglück, B., Flynn, J., and M. Leuchner, (2010), Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies, *Atmospheric Environment*, 44, 4107–4115.

Mielke, L.H., A. Furgeson, and H.D. Osthoff, (2011), Observation of ClNO₂ in a mid-continental urban environment, *Environmental Science & Technology*, 45(20), 8889–8896, doi:10.1021/es201955u.

Mielke, L.H., J. Stutz, C. Tsai, S.C. Hurlock, J.M. Roberts, P.R. Veres, K.D. Froyd, P.L. Hayes, M.J. Cubison, J.S. Jimenez, R.A. Washenfelder, C.M. Young, J.B. Gilman, J.A. de Gouw, J.H. Flynn, N. Grossberg, B.L. Lefer, J. Liu, R.J. Weber, and H.D. Osthoff, (2013), Heterogeneous

formation of nitryl chloride and its role as a nocturnal NO_x reservoir species during CalNex-LA 2010, *Journal of Geophysical Research Atmospheres*, 118, 10,638–10,652, doi:10.1002/jgrd.50783.

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, and F.C. Fehsenfeld, (2009), Relationship between photochemical ozone production and NO_x oxidation in Houston, Texas, *Journal of Geophysical Research*, 114, doi:10.1029/2008JD01688.

Olaguer, E.P., B. Rappenglück, B. Lefe, J. Stutz, J. Dibb, R. Griffin, W.H. Brune, M. Shauck, M. Buhr, H. Jeffries, W. Wiuete, and J.P. Pinto, (2009), Deciphering the role of radical precursors during the Second Texas Air Quality Study, *Journal of the Air & Waste Management Association*, 59, 11.

Olaguer, E.P., (2013), Application of an adjoint neighborhood-scale chemistry transport model to the attribution of primary formaldehyde at Lynchburg Ferry during TexAQS II, *Journal of Geophysical Research Atmospheres*, 118, 4936–4946.

Olaguer, E.P., C.E. Kolb, B. Lefer, B. Rappenglück, R. Zhang, and J.P. Pinto, (2014), Overview of the SHARP campaign: Motivation, design, and major outcomes, *Journal of Geophysical Research Atmospheres*, 119, 2597–2610, doi:10.1002/2013JD019730.

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, and S.S. Brown, (2008), High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nature Geoscience*, 1, 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, and E.J. Williams, (2009), 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, 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, and S.C. Herndon, (2012), Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region, *Atmospheric Chemistry and Physics*, 12, doi:10.5194/acp-12-3273-2012.

Perring, A.E., S.E. Pusede, and R.C. Cohen, (2013), An observational perspective on the atmospheric impacts of alkyl and multifunctional nitrates on ozone and secondary organic aerosol, *Chemical Reviews*, 113, doi:10.1021/cr300520x.

Phillips, G.J., M.J. Tang, J. Thieser, B. Brickwedde, G. Schuster, B. Bohn, J. Lelieveld, and J.N. Crowley, (2012), Significant concentrations of nitryl chloride observed in rural continental

- Europe associated with the influence of sea salt chloride and anthropogenic emissions, *Geophysical Research Letters*, 39, L10811, doi:10.1029/2012GL051912.
- Pikelnaya, O., J.H. Flynn, C. Tsai, and J. Stutz, (2013), Imaging DOAS detection of primary formaldehyde and sulfur dioxide emissions from petrochemical flares, *Journal of Geophysical Research Atmospheres*, 118, 8716–8728, doi:10.1002/jgrd.50643.
- Rappenglück, B., P.K. Dasgupta, M. Leuchner, Q. Li, and W. Luke, (2010), Formaldehyde and its relation to CO, PAN, and SO₂ in the Houston-Galveston airshed, *Atmospheric Chemistry and Physics*, 10(5), 2413–2424, doi:10.1029/2008JD009865.
- Riedel, T.P., T.H. Bertram, T.A. Crisp, E.J. Williams, B.M. Lerner, A. Vlasenko, S.-M. Li, J. Gilman, J. de Gouw, D.I.M. Bon, N.L. Wagner, S.S. Brown, and J.A. Thornton, (2012), Nitryl chloride and molecular chlorine in the coastal marine boundary layer, *Environmental Science & Technology*, 46 (19), 10463-10470, DOI: 10.1021/es204632r.
- Rindelaub, J. D., K.M. McAvey, and P.B. Shepson, (2015), The photochemical production of organic nitrates from pinene and loss via acid-dependent particle phase hydrolysis, *Atmospheric Environment*, 100, 193–201, doi:10.1016/j.atmosenv.2014.11.010.
- Robinson, A.L., N.M. Donahue, M.K. Shrivastava, E.A. Weitkamp, A.M. Sage, A.P. Grieshop, T.E. Lane, J.R. Pierce, and S.N. Pandis, (2007), Rethinking organic aerosols: Semivolatile emissions and photochemical aging, *Science*, 315, 1259–1262, 2007.
- Rollins, A.W., J.D. Smith, K.R. Wilson, and R.C. Cohen, (2010), Real time in situ detection of organic nitrates in atmospheric aerosols, *Environmental Science & Technology*, 44, 5540–5545, doi:10.1021/es100926x.
- Rollins, A.W., S. Pusede, P. Wooldridge, K.E. Min, D.R. Gentner, A.H. Goldstein, S. Liu, D.A. Day, L.M. Russell, C.L. Rubitschun, J.D. Surratt, and R.C. Cohen, (2013), Gas/particle partitioning of total alkyl nitrates observed with TD-LIF in Bakersfield, *Journal of Geophysical Research Atmospheres*, 118, 6651–6662, doi:10.1002/jgrd.50522.
- 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, and D.T. Sueper, (2003), Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas, *Journal of Geophysical Research*, 108, doi:10.1029/2002JD003070.
- Sarwar, G., H. Simon, P. Bhave, and G. Yarwood, (2012), Examining the impact of heterogeneous nitryl chloride production on air quality across the United States, *Atmospheric Chemistry and Physics*, 12, 6455-6473, doi:10.5194/acp-12-6455-2012.
- Sarwar, G., H. Simon, J. Xing, and R. Mathur, (2014), Importance of tropospheric ClNO₂ chemistry across the Northern Hemisphere, *Geophysical Research Letters*, 41, 4050–4058, doi:10.1002/2014GL059962.

Seinfeld J.H., and 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. McGaughy, D.T. Allen, S.S. Brown, H.D. Osthoff, J.M. Roberts, D. Byun, and D. Lee, (2009), Modeling the impact of ClNO₂ on ozone formation in the Houston area. *Journal of Geophysical Research* 114, doi:10.1029/2008JD010732.

Simpson, W.R., S.S. Brown, A. Saiz-Lopez, J.A. Thornton, and R. von Glasow, (2015), Tropospheric halogen chemistry: Sources, cycling, and impacts. *Chemical Reviews*, 115(10), 4035-4062, doi:10.1021/cr5006638.

Sindelarova, K., C. Granier, I. Bouarar, A. Guenther, S. Tilmes, T. Stavrou, J.-F. Muller, U. Kuhn, P. Stefani, and W. Knorr, (2014), Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. *Atmospheric Chemistry and Physics*, 14(17), 9317-9341.

Sommariva, R., Bates, T., Bon, D., Brookes, D., Gouw, J., Gilman, J., Herndon, S., Kuster, W., Lerner, B., Monks, P., Osthoff, H., Parker, A., Roberts, J., Tucker, S., Warneke, C., Williams, E., Zahniser, M., and S. Brown, (2011), Modelled and measured concentrations of peroxy radicals and nitrate radical in the U.S. Gulf Coast region during TexAQS 2006, *Journal of Atmospheric Chemistry*, 68, 331–362, doi:10.1007/s10874-012-9224-7, 2011.

Spataro, F., A. Ianniello, G. Esposito, I. Allegrini, T. Zhu, and M. Hu, (2013), Occurrence of atmospheric nitrous acid in the urban area of Beijing (China), *Science of the Total Environment* 447, 210–224.

Stemmler, K., M. Ammann, C. Donders, J. Kleffman, and C. George, (2006), Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, *Nature*, 440, 195-198. <http://dx.doi.org/10.1038/nature04603>.

Stutz, J., K. Wong, L. Lawrence, L. Ziemba, J. Flynn, and B. Rappengluck, (2009), Nocturnal NO₃ Radical Chemistry in Houston, Texas, *Atmospheric Environment*, 44(33), 4099-4106, doi 10.1016/j.atmosenv.2009.03.004.

Surratt, J.D., A.W.H. Chan, N.C. Eddingsaas, M. Chan, C.L. Loza, A.J. Kwan, S.P. Hersey, R.C. Flagan, P.O. Wennberg, and J.H. Seinfeld, (2010), Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *Proceedings of the National Academy of Sciences USA*, 107, 6640–6645, doi:10.1073/pnas.0911114107.

Surratt, J.D., S.M. Murphy, J.H. Kroll, N.L. Ng, L. Hildebrandt, A. Sorooshian, R. Szmigielski, R. Vermeylen, W. Maenhaut, M. Claeys, R.C. Flagan, and J.H. Seinfeld, (2006), Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, *Journal of Physical Chemistry A*, 110, 9665–9690, doi:10.1021/jp061734m.

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, and D.T. Allen,

(2003), Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas. *Atmospheric Environment*, 37, 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, and S.S. Brown, (2010), A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, *Nature*, 464, doi:10.1038/nature08905.

Tsigaridis, K., and M. Kanakidou, (2003), Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis, *Atmospheric Chemistry and Physics*, 3(5), 1849-1869.

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, and W. Zheng, (2010), Characterization of NO_x, SO₂, ethene, and propene from industrial emission sources in Houston, Texas, *Journal of Geophysical Research Atmospheres*, 115, D16311, doi:10.1029/2009jd013645.

Whitten, G.Z., G. Heo, Y. Kimura, E.C. McDonald-Buller, D.T. Allen, D.T., W.P.L. Carter, and G. Yarwood, (2010), A new condensed toluene mechanism for Carbon Bond: CB05-TU, *Atmospheric Environment*, 44(40), 5346-5355.

Wong, K.W., C. Tsai, B. Lefer, C. Haman, N. Grossberg, W.H. Brune, X. Ren, W. Luke, and J. Stutz, (2012), Daytime HONO vertical gradients during SHARP 2009 in Houston, TX. *Atmospheric Chemistry and Physics*, 12, 635-652. <http://dx.doi.org/10.5194/acp-12-635-2012>.

Xiao, X., D.S. Cohan, D.W. Byun, and F. Ngan, (2010), Highly nonlinear ozone formation in the Houston region and implications for emission controls, *Journal of Geophysical Research Atmospheres*, 115, D23309, doi:10.1029/2010jd014435, 2010.

Yarwood, G., S. Rao, M. Yocke, and G.Z. Whitten, (2005) Updates to the Carbon Bond Mechanism: CB05. Report to the U.S. Environmental Protection Agency, RT-04-00675, December 2005. Available at http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf.

Yarwood, G., G.Z. Whitten, J. Jung, G. Heo, and D.T. Allen, (2010), Development, evaluation and testing of version 6 of the Carbon Bond chemical mechanism (CB6). Final Report to the Texas Commission on Environmental Quality, Work Order No. 582-7-84005-FY10-26.

Yarwood, G., T. Sakulyanontvittaya, U. Nopmongcol, and B. Koo, (2014), Ozone depletion by bromine and iodine over the Gulf of Mexico, Final Report prepared for the Texas Commission on Environmental Quality, Austin, Texas (November 2014).

Ying, Q., J. Li, and S.H. Kota, (2015), Significant contributions of isoprene to summertime secondary organic aerosol in eastern United States, *Environmental Science & Technology*, 49 (13), 7834-7842, doi: 10.1021/acs.est.5b02514.

- Yuan, B., W.W. Hu, M. Shao, M. Wang, W.T. Chen, S.H. Lu, L.M. Zeng, and M. Hu, (2013), VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China, *Atmospheric Chemistry and Physics*, 13, 8815–8832, doi:10.5194/acp-13-8815-2013.
- Zhou, W., D.S. Cohan, and B.H. Henderson, (2014), Slower ozone production in Houston, Texas following emission reductions: evidence from Texas Air Quality Studies in 2000 and 2006, *Atmospheric Chemistry and Physics*, 14, 2777-2788, doi:10.5194/acp-14-2777-2014, 2014.
- Zhou, X., N. Zhang, M. TerAvest, D. Tang, J. Hou, S. Bertman, M. Alaghmand, P.B. Shepson, M.A. Carroll, S. Griffith, S. Dusanter, and P.S. Stevens, (2011), Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, *Nature Geoscience*, 4, 440-443. <http://dx.doi.org/10.1038/ngeo1164>.
- Zhou, X., G. Huang, K. Civerolo, U. Roychowdhury, and K.L. Demerjian, (2007), Summertime observations of HONO, HCHO, and O₃ at the summit of Whiteface Mountain, New York, *Journal of Geophysical Research*, 112, D08311. <http://dx.doi.org/10.1029/2006JD007256>.
- Zhang, R., J. Zheng, A. Zhalizov, S. North, and D. Collins, (2009), Surface-induced Oxidation of Organics in the Troposphere (SOOT). Houston Advanced Research Center (HARC), H-101, November 20, 2009.
- Zhang H, J. Li, Q., Ying, B.B. Guven, and E.P. Olaguer, (2013), Source apportionment of formaldehyde during TexAQs 2006 using a source-oriented chemical transport model, *Journal of Geophysical Research Atmospheres*, 118, 1525–35.
- Ziemba, L.D., J.E. Dibb, R.J. Griffin, C.H. Anderson, S.I. Whitlow, B.L. Lefer, B. Rappengluck, and J. Flynn, (2010), Heterogeneous conversion of nitric acid to nitrous acid on the surface of primary organic aerosol in an urban atmosphere, *Atmospheric Environment*, 44, 33, 4081-4089.

2.4 Atmospheric physical processes and long-range transport of pollutants

2.4.1 Overview

Models of atmospheric physical processes, emissions, and atmospheric chemistry are all incorporated into photochemical air quality models. The photochemical air quality models mathematically and numerically process the information to yield predictions of air pollutant concentrations. The models are used to quantitatively assess the potential effectiveness of air quality management strategies. Because of their importance in air quality management, AQRP projects have focused on improving model performance by improving the description of emissions and atmospheric chemistry (described in previous sections), as well as by improving models of physical pollutant loss mechanisms, cloud characterizations, cloud processes, and wind fields. This Section describes those model improvements, as well as analyses performed to understand the long-range transport of pollutants.

2.4.2 Atmospheric physical processes and long-range transport of pollutants: Assessment from AQRP projects 2010-2015

Regionally high ozone episodes and synoptic-scale weather patterns

Continental-scale weather patterns establish the frequency of local meteorological conditions favorable for high ozone concentrations, such as high temperatures, low wind speeds, clear skies, and stagnation (e.g., Jacob and Winner, 2009; Ngan et al., 2011; Zhu et al., 2013). The synoptic weather conditions during high ozone episodes in eastern Texas often exhibit a ridge of high pressure in the lower atmosphere that extends south or southwest into the region (McGaughey et al., 2013). This large-scale circulation pattern often occurs in a post-frontal environment that is associated with the long-range (multi-day) transport of continental air, which is characterized by elevated concentrations of ozone and/or its precursor compounds, into Texas from geographic areas located to the north and/or east of the state (Rappenglück et al., 2008; Ngan et al., 2011; 2012; AQRP Project 13-016, Morris and Lefer, 2013; AQRP Project 14-006, Alrick and Morris, 2015; McGaughey et al., 2015). These background ozone concentrations entering Texas have been shown to vary by transport direction and season (Nielsen-Gammon et al., 2005; Berlin et al., 2013; Morris et al., 2013), and are correlated, in part, to the predominant continental-scale weather patterns. For example, the Bermuda High, a quasi-permanent high-pressure system centered over the North Atlantic Ocean in summer, has a significant influence on surface ozone concentrations in the eastern U.S. (Hogrefe et al., 2004; Hegarty et al., 2007; Li et al., 2012; Zhu et al., 2013; Shen et al., 2015). In a large-scale meteorological analysis specific to Texas during 1998-2013, AQRP Project 14-010 (Wang, 2015) developed a linear regression model that captured 58% - 72% of the interannual summer variance of monthly mean Houston-Galveston-Brazoria maximum daily average 8-hour (MDA8) ozone concentrations; variations in the westernmost extent of the Bermuda High was the most important predictor of monthly ozone concentrations in this region.

Improved representation of vertical mixing and land surface processes for meteorological modeling

Because large-scale meteorological influences are often weak during conditions of poor air quality, the potential impacts from local-scale circulations (such as terrain flows, sea/land breezes, nocturnal jets) become especially important (Olague et al., 2009). Numerous studies have evaluated treatments of vertical diffusion and convective mixing in support of Texas air

quality modeling applications in recent years (e.g., Emery et al., 2009; ENVIRON, 2011; Tang et al., 2011; Li and Rappengluck, 2014; Haman et al., 2014) as well as sensitivity of near-surface meteorological predictions to the choice of planetary boundary layer scheme (e.g., Hu et al., 2010, 2013; Yerramilli et al., 2010; Kolling et al., 2013; Cuichiara et al., 2014; Wilmot et al., 2014) and sensitivity to land surface modeling (Cheng et al., 2008; Misenis and Zhang, 2010). 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 planetary boundary layer height over the Houston area. In a similarly-focused study, AQRP Project 12-TN1 (Tong et al., 2013) analyzed the impact of different combinations of surface and planetary boundary layer schemes on the over-prediction of nighttime near-surface wind speeds in the Houston-Galveston-Brazoria area; although the simulation of physically-relevant parameters such as friction velocity were improved, the overall model biases were aggravated suggesting that optimization of WRF physics schemes might be needed.

Meteorological models used in support of air quality modeling applications typically incorporate data assimilation (i.e., “nudging”) to observations or other analyses to reduce uncertainties in near-surface meteorological predictions (e.g., Ngan et al., 2012, Li and Rappengluck, 2014; TCEQ, 2015; AQRP Project 14-014, Choi and Li, 2015). One of the most successful efforts to reduce uncertainties in the simulation of daytime lower-tropospheric winds and planetary boundary layer heights has been the assimilation of radar wind profiler data (e.g., Nielsen-Gammon et al., 2007; Zhang et al., 2007; Stuart et al., 2007; TCEQ, 2015). AQRP Project 14-004 (Loughner and Follette-Cook, 2015) used an iterative observational and data assimilation technique newly developed by EPA (Appel et al., 2014) to improve WRF’s simulation of the sea/bay breezes that proved critical to capturing the magnitude and spatial distribution of ozone concentrations in Houston during 2013. AQRP Project 14-022 (McNider et al., 2015) investigated a technique that utilized the difference between satellite-observed and land surface model-simulated skin temperatures to nudge soil moisture and thermal resistance. Root mean square error (RMSE) and bias was calculated for a control WRF run and for the nudging case using skin temperatures (evaluated by the satellite dataset) as the performance metric. The results for the model grid domain that included the continental U.S. and surrounding regions showed improvements in bias across much of the region; however, increased bias in limited areas caused a slight overall increase in the absolute bias. RMSE was improved by approximately 20% with even larger improvements in Texas. An evaluation of WRF wind speed and wind direction performance compared to NWS observations demonstrated slight decreases in both bias and RMSE. Because skin temperatures are physically related to relevant land surface characteristics, the results suggested that simple land surface models constrained by observations using similar data assimilation techniques can improve the specification of land surface parameters leading to improved meteorological predictions.

Simulation of clouds and precipitation

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 (Olague et al., 2009), suggesting the need for flexibility in the selection of modeling parameterizations (TCEQ, 2011).

In support of Texas applications, Pour-Biazar et al. (2007) used GOES satellite data to correct the photolysis rates in CMAQ for a TexAQS 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 to 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. To capture the effects of sub-grid clouds (i.e., clouds that are not fully resolved by air quality grid models), AQR Project 14-025 (Emery et al., 2015) developed a “Cloud-in-Grid” treatment that simulates the impact of vertical convective transport for both in-cloud and ambient fractions of the grid column. A comparison to limited observational aircraft data demonstrated improvement in the simulation of boundary layer concentrations of ozone and nitrogen oxides.

Project 14-022 (McNider et al., 2015) found that large differences between WRF and satellite insolation at the surface was largely due to the placement of clouds. A set of simulations was performed that employed the NASA Short-term Prediction Research and Transition Center (SPoRT) Geostationary Operational Environmental Satellite (GOES)-derived insolation product that had better performance statistics against pyranometer data compared to a control WRF simulation. Using National Weather Service (NWS) 2-meter temperature as the performance metric, replacement of satellite insolation into the WRF control run reduced model bias and error within Texas; however, the overall performance across the entire continental U.S. and surrounding regions was slightly degraded. McNider et al. (2015) indicated that the differences in results between the satellite and WRF insolation cases appeared to be related to surface albedo and that using satellite-derived albedo in place of WRF defaults might improve performance; however, further investigation is needed.

Contributions of North American Background (NAB) ozone to Texas air quality

Over the past decade, hemispheric transport of ozone and pollutants with longer atmospheric lifetimes to and from the United States has received increasing recognition as potential influences on local and regional air quality management. The definition of “background ozone” can vary widely, and its estimation can depend on global-scale models and/or ambient observations. Within the United States, North American Background (NAB) ozone, formerly known as Policy Relevant Background (PRB) ozone, is a specific construct that has been instrumental to the establishment of the NAAQS for ozone. The EPA (2013) defines NAB ozone as concentrations that would occur in the absence of anthropogenic emissions in continental North America. Contributors to NAB include emissions that react to form ozone from anthropogenic sources outside North America and natural sources globally (e.g., wildfires,

lightning, biogenic except agricultural activities) and stratospheric-tropospheric exchange of ozone.

Establishing NAB ozone concentrations throughout the United States currently requires the application of global-scale chemical transport models (CTMs) alone or in combination with regional CTMs. Recent modeling studies have estimated NAB ozone concentrations to vary between 25 ppb and 50 ppb across the United States (e.g., Zhang et al., 2011; Emery et al., 2012; Fiore et al., 2014), with maximum values (>60 ppb) in western intermountain regions attributed, in part, to stratospheric-tropospheric exchange processes (e.g., Lin et al., 2012; AQR Project 12-011, Emery et al., 2013; Lefohn et al., 2014), wildfires (e.g., Mueller and Mallard, 2011; Jaffe et al., 2012; Zhang et al., 2014), and intercontinental pollution (e.g., Brown-Steiner and Hess, 2011; Verstraeten et al., 2015).

Regional and global modeling studies have specifically examined the contributions of long-range transport on Texas air quality. Using a regional CAMx episode for June 2006 with boundary conditions from GEOS-Chem, McDonald-Buller et al. (2014) found median NAB ozone concentrations were 18 - 22 ppb in eastern Texas urban areas and 20 - 29 ppb in El Paso, consistent with other studies that have found higher concentrations at intermountain west sites (e.g., Emery et al., 2012; Zhang et al., 2014). NAB ozone concentrations increased with altitude over Texas, with less pronounced gradients at higher elevation sites in west Texas. Tai et al. (2013) investigated the effects of removing anthropogenic emissions from geographic regions outside of North America (zROW – i.e., zero out the rest of the world) on predicted ozone concentrations in Texas using GEOS-Chem for selected years during 2006 through 2012. Monthly MDA8 ozone concentrations were relatively lower in El Paso than the Dallas-Fort Worth and Houston urban areas but were subject to higher contributions by sources outside of North America (exceeding 10 ppb in the winter). Anthropogenic emissions were projected to increase in Asia and the Middle East but decline in member countries of the Organization for Economic Cooperation and Development (OECD90) between 2012 and 2018; emissions reductions in Western Europe during this time period were projected to provide at least some benefit to the Eastern U.S., particularly in the Gulf Coast States (Tai et al., 2013).

Boundary conditions for regional chemical transport models

The use of regional-scale photochemical models allows for refined grid resolution, geographic topography, emissions inventories, and meteorological data that may not be achievable with global-scale models because of their computational intensity or that present challenges to their performance. However, regional chemical transport models, such as CMAQ (Foley et al., 2010) and CAMx (ENVIRON, 2014) require lateral and top boundary conditions that are now routinely obtained from global-scale models (Giordano et al., 2015). Common global models employed for North American studies have included the Goddard Earth Observing System – Chemistry model (GEOS-Chem; Bey et al., 2001), The Model for Ozone and Related chemical Tracers (MOZART-4; Emmons et al., 2010) and AM3 (Donner et al., 2011). Because the outer boundaries of regional modeling domains are often located over remote maritime areas, evaluation and validation of model predictions is challenging; recent studies have employed satellite datasets (Tang et al., 2009; Pfister et al., 2011; Henderson et al., 2014; McGaughey et al., 2014), comparisons with observations collected at ground-based monitoring stations in remote U.S. regions (e.g., refer to review by McDonald-Buller et al., 2011), ozonesondes (Pfister

et al., 2011; Li and Rappenglück, 2014), and/or aircraft measurements (Tang et al., 2009; Pfister et al., 2011).

AQRP Project 12-011 (Emery et al., 2013) developed boundary condition inputs for CAMx utilizing output from three global models (GEOS-Chem, MOZART, and AM3) and conducted an evaluation of surface ozone predictions focused on the southwest, south central, and southeast regions of the U.S. surrounding Texas and the Gulf of Mexico. In general, performance of the models tracked each other throughout the 2008 simulation, with differences associated with the representation of lightning NO_x and stratospheric intrusions. AM3 performance was superior in the southwest where the influence of higher ozone concentrations in the upper troposphere and lower stratosphere played a substantial role in the springtime regional surface ozone pattern. These findings and those of other studies (e.g. McDonald-Buller et al., 2011) suggest the utility of continuing to evaluate and further the evolution of multiple global models as resources for regional modeling simulations.

Dry deposition

Dry deposition is broadly defined as the transport of gaseous and particulate species from the atmosphere by turbulent transfer to surfaces in the absence of precipitation (Seinfeld and Pandis, 2012). Dry deposition is estimated to account for 20-25% of total ozone removal from the troposphere globally (Lelieveld and Dentener, 2000; Wild, 2007). On a regional level in Texas, dry deposition represents the most important physical removal mechanism for ozone during the warm spring through early fall seasons (McDonald-Buller et al., 2001); therefore, accurate estimates of dry deposition of ozone and its precursors are required for air quality modeling and management.

In regional air quality models such as CAMx or CMAQ, dry deposition is often treated as a first-order removal mechanism, where a characteristic dry deposition velocity V_d (ratio of deposition flux and concentration) is used to describe the process. Dry deposition of a gas is modeled as the product of its dry deposition velocity and concentration. Dry deposition models, such as those of Wesely (1989) and more recently of Zhang et al. (2003) that are included as options in CAMx, typically employ a resistance approach analogous to Ohm's law in electrical circuits. Three resistances to transport and surface uptake are included: an aerodynamic resistance, quasi-laminar sub-layer resistance, and surface resistance.

Validation of dry deposition models against observations, as well as intercomparisons between models have been conducted (Zhang et al., 2002; Michou et al., 2005; Schwede et al., 2011; Park et al., 2014; Val Martin et al., 2014; Wu et al., 2011), yet significant uncertainties remain (Pleim and Ran, 2011). Dry deposition velocities remain uncharacterized for many compounds or require reconciliation between predictions from algorithms in global and regional chemical transport models and observations (e.g. Nguyen et al., 2015). Observations of ozone dry deposition velocities are extremely limited in Texas, making it difficult to evaluate model estimates. Huang et al. (2015) identified a study, by Kawa (1986), that reported ozone V_d in the range of 1.1 to 1.2 cm/s using an eddy covariance technique over the Big Thicket National Preserve (forest) located in East Texas in June of 1982.

Similar to models used to estimate biogenic emissions, dry deposition algorithms require characterization of land use and land cover, as well as meteorological parameters for evaluating component resistances. Characterizing land cover, in particular in forested and heavily vegetated areas, has been a primary consideration for determining surface resistances; the heterogeneity of the urban environment has typically not been represented in the dry deposition algorithms used in regional-scale transport models. AQRP Project 10-021 (Corsi et al., 2011) conducted laboratory experiments to determine the surface resistance of fresh and weathered built environment surface materials, developed a refined characterization of the urban built environment of Austin, Texas using extensive geospatial data, and examined the effects on the dry deposition of ozone. Changes in predicted daily maximum 8-hour average ozone concentrations were primarily attributed to deposition to urban vegetation and highlighted the importance of characterizing Texas urban landscapes undergoing rapid development.

Responses of vegetation to changes in climate have the potential to alter dry deposition velocities. Recently Huang et al. (2015) modeled seasonal and interannual changes in estimated ozone dry deposition velocities and component resistances over eastern Texas during representative drought years (2006 and 2011). Predicted ozone dry deposition velocities increased during the spring but decreased during the summer and fall seasons reflecting complex and competing responses of deposition pathways (i.e., stomatal and non-stomatal) in vegetated areas. Forests exhibited the most significant reductions in simulated dry deposition velocities. Results from this study emphasized the need for field measurements and the importance of understanding the spatial distribution of impacts on dry deposition over eastern Texas and other regions of the world subject to recurring drought.

2.4.3 References

AQRP Projects:

AQRP Project 10-021: Corsi, R., E. McDonald-Buller, E. Darling, Y. Kimura, and D. Poppendieck, (2011), Dry deposition of ozone to built environment surfaces, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 12-011: Emery, C., E. Tai, and G. Yarwood, (2013), Using global and regional models to represent background ozone entering Texas. Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 12-TN1: Tong D., P. Lee, and L. Pan, (2013), Investigation of surface layer parameterization of the WRF model and its impact on the observed nocturnal wind speed bias, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 13-016: Morris, G., and B. Lefer, (2013), Ozonesonde launches from the University of Houston and Smith Point, Texas in support of DISCOVER-AQ, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-004: Loughner, C.P., and M. Follette-Cook, (2015), Emission source region contributions to a high surface ozone episode during DISCOVER-AQ, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-006: Alrick, D., and G. Morris, (2015), Characterization of boundary layer meteorology during DISCOVER-AQ, Houston, 2013, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-010: Wang, Y., (2015), Impact of large-scale circulation patterns on surface ozone concentrations in Houston-Galveston-Brazoria (HGB), Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-014: Choi, Y. and X. Li, (2015), Constraining NO_x emissions using satellite NO₂ column measurements over the southeast Texas, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-022: McNider, R. T., K. Doty, and Y. L. Wu, (2015), Use of satellite data to improve specifications of land surface parameters, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-025: Emery, C., J. Johnson, D.J. Rasmussen, W. C. Hsieh, G. Yarwood, J. Nielsen-Gammon, K. Bowman, R. Zhang, Y. Lin, and L. Siu, (2015), Development and Evaluation of an Interactive Sub-Grid Cloud Framework for the CAMx Photochemical Model, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

Other:

Appel, K.W., R.C. Gilliam, J.E. Pleim, G.A. Pouliot, D.C. Wong, C. Hogrefe, S.J. Roselle, and R. Mathur, (2014), Improvements to the WRF-CMAQ modeling system for fine-scale air quality simulations, EM, September 2014, 16-21.

Berlin, S.R., A.O. Langford, M. Estes, M., M. Dong, and D.D. Parrish, (2014), Magnitude, decadal changes, and impact of regional background ozone transported into the greater Houston, Texas, Area, Environmental Science & Technology, 47, 13985–13992.

Bey, I., D.J. Jacob, R.M. Yantosca, J.A. Logan, B.D. Field, A.M. Fiore, Q. Li, H.Y. Liu, L.J. Mickley, and M. Schultz, (2001), Global modeling of tropospheric chemistry with assimilated meteorology: model description and evaluation, Journal of Geophysical Research, 106, 23073–23096.

Brown-Steiner, B., and P. Hess, (2011), Asian influence on surface ozone in the United States: a comparison of chemistry, seasonality, and transport mechanisms, Journal of Geophysical Research, 116, <http://dx.doi.org/10.1029/2011jd015846>.

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

Cheng, F.Y., and D.W. Byun, (2008), 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, doi:10.1016/j.atmosenv.2008.02.059.

Cuchiara, G., X. Li, and B. Rappenglück, (2014) Intercomparison of planetary boundary layer parameterization and its impacts on surface ozone concentration in the WRF/Chem model for a case study in Houston/Texas, *Atmospheric Environment*, 96, 175-185, <http://dx.doi.org/10.1016/j.atmosenv.2014.07.013>.

Donner, L.J., B.L. Wyman, R.S. Hemler, L.W. Horowitz, Y. Ming, M. Zhao, J.C. Golaz, P. Ginoux, S.J. Lin, M.D. Schwarzkopf, J. Austin, G. Alaka, W.F. Cooke, T.L. Delworth, S.M. Freidenreich, C.T. Gordon, S.M. Griffies, I.M. Held, W.J. Hurlin, S.A Klein, T.R. Knutson, A.R. Langenhorst, H.C. Lee, Y. Lin, B.I. Magi, S.L. Malyshev, P.C.D. Milly, V. Naik, M.J. Nath, R. Pincus, J.J. Ploshay, V. Ramaswamy, C.J. Seman, E. Shevliakova, J.J. Sirutis, W.F. Stern, R.J. Stouffer, R.J. Wilson, M. Winton, A.T. Wittenberg, and F. Zeng, (2011), The dynamical core, physical parameterizations, and basic simulation characteristics of the atmospheric component AM3 of the GFDL Global Coupled Model CM3, *Journal of Climate*, 24, 3484–3519, <http://dx.doi.org/10.1175/2011JCLI3955.1>.

Emery, C., J. Johnson, P. Piyachaturawat, and G. Yarwood, (2009), 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, and G. Yarwood, (2010), Improving cloud impacts on photolysis using an on-line radiation model in CAMx. The 9th Annual CAMS Conference, Chapel Hill, NC, October 2010.

Emmons, L.K., S. Walters, P.G. Hess, J.F. Lamarque, G.G. Pfister, D. Fillmore, C. Granier, A. Guenther, D. Kinnison, T. Laepple, J. Orlando, X. Tie, G. Tyndall, C. Wiedinmyer, S.L. Baughcum, and S. Kloster, (2010), Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), *Geoscientific Model Development*, 3, 43-67, www.geosci-model-dev.net/3/43/2010/, doi:10.5194/gmd-3-43-2010.

EPA, (2013), Integrated science assessment of ozone and related photochemical oxidants, EPA/600/R-10/076F, Office of Research and Development National Center for Environmental Assessment-RTP Division.

Emery, C., J. Jung, N. Downey, J. Johnson, M. Jimenez, G. Yarwood, and R. Morris, (2012), Regional and global modeling estimates of policy relevant background ozone over the United States, *Atmospheric Environment* 47, 206-217.

ENVIRON, (2011), 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.

ENVIRON, (2014), User's Guide: Comprehensive Air Quality Model with Extensions (CAMx), Version 6.1. Prepared by ENVIRON International Corporation, Novato, CA, April 2014. Available at: www.camx.com.

Fiore, A.M., J.T. Oberman, M.Y. Lin, L. Zhang, O.E. Clifton, D.J. Jacob, V. Naik, L.W. Horowitz, J.P. Pinto, and G.P. Milly, (2014), Estimating North American background ozone in U.S. surface air with two independent global models: Variability, uncertainties and recommendations, *Atmospheric Environment*, 96, 284-300, 2014.

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, and J. Crawford, (2010), Impact of clouds and aerosols on ozone production in Southeast Texas, *Atmospheric Environment* 44, doi:10.106/j.atmosenv.2009.09.005.

Foley, K.M., S.J. Roselle, K.W. Appel, P.V. Bhave, J.E. Pleim, T.L. Otte, R. Mathur, G. Sarwar, J.O. Young, R.C. Gilliam, C.G. Nolte, J.T. Kelly, A.B. Gilliland, and J.O. Bash, (2010), Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7, *Geoscientific Model Development*, 3, 205–226, doi:10.5194/gmd-3-205-2010.

Giordano, L., D. Brunner, J. Flemming, U. Im, C. Hogrefe, R. Bianconi, A. Badia, A. Balzarini, R. Baro, R. Belassio, C. Chemel, G. Curci, R. Forkel, P. Jimenez-Guerrero, M. Hirtl, A. Hodzic, L. Honzak, O. Jorba, C. Knote, J.J.P. Kuenen, P.A. Makar, A. Manders-Groot, L. Neal, J.L. Perez, G. Piravano, G. Pouliot, R. San Jose, N. Savage, W. Schroder, R.S. Sokhi, D. Syrakov, A. Torian, K. Werhahn, R. Wolke, K. Yahya, R. Zabkar, Y. Zhang, J. Zhang, and S. Galmarini, (2015), Assessment of the MACC reanalysis and its influence as chemical boundary conditions for regional air quality modeling in AQMEII-2, *Atmospheric Environment*, 115, 371-388.

Haman, C.L., E. Couzo, J.H. Flynn, W. Vizuete, B. Heffron, B.L. Lefer, (2014), Relationship between boundary layer heights and growth rates with ground-level ozone in Houston, Texas, *Journal of Geophysical Research* <http://dx.doi.org/10.1002/2013JD020473>.

Hegarty, J., H. Mao, and R. Talbot., (2007), Synoptic controls on summertime surface ozone in the northeastern United States, *Journal of Geophysical Research*, 112, D14306, 2007.

Henderson, B.H., F. Akhtar, H.O.T. Pye, S.L. Napelenok, and W.T. Hutzell, (2014), A database and tool for boundary conditions for regional air quality modeling: description and evaluation, *Geoscientific Model Development*, 7(1), 339–360. <http://doi.org/10.5194/gmd-7-339-2014>.

Hogrefe, C., J. Biswas, B. Lynn, K. Civerolo, J.-Y. Ku, J. Rosenthal, C. Rosenzweig, R. Goldberg, and P.L. Kinney, (2004), Simulating regional-scale ozone climatology over the eastern United States: Model evaluation results, *Atmospheric Environment*, 38, 2627-2638, 2004.

Hu, X., J. Nielsen-Gammon, and F. Zhang, (2010), Evaluation of three planetary boundary layer schemes in the WRF model. *Journal of Applied Meteorology and Climate*, 49, 1831-1844, <http://dx.doi.org/10.1175/2010JAMC2432.1>.

Hu, X., P.M. Klein, and M. Xue, (2013), Evaluation of the updated YSU planetary boundary layer scheme within WRF for wind resource and air quality assessments, *Journal of Geophysical Research Atmospheres*, 118, 10,490-10,505. <http://dx.doi.org/10.1002/jgrd.50823>.

Huang, L., E.C. McDonald-Buller, G. McGaughey, Y. Kimura, and D.T. Allen, (2015), The impact of drought on ozone dry deposition over eastern Texas, submitted to Atmospheric Environment.

Jacob, D. J., and D.A. Winner, (2009), Effect of climate change on air quality, Atmospheric Environment, 43(1), 51-63, 2009.

Jaffe, D.A. and N.I. Wigder, (2012) Ozone production from wildfires: a critical review, Atmospheric Environment, 51, 1-10.

Kawa, S.R., (1986), Ozone deposition, scalar budgets and radiative heating over Texas coastal forest and ocean. Department of Atmospheric Science, Colorado State University.

Kolling, J., J. Pleim, H. Jeffries, and W. Vizuete, (2013), A multisensor evaluation of the asymmetric convection model, version 2, in Southeast Texas, Journal of the Air & Waste Management Association, 63(1), 41e53. <http://dx.doi.org/10.1080/10962247.2012.732019>.

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, and E.J. Williams, (2010), Convective venting and surface ozone in Houston during TexAQS 2006, Journal of Geophysical Research, 115, 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, and R.J. Zamora, (2011), 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, doi:10.5194/acp-11-2127-2011.

Lefohn, A.S., Emery, C., Shadwick, D., Wernli, H., Jung, J., S.J. Oltmans,, (2014), Estimates of background surface ozone concentrations in the United States based on model-derived source apportionment, Atmospheric Environment, 84, 275-288.

Lelieveld, J., and F.J. Dentener, (2000), What controls tropospheric ozone? Journal of Geophysical Research: Atmospheres, 105, 3531–3551.

Lin, M., A.M. L.W. Fiore, O.R. Horowitz, V.R. Cooper, J. Naik, B.J. Holloway, A.M. Johnson, S.J. Middlebrook, I.B. Oltmans, T.B. Pollack, J.X. Ryerson, C. Warner, C. Wiedinmyer, J. Wilson, and B. Wyman, (2012), Transport of Asian ozone pollution into surface air over the western United States in spring, Journal of Geophysical Research Atmospheres, 117, D00V07, DOI: 10.1029/2011JD016961.

Li, L., W. Li, and Y. Kushnir, (2012), Variation of North Atlantic Subtropical High western ridge and its implication to the Southeastern US summer precipitation, Climate Dynamics, 39, 1401-1412.

Li, X., and B. Rappenglück, (2014), A WRF-CMAQ study on spring time vertical ozone structure in southeast Texas, *Atmospheric Environment*, 97, 363-385.

McDonald-Buller, E., C. Wiedinmyer, Y. Kimura, and D. Allen, (2001), Effects of land use data on dry deposition in a regional photochemical model for eastern Texas, *Journal of the Air & Waste Management Association*, 51(8), 1211–1218. doi:10.1080/10473289.2001.10464340.

McDonald-Buller, E., Y. Kimura, G. McGaughey, and D.T. Allen, (2014), Predictions of North American background ozone in Texas, Presented at the 13th annual CMAS conference, Chapel Hill, NC, October 27-20, 2014, https://www.cmascenter.org/conference/2014/abstracts/elena_mcdonald-buller_predictions_north_2014.pdf

McDonald-Buller, E.C., D.T. Allen, N. Brown, D.J. Jacob, D. Jaffe, C.E. Kolb, A.S. Lefohn, S. Oltmans, D.D. Parrish, G. Yarwood, and I. Zhang, (2011) Establishing policy relevant background (PRB) ozone concentrations in the United States, *Environmental Science & Technology*, 45, 9484-9497. <http://dx.doi.org/10.1021/es2022918>.

McGaughey, G., D.T. Allen, E.C. McDonald-Buller, S. Smith, and T. Howard, (2011), Analysis of O₃ and NO₂ boundary conditions for regional chemical transport modeling of southeastern Texas using satellite observations. Prepared for Texas Air Research Center (TARC), Prepared by the Center for Energy and Environmental Resources, The University of Texas at Austin, August 31, 2011.

McGaughey, G., C. Durrenberger, and E.C. McDonald-Buller, (2013), Conceptual model for ozone for the Austin area. Prepared for the Capital Area Council of Governments (CAPCOG) and Texas Commission on Environmental Quality (TCEQ) by The University of Texas at Austin, 2013.

McGaughey, G., C. Durrenberger, and E.C. McDonald-Buller, (2015), Conceptual model for ozone for the Victoria area. Prepared for the City of Victoria and Texas Commission on Environmental Quality (TCEQ) by The University of Texas at Austin, 2015.

Michou, M., P. Laville, D. Serça, A. Fotiadi, P. Bouchou, and V.H. Peuch, (2005), Measured and modeled dry deposition velocities over the ESCOMPTE area, *Atmospheric Research*, 74, 89–116. doi:10.1016/j.atmosres.2004.04.011

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

Mueller, S.F., and J.W. Mallard, (2011), Contributions of natural emissions to ozone and PM_{2.5} as simulated by the Community Multiscale Air Quality (CMAQ) model, *Environmental Science & Technology*, 45(11), 4817-4823. doi: 10.1021/es103645m.

Ngan, F., and D. Byun, (2011), 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*, 50,485-50,499.

Ngan, F., D. Byun, H. Kim, D. Lee, B. Rappengluck, and A. Pour-Biazar, (2012), Performance assessment of retrospective meteorological inputs for use in air quality modeling during TexAQS 2006. *Atmospheric Environment*, 54, 86-96.

Nguyen, T.B., J.D. Crouse, A.P. Teng, J.M.S. Clair, F. Paulot, G.M. Wolfe, and P.O. Wennberg, (2015), Rapid deposition of oxidized biogenic compounds to a temperate forest, *Proceedings of the National Academy of Sciences*, 112(5), E392-E401.

Nielsen-Gammon, J.W., J. Tobin, A. McNeel, and G. Li, (2005), 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., R.T. McNider, W.M. Angevine, A.B. White, and K. Knupp, (2007), Mesoscale model performance with assimilation of wind profiler data: Sensitivity to assimilation parameters and network configuration, *Journal of Geophysical Research Atmospheres*, 112, doi:10.1029/2006jd007633.

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

Park, R.J., S.K. Hong,, H.A. Kwon, S. Kim, A. Guenther, J.H. Woo, and C.P. Loughner, (2014), An evaluation of ozone dry deposition simulations in East Asia, *Atmospheric Chemistry and Physics*, 14(15), 7929–7940. doi:10.5194/acp-14-7929-2014

Pfister, G.G., D.D. Parrish, H. Worden, L.K. Emmons, D.P. Edwards, C. Wiedinmyer, G.S. Diskin, G. Huey, S.J. Oltmans, V. Thouret, A. Weinheimer, and A. Wisthaler, (2011), Characterizing summertime chemical boundary conditions for airmasses entering the US West Coast, *Atmospheric Chemistry and Physics*, 11, 1769–1790, doi:10.5194/acp-11-1769-2011, 2011. 5767

Pleim, J., and L. Ran, (2011), Surface flux modeling for air quality applications, *Atmosphere*, 2(4), 271–302. doi:10.3390/atmos2030271.

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, and R. Cameron, (2007), 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, and R.T. McNider, (2011), 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.

Rappengluck, B., R. Perna, S. Zhong, and G.A. Morris, (2008), 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, D17315, doi:10.1029/2007JD009745.

Schwede, D., L. Zhang, R. Vet, and G. Lear, (2011), An intercomparison of the deposition models used in the CASTNET and CAPMoN networks, *Atmospheric Environment*, 45(6), 1337–1346. doi:10.1016/j.atmosenv.2010.11.050

Seinfeld, J.H., and S.N. Pandis, (2012), *Atmospheric chemistry and physics: from air pollution to climate change*. John Wiley & Sons.

Shen, L., L.J. Mickley and A.P.K. Tai, (2015), Influence of Synoptic Patterns on Surface Ozone Variability over the Eastern United States from 1980 to 2012, *Atmospheric Chemistry and Physics Discussions*, 15, 13073-13108, 2015.

Stuart, A.L., A.Aksoy, F. Zhang, and J.W. Nielsen-Gammon, (2006), Ensemble-based data assimilation and targeted observation of a chemical tracer in a sea breeze model, *Atmospheric Environment* 41, doi:10.1016/j.atmosenv.2006.11.046.

Tai, E., O. Nopmongkol, J. Jung, J. King, Y. Alvarez, and G. Yarwood, (2013), Foreign contributions to Texas' ozone, Prepared for the Texas Commission on Environmental Quality, August 2013, WO 582-11-10365-FY13-14 Final Report.

Tang, Y., P. Lee, M. Tsidulko, H.-C. Huang, J.T. McQueen, G.J. DiMego, L.K. Emmons, R.B. Pierce, A.M. Thompson, H.-M. Lin, D. Kang, D. Tong, S. Yu, R. Mathur, J.E. Pleim, T.L. Otte, G. Pouliot, J.O. Young, K.L. Schere, P.M. Davidson, and I. Stajner, (2009), The impact of chemical lateral boundary conditions on CMAQ predictions of tropospheric ozone over the continental United States, *Environmental Fluid Mechanics*, 9, 43-58, doi: 10.1007/s10652-008-9092-5.

Tang, W., D.S. Cohan, G.A. Morris, D.W. Byun, and W.T. Luke, (2011) Influence of vertical mixing uncertainties on ozone simulation in CMAQ, *Atmospheric Environment*, 45, 2898-2909.

TCEQ, (2011), 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.

TCEQ, (2015), Dallas-Fort Worth Attainment Demonstration SIP Revision for the 1997 Eight-Hour Ozone Standard, Austin, TX, Meteorological modeling for the DFW attainment

demonstration SIP revision for the 2008 eight-hour ozone standard, https://www.tceq.texas.gov/assets/public/implementation/air/sip/dfw/dfw_ad_sip_2015/AD/Adoption/DFW_SIP_Appendix_A_060315.pdf, accessed August 2015.

Val Martin, M., C.L. Heald, and S.R. Arnold, (2014), Coupling dry deposition to vegetation phenology in the Community Earth System Model: Implications for the simulation of surface O₃, *Geophysical Research Letters*, 41(8), 2988–2996. doi:10.1002/2014GL059651.

Verstraeten, W.W., J.L. Neu, J.E. Williams, K.W. Bowman, J.R. Worden, and K.F. Goersma, (2015), Rapid increases in tropospheric ozone production and export from China, *Nature Geoscience*, 8(9), 690-695, doi:10.1038/ngeo2493.

Wesely, M. L., (1989), Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, *Atmospheric Environment*, 23(6), 1293–1304.

Wild, O., (2007), Modelling the global tropospheric ozone budget : Exploring the variability in current models, *Atmospheric Chemistry and Physics*, 7(10), 2643–2660.

Wilmot, C.-S.M., B. Rappenglück, and X. Li, (2014), MM5 v3.6.1 and WRF v3.2.1 model comparison of standard and surface energy variables in the development of the planetary boundary layer. *Geoscientific Model Development Discussions*, 7, 2705-2743. <http://dx.doi.org/10.5194/gmdd-7-1-2014>.

Wu, Z., X. Wang, F. Chen, A.A. Turnipseed, A.B. Guenther, D. Niyogi, U. Charusombat, B. Xia, J.W. Munger, and K. Alapaty, (2011), Evaluating the calculated dry deposition velocities of reactive nitrogen oxides and ozone from two community models over a temperate deciduous forest, *Atmospheric Environment*, 45(16), 2663-2674.

Yerramilli, A., V. Challa, V. Dodla, H. Dasari, J. Young, C. Patrick, J. Baham, R. Hughes, M. Hardy, and S. Swanier, (2010), Simulation of surface ozone pollution in the central Gulf Coast region using WRF/Chem model: sensitivity to PBL and land surface physics. *Advances in Meteorology*, <http://dx.doi.org/10.115/2010/319138>.

Zhang, L., J.R. Brook, and R. Vet, (2002), On ozone dry deposition — with emphasis on non-stomatal uptake and wet canopies, *Atmospheric Environment*, 36(30), 4787–4799.

Zhang, L., J.R. Brook, and R. Vet, (2003), A revised parameterization for gaseous dry deposition in air-quality models, *Atmospheric Chemistry and Physics*, 3(6), 2067-2082.

Zhang, F., N. Bei, J.W. Nielsen-Gammon, L. Guohui, R. Zhang, A. Stuart, A. Aksoy, (2007), 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.

Zhang, L., D.J. Jacob, N.V. Downey, D.A. Wood, D. Blewitt, C.C. Carouge, A. van Donkelaar, D.B.A. Jones, L.T. Murray, and Y. Wang, (2011), Improved estimate of the policy-relevant

background ozone in the United States using the GEOSChem global model with horizontal resolution over North America, *Atmospheric Environment*, 45, 6769-6776.

Zhang, L., D.J. Jacob, X. Yue, N.V. Downey, D.A. Wood, and D. Blewitt, (2014), Sources contributing to background surface ozone in the US Intermountain West, *Atmospheric Chemistry and Physics*, 14, 5295-5309. <http://dx.doi.org/10.5194/acp-14-5295-2014>.

Zhu, J. and X. Liang, (2013), Impacts of the Bermuda High on Regional Climate and Ozone over the United States, *Journal of Climate*, 26, 1018-1032, 2013.

2.5 Particulate matter

2.5.1 Overview

Most of the research of the AQRP program has focused on improving the understanding of emissions, chemistry and atmospheric physical processes that lead to ozone formation and accumulation. This is because ozone is the air pollutant for which the State has the greatest number of regions that do not meet the NAAQS. With the recent tightening of the NAAQS for fine particulate matter, however, some regions in Texas are approaching non-attainment for fine particulate matter as well; a number of AQRP projects have been funded to specifically address particulate matter. These projects are summarized in this Section.

2.5.2 Particulate matter sources and composition in Southeastern Texas: Assessment from AQRP projects 2010-2015

Over the past 15 years, measurements during field campaigns have been made to better characterize particulate matter size, composition and concentrations in southeastern 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 (i.e., particles with diameters less than or equal to 2.5 micrometers) in southeastern Texas (Russell et al., 2004). Measurements conducted during the SHARP, TexAQS/GoMACCS 2006, and more recently DISCOVER-AQ campaigns have sought to continue to improve the spatial and temporal characterization of fine particulate matter composition and sources and to develop new measurement approaches for characterizing aerosol concentration, size distribution, and optical properties (AQRP Project 14-005, Brooks and Yang, 2015). In 2012, the EPA promulgated a more stringent primary annual NAAQS for fine particulate matter of $12 \mu\text{g m}^{-3}$, a decrease from the level of the 1997 standard of $15 \mu\text{g m}^{-3}$. Although the Houston area has experienced declines in fine particulate mass matter concentrations over the past decade at regulatory monitoring sites, it remains close to the level of nonattainment with the 2012 federal standard. As of January 15, 2015, the Houston area was designated by the EPA as “unclassifiable/attainment” (HGAC, 2015).

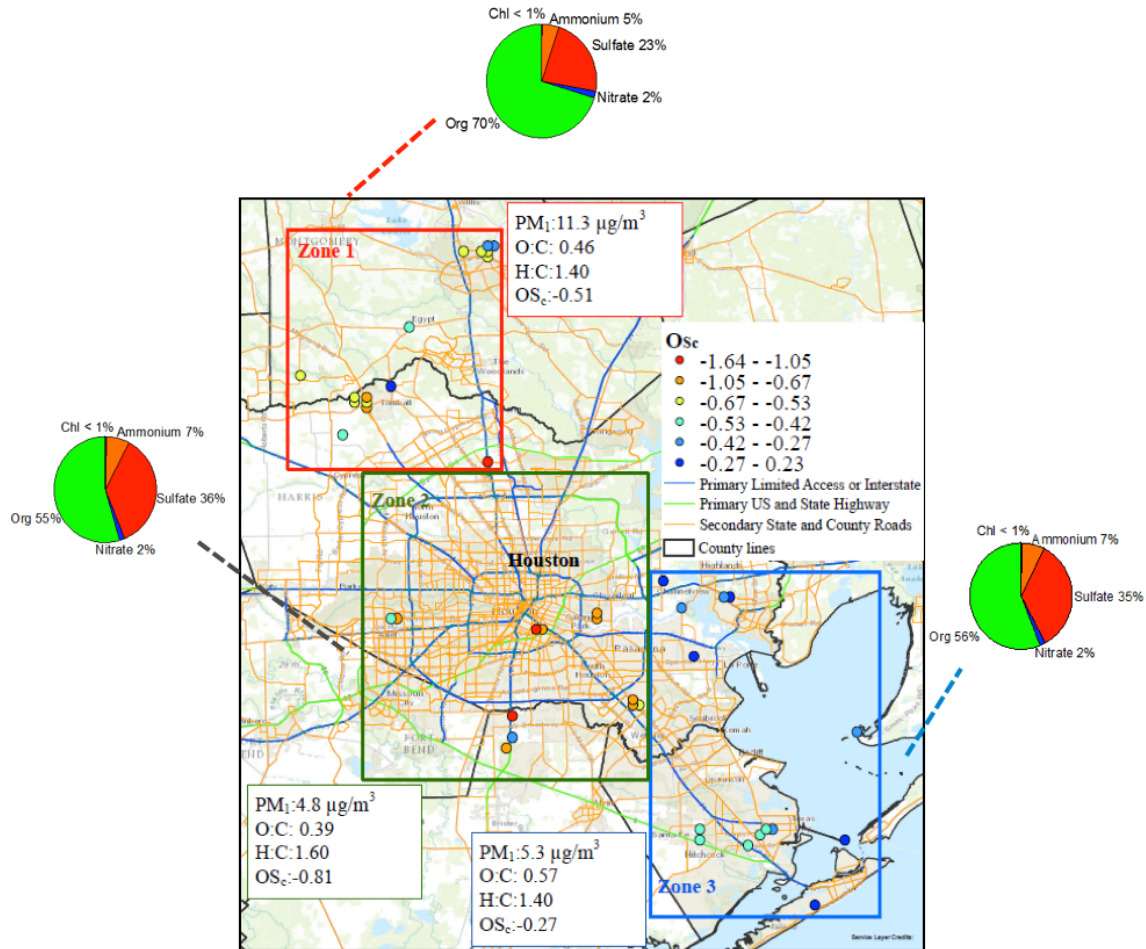
Zhang et al. (2015) have a recent critical review of urban fine particulate matter with an overview of Houston and other metropolitan areas (Beijing, Los Angeles, and Mexico City) that have had intensive atmospheric field measurement campaigns. AQRP Projects 13-022 (Griffin et al., 2014) and 14-009 (Griffin and Lefer, 2015) provided a recent characterization of the spatial variation of submicron particulate matter composition across Houston during the DISCOVER-AQ campaign. Figure 2.5.1, which is drawn from this work, indicates the relative importance of organic aerosol and sulfate as particulate matter species (Griffin and Lefer, 2015). Positive Matrix Factorization (PMF) analysis was applied for zonal-based identification of organic aerosol components, including hydrocarbon-like organic aerosol (HOA), which is a proxy for POA, and various forms of oxygenated organic aerosol (OOA-I representing less aged fresh SOA and OOA-II representing aged and oxidized regional SOA). Secondary organic aerosol represented more than 90% of organic aerosol in Zones 1 (northwest Houston) and 3 (east and southeast Houston); the OOA-I factor was more important than the OOA-II factor, suggesting overall the influences of regional transport and anthropogenic and biogenic VOC emission sources. Sources likely differed between zones. For example, higher levels of isoprene and

monoterpenes were predicted in northwest Houston than the other zones. Monoterpene concentrations exhibit statistically significant moderate correlation with levels of SOA and OOA-I in this zone; Principal Component Analysis (PCA) suggested that monoterpenes may impact SOA formation through oxidation by nitrate radical. Although the composition of OA in Zone 2 (central Houston) also indicated the dominant contribution of SOA (67%), it had a more primary character than the other zones suggesting greater impacts by sources of primary aerosol such as motor vehicles.

Radiocarbon measurements made during DISCOVER-AQ for AQRP Projects 12-032 (Sheesley and Usenko, 2013) and 14-029 (Sheesley and Usenko, 2015) distinguished fossil (i.e., primary fossil fuel combustion and SOA produced in the atmosphere from fossil-derived volatile organic carbon) and contemporary sources (i.e., primary biogenic emissions, biomass combustion and SOA produced in the atmosphere from biogenic- and biomass combustion-derived volatile organic carbon) at selected sites in Houston. Moody Tower, a site indicative of urban Houston, had a consistent primary motor vehicle exhaust contribution of 18-27%, a fossil SOA contribution that varied from 5% to 33% depending on atmospheric conditions, and biogenic SOA contribution ranging from 40% to 75%. Conroe, a site indicative of aged urban aerosol combined with biogenics located north of Houston, had a lower contribution of motor vehicle exhaust (5% to 10%), a similarly variable fraction of fossil SOA (4% to 25%), and a biogenics contribution of 60% to 79%.

These findings were broadly consistent with those of earlier studies that have been conducted during field campaigns in southeastern Texas over the past 15 years. Measurements made during TexAQS 2000 and GC-ARCH (Allen, 2005) indicated that fine particulate matter composition in southeast Texas was dominated by sulfate primarily from regional sources and organic carbon of regional and local origin. Fires can be an important event-based contribution to fine particulate matter mass. Secondary organic aerosol formation was associated with reactions of biogenic and anthropogenic precursors. Particle size distributions were not spatially homogeneous; industrial sites had higher concentrations of ultrafine particles than more residential sites. Yu and Cowin (2009) found that the averages and ranges of organic, elemental, and total during the SHARP campaign were comparable to observations in the early 2000s (Allen, 2004, 2005). The average OC to EC ratio was 6.9, indicating that secondary organic aerosols were a component in the carbonaceous aerosols observed in Houston. Bahreini et al. (2009) found greater organic aerosol mass downwind of the Houston industrial center relative to the urban area during TexAQS 2006. Observed ratios of the enhancement above background in OA, Δ OA, to the enhancement above background in carbon monoxide (CO), Δ CO, downwind of the Houston urban center were within a factor of two of the same values in plumes from urban areas in the northeastern United States (de Gouw, 2008) indicating similar concentrations of precursors and chemical processes. However, Δ OA/ Δ CO in plumes originating from the Houston Ship Channel exceeded that in the urban area by factors ranging from 1.5 to 7.

Figure 2.5.1. From Griffin and Lefer (2015; ref. Table 12): Average contribution of particulate matter constituents, concentrations, and oxidation metrics in three analysis zones defined by average carbon oxidation state (OS_c) and geography. Zone 1- northwest Houston; Zone 2 - greater central Houston; Zone 3 - east and southeast Houston. Average concentrations ($\mu\text{g m}^{-3}$) and associated standard deviations (in parentheses) of PM species in the defined analysis zones are shown in the accompanying table.



Zone	OA	Sulfate	Nitrate	Ammonium	Chloride
1	8.16 (± 3.54)	2.4 (± 0.60)	0.23 (± 0.15)	0.53 (± 0.15)	0.019 (± 0.007)
2	2.68 (± 1.73)	1.68 (± 1.01)	0.08 (± 0.09)	0.37 (± 0.26)	0.013 (± 0.008)
3	3.03 (± 1.9)	1.58 (± 0.63)	0.08 (± 0.047)	0.33 (± 0.16)	0.0076 (± 0.004)

2.5.3 References

AQRP Projects:

AQRP Project 12-032: Sheesley, R., and S. Usenko, (2013), Collect, analyze, and archive filters at two DISCOVER-AQ Houston focus areas: Initial characterization of PM formation and emission, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 13-022: Griffin, R. B. Lefer, and R. Talbot, (2014), Surface measurements of PM, VOCs and photochemically relevant gases in support of DISCOVER-AQ, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-005: Brooks, S. and P. Yang, (2015), Sources and Properties of Atmospheric Aerosol in Texas: DISCOVER-AQ Measurements and Validation, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-009: Griffin, R. and B. Lefer, (2015), Analysis of surface particulate matter and trace gas data generated during the Houston operations of DISCOVER-AQ, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

AQRP Project 14-029: Sheesley, R., and S. Usenko, (2015), Spatial and temporal resolution of primary and secondary particulate matter in Houston during DISCOVER-AQ, Prepared for the Texas Air Quality Research Program, <http://aqrp.ceer.utexas.edu/>

Other:

Allen D., (2005), 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.

Allen, D., (2004), 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.

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, and F.C. Fehsenfeld, (2009), Organic aerosol formation in urban and industrial plumes near Houston and Dallas, Texas. *Journal of Geophysical Research*, 114, doi:10.1029/2008JD011493.

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, and E.J. Williams, (2008), 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, doi:10.1029/2007JD009243.

Houston Galveston Area Council (HGAC), (2015), Houston-Galveston-Brazoria (HGB) PM2.5 advance path forward update, Prepared in partnership by members of the H-GAC regional air quality planning advisory committee, 2015 update, <http://www.hgac.com/taq/airquality/raqpac/documents/2015/June25/Path%20Forward%20DRAFT%202015%20Base%20Document%20-%20Final.pdf>

Russell, M., D. Allen, D. Collins, and M. Fraser, (2004), Daily, seasonal, and spatial trends in PM2.5 mass and composition in Southeast Texas, *Aerosol Science and Technology* 38 (S1), 14-26.

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

Zhang, R., G. Wang, S. Guo, M.L. Zamora, Q. Ying, Y. Ling, W. Wang, M. Hu, and Y. Wang, (2015), Formation of urban fine particulate matter, *Chemical Reviews*, 115(10), 3803-55, doi: 10.1021/acs.chemrev.5b00067.

3. Summary of Projects and Publications from the Air Quality Research Program (AQRP, 2010-2015)

Fifty research projects and two science synthesis projects were funded by the AQRP between 2010 and 2015. The 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>).

Table 3-1. AQRP Research Projects 2010-2012

Project Number	Title
<i>Dallas-Fort Worth Area Studies</i>	
10-DFW, 11-DFW	Logistical Support for Dallas-Fort Worth (Barnett Shale) Measurement Study
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
<i>Houston Area Studies</i>	
10-032	SHARP Data Analysis: Radical Budget and Ozone Production
10-045	Quantification of Hydrocarbon, NO _x and SO ₂ Emissions from Petrochemical Facilities in Houston: Interpretation of the 2009 FLAIR Dataset
12-013	Development of Transformation Rate of SO ₂ to Sulfate for the Houston Ship Channel using the TexAQS 2006 Field Study Data
14-010	Impact of large-scale circulation patterns on surface ozone concentrations in HGB
<i>DISCOVER-AQ (Houston) Studies</i>	
12-004	Logistical Support for DISCOVER-AQ Measurement Study
13-005	Quantification of industrial emissions of VOCs, NO ₂ and SO ₂ by SOF and mobile DOAS during DISCOVER-AQ
13-016	Ozonesonde launches from the University of Houston and Smith Point, Texas in Support of DISCOVER-AQ
13-022	Surface Measurements of PM, VOCs, and Photochemically Relevant Gases in Support of DISCOVER-AQ
13-024	Surface Measurement of Trace Gases in Support of DISCOVER-AQ in Houston in Summer 2013
12-032	Collect, Analyze, and Archive Filters at two DISCOVER-AQ Houston Focus Areas
14-002	Analysis of Airborne Formaldehyde Data Over Houston Texas Acquired During the 2013 DISCOVER-AQ and SEAC4RS Campaigns
14-004	Emission Source region contributions to a high surface ozone episode during DISCOVER-AQ
14-005	Sources and Properties of Atmospheric Aerosol in Texas: DISCOVER-AQ Measurements and Validation
14-006	Characterization of Boundary-Layer Meteorology during DISCOVER-AQ Using Radar Wind Profiler and Balloon Sounding Measurements
14-007	Improved Analysis of VOC, NO ₂ , SO ₂ and HCHO data from SOF, mobile DOAS

	and MW-DOAS during DISCOVER-AQ
14-009	Analysis of Surface Particulate Matter and Trace Gas Data Generated during the Houston Operations of DISCOVER-AQ
14-014	Constraining NO _x Emissions Using Satellite NO ₂ and HCHO Column Measurements over Southeast Texas
14-020	Analysis of Ozone Formation Sensitivity in Houston Using the Data Collected during DISCOVER-AQ and SEAC4RS
14-024	Sources of Organic Particulate Matter in Houston: Evidence from DISCOVER-AQ Data, Modeling and Experiments
14-026	Quantifying ozone production from light alkenes using novel measurements of hydroxynitrate reaction products in Houston during the NASA SEAC4RS project
14-029	Spatial and temporal resolution of primary and secondary particulate matter in Houston during DISCOVER-AQ
<i>Flares and Emission Inventories</i>	
10-006	Quantification of Industrial Emissions of VOCs, NO ₂ and SO ₂ 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
12-011	Investigation of Global Modeling and Lightning NO _x Emissions as Sources of Regional Background Ozone in Texas
12-018	The Effects of Uncertainties in Fire Emissions Estimates on Predictions of Texas Air Quality
14-011	Targeted Improvements in the Fire Inventory from NCAR (FINN) Model for Texas Air Quality Planning
14-023	Assessment of Two Remote Sensing Technologies to Control Flare Performance
<i>Emissions and Chemistry of Biogenic Volatile Organic Compounds</i>	
14-003	Update and evaluation of model algorithms needed to predict Particulate Matter from Isoprene
14-008	Investigation of Input Parameters for Biogenic Emissions Modeling in Texas during Drought Years
14-016	Improved Land Cover and Emission Factor Inputs for Estimating Biogenic Isoprene and Monoterpene Emissions for Texas Air Quality Simulations
14-017	Incorporating Space-borne Observations to Improve Biogenic Emission Estimates in Texas
14-030	Improving Modeled Biogenic Isoprene Emissions under Drought Conditions and Evaluating Their Impact on Ozone Formation
<i>Modeling and Atmospheric Chemistry</i>	
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	NO _x 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 NO _x Sinks and Recycling in

	Atmospheric Chemical Mechanisms
12-006	Environmental chamber experiments and CMAQ modeling to improve mechanisms to model ozone formation from HRVOCs
12-012	Interactions Between Organic Aerosol and NO _y : Influence on Oxidant Production
12-028	Implementation and evaluation of new HONO mechanisms in a 3-D Chemical Transport Model for Spring 2009 in Houston
12-TN1	Investigation of surface layer parameterization of the WRF model and its impact on the observed nocturnal wind speed bias
12-TN2	Development of IDL-based geospatial data processing framework for meteorology and air quality modeling
14-022	Use of satellite data to improve specifications of land surface parameters
14-025	Development and Evaluation of an Interactive Sub-Grid Cloud Framework for the CAMx Photochemical Model
<i>State of the Science Evaluations</i>	
10-SSA	State of the Science Synthesis, 2012
	State of the Science Synthesis, 2015

PUBLICATIONS

FY10-11

10-006

Johansson, J., Johan Mellqvist, Jerker Samuelsson, Brian Offerle, Jana Moldanova, Bernhard Rappenglück, Barry Lefer, and James Flynn (2014), Formaldehyde Quantitative Measurements and Modeling of Industrial Formaldehyde Emissions in the Greater Houston Area during Campaigns in 2009 and 2011, *Journal of Geophysical Research: Atmospheres*, 119, DOI: 10.1002/2013JD020159

Johansson, J. K. E., J. Mellqvist, J. Samuelsson, B. Offerle, B. Lefer, B. Rappenglück, J. Flynn, and G. Yarwood(2014), Emission measurements of alkenes, alkanes, SO₂, and NO₂ from stationary sources in Southeast Texas over a 5 year period using SOF and mobile DOAS, *J. Geophys. Res. Atmos.*, 119, doi:10.1002/2013JD020485.

10-008

Digar, A., D.S. Cohan, X. Xiao, K.M. Foley, B. Koo, and G. Yarwood (2013). Constraining ozone-precursor responsiveness using ambient measurements. *Journal of Geophysical Research*, 118(2), 1005-1019, doi:10.1029/2012JD018100.

10-009

The following papers were published in the journal *Industrial & Engineering Chemistry Research* in a Special Issue on Industrial Flaring:

Torres, V.M., Herndon, S., Wood, E., Al-Fadhli, F.M., Allen, D.T., Emissions of Nitrogen Oxides from Flares Operating at Low Flow Conditions, *Industrial & Engineering Chemistry Research*, 51, 12600-12605, DOI: 10.1021/ie300179x (2012)

Pavlovic, R.T., Al-Fadhli, Kimura, Y., Allen, D.T., and McDonald-Buller, E.C. Impacts of Emission Variability and Flare Combustion Efficiency on Ozone Formation in the Houston-Galveston-Brazoria Area, *Industrial & Engineering Chemistry Research*, 51, 12593-12599, DOI: 10.1021/ie203052w (2012).

Knighton, W.B., Herndon, S.C., Franklin, J.F., Wood, E.C., Wormhoudt, J., Brooks, W., Fortner, E.C., and Allen, D.T. Direct measurement of volatile organic compound emissions from industrial flares using real-time on-line techniques: Proton Transfer Reaction Mass Spectrometry and Tunable Infrared Laser Differential Absorption Spectroscopy, *Industrial & Engineering Chemistry Research*, 51, 12674-12684, DOI: 10.1021/ie202695v (2012)

Torres, V.M., Herndon, S., Kodesh, Z., Nettles, R., and Allen, D.T. "Industrial flare performance at low flow conditions: Part 1. Study Overview" *Industrial & Engineering Chemistry Research*, 51, 12559-12568, 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*, 51, 12569-12576, DOI: 10.1021/ie202675f (2012)

Herndon, S.C., Nelson, D.D., Wood, E.C., Knighton, W.B., Kolb, C.E., Kodesh, Z., Torres, V.M., and Allen, D.T., Application of the carbon balance method to flare emissions characteristics, *Industrial & Engineering Chemistry Research*, 51, 12577-12585, DOI: 10.1021/ie202676b (2012)

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*, 51, 12663-12673, DOI: 10.1021/ie201400z (2012).

The following presentations were given at the Air & Waste Management Association June 2012 Conference, and papers were published in the Conference Proceedings:

Torres, V.M., Allen, D.T., Herndon, S. and Kodesh, Z., Overview of the Texas Commission on Environmental Quality 2010 Flare Study, Air and Waste Association Annual Meeting, Extended Abstract 2012-A-437-AWMA, San Antonio, June, 2012.

Torres, V.M., Al-Fadhli, F.M., Allen, D.T., Herndon, S., and Wood, E., NO_x Emissions from Industrial Flaring, Air and Waste Association Annual Meeting, Extended Abstract 2012-A-315-AWMA, San Antonio, June, 2012.

10-015

The following papers are currently under development:

Measurements of Nitryl Chloride in Several Metropolitan Areas and Comparison with Regional Models

J.M. Roberts, H. Osthoff, E.J. Williams, B. Lerner, J.A. Neuman, J.B. Nowak, S.B. Brown, W.P. Dube, N.L. Wagner, T.B. Ryerson, I.B. Pollack, J.S. Holloway, A. Middlebrook, R. Bahreini, B. Koo, G. Yarwood

In preparation for Journal of Geophysical Research

Hydrochloric acid at the Pasadena ground site during CalNex 2010 and its role as a source of aerosol chloride

J.M. Roberts, P.R. Veres, A.K. Cochran, C. Warneke, J. de Gouw, R. Weber, R. Ellis, T. Vandenboer, J. Murphy, B. Koo, G. Yarwood

In preparation for Journal of Geophysical Research

10-020

Brown, S. S. et al. (2012), Effects of NO_x control and plume mixing on nighttime chemical processing of plumes from coal-fired power plants, *J. Geophys. Res.*, 117, D07304, doi:[10.1029/2011JD016954](https://doi.org/10.1029/2011JD016954).

Brown, S. S., Dubé, W. P., Bahreini, R., Middlebrook, A. M., Brock, C. A., Warneke, C., de Gouw, J. A., Washenfelder, R. A., Atlas, E., Peischl, J., Ryerson, T. B., Holloway, J. S., Schwarz, J. P., Spackman, R., Trainer, M., Parrish, D. D., Fehsenfeld, F. C., and Ravishankara, A. R.: Biogenic VOC oxidation and organic aerosol formation in an urban nocturnal boundary layer: aircraft vertical profiles in Houston, TX, *Atmos. Chem. Phys.*, 13, 11317-11337, doi:10.5194/acp-13-11317-2013, 2013.

In preparation for Atmosphere:

Reactive Plume Modeling to Investigate NO_x Reactions and Transport at Night

Prakash Karamchandani, Shu-Yun Chen, Greg Yarwood, Steven S. Brown, David Parrish

In preparation for Atmosphere:

Modeling Overnight Power Plant Plume Impacts on Next-Day Ozone Using a Plume-in-Grid Technique

Greg Yarwood, Chris Emery, Steven S. Brown, David Parrish

10-021

The Project Investigators presented findings from this project at the Air & Waste Management Association June 2012 Conference. The title of the submitted abstract was *Dry Deposition of Ozone to Built Environment Surfaces* and the authors are Yosuke Kimura, Dustin Poppendeck, Erin Darling, Elena McDonald-Buller, and Richard Corsi

10-022

Kanwar Devesh Singh, Tanaji Dabade, Hitesh Vaid, Preeti Gangadharan, Daniel Chen, Helen H. Lou, Xianchang Li, Kuyen Li, and Christopher B. Martin "Computational Fluid Dynamics Modeling of Industrial Flares Operated in Stand-By Model," *Industrial & Engineering Chemistry Research* **2012** 51 (39), 12611-12620

Kanwar Devesh Singh, Preeti Gangadharan, Daniel Chen, Helen H. Lou, Xianchang Li, P. Richmond, " Parametric Study of Ethylene Flare Operations and Validation of a Reduced Combustion Mechanism," *Engineering Applications of Computational Fluid Mechanics*, Vol. 8, No. 2, pp. 211–228 (2014).

Hitesh S. Vaid, Kanwar Devesh Singh, Helen H. Lou, Daniel Chen, Peyton Richmond, "A Run Time Combustion Zoning Technique towards the EDC Approach in Large-Scale CFD Simulations," *International Journal of Numerical Methods for Heat and Fluid Flow*, Vol. 24 No. 1, 2014, pp. 21-35.

K. Singh, T. Dabade, H. Vaid, P. Gangadharan, D. Chen, H. Lou, X. Li, K. Li, C. Martin, "Computational Fluid Dynamics Modeling of Industrial Flares Operated in Stand-By Mode," *Industrial Flares special issue, Ind. & Eng. Chem. Research*, 51 (39), 12611-12620, October, 2012.

H. Lou, D. Chen, C. Martin, X. Li, K. Li, H. Vaid, K. Singh, P. Gangadharan, "Optimal Reduction of the C1-C3 Combustion Mechanism for the Simulation of Flaring, " *Industrial & Engineering Chemistry Research, Industrial flares special issue*, 51 (39), 12697-12705, October,

2012.

H. Lou, C. Martin, D. Chen, X. Li, K. Li, H. Vaid, A. Tula, K. Singh, "Validation of a Reduced Combustion Mechanism for Light Hydrocarbons," *Clean Technologies and Environmental Policy*, Volume 14, Issue 4, pp 737-748, August 2012, DOI 10.1007/s10098-011-0441-6.

Helen H. Lou, Christopher B. Martin, Daniel Chen, Xianchang Li, Kyuen Li, Hitesh Vaid, Anjan Tula Kumar, Kanwar Devesh Singh, & Doyle P. Bean, "A reduced reaction mechanism for the simulation in ethylene flare combustion," *Clean Technologies and Environmental Policy*, Volume 14, Issue 2, pp 229-239, April 2012, doi:10.1007/s10098-011-0394-9.

10-024

E.T. Gall, R.J. Griffin, A.M. Steiner, J.E. Dibb, E. Scheuer, L. Gong, A.P. Rutter, B.K. Cevik, S. Kim, B. (2016) Lefer, and J. Flynn, Evaluation of nitrous acid sources and sinks in urban outflow, *Atmos. Environ.*, 127, 272-282.

B. Karakurt Cevik, A.P. Rutter, L. Gong, R.J. Griffin, J.H. Flynn, B.L. Lefer, and S. Kim (2016), Estimates of air mass aging using particle and other measurements near Fort Worth, *Atmos. Environ.*, 126, 45-54.

A.P. Rutter, R.J. Griffin, B. Karakurt Cevik, K.M. Shakya, L. Gong, S. Kim, J.H. Flynn, and B.L. Lefer (2015), Sources of air pollution in a region of oil and gas development downwind of a large city, *Atmos. Environ.*, 120, 89-99.

S. Kim, A.B. Guenther, B. Lefer, J. Flynn, R. Griffin, A.P. Rutter, L. Gong, and B. Karakurt Cevik (2015), Field observations of the role of stabilized Criegee radicals in sulfuric acid production in a high biogenic VOC environment, *Environ. Sci. Technol.*, 49, 3383-3391.

L. Gong, R. Lewicki, R.J. Griffin, A. Rutter, F.K. Tittel, B.L. Lefer, J.H. Flynn, J.E. Dibb, and E. Scheuer (2012), Gas-particle partitioning of ammonia in the Fort Worth, TX area, *American Association for Aerosol Research Annual Conference*, Minneapolis, MN, October 2012. (poster)

B. Karakurt Cevik, L. Gong, R. Lewicki, R.J. Griffin, A. Rutter, F.K. Tittel, B.L. Lefer, J.H. Flynn, J.E. Dibb, and E. Scheuer (2012), Comparison of estimates of air mass aging using particle and other measurements near Fort Worth, TX, *American Association for Aerosol Research Annual Conference*, Minneapolis, MN.

A. P. Rutter, B. Karakurt Cevik, K.M. Shakya, L. Gong, C. Gutierrez, M. Calzada, S. Kim, R.J. Griffin, J.H. Flynn, and B.L. Lefer, Source apportionment of organic aerosols and VOCs near Fort Worth, TX (2012), *American Association for Aerosol Research Annual Conference*, Minneapolis, MN.

S. Kim, A.B. Guenther, T. Karl, B.L. Lefer, J.H. Flynn, R.J. Griffin, and A.P. Rutter, Sub-urban OH response to isoprene chemistry: A case study in the Dallas Fort-Worth area (2012), *American Geophysical Union Winter Meeting*, San Francisco, CA, December 2012. (poster)

10-032

Ren, X., D. van Duin, M. Cazorla, S. Chen, J. Mao, L. Zhan, W. H. Brune, J. H. Flynn, N. Grossberg, B. L. Lefer, B. Rappengluck, K. W. Wong, C. Tsai, J. Stutz, J. E. Dibb, B. T. Jobson, W. T. Luke and P. Kelley (2013), Atmospheric oxidation chemistry and ozone production: Results from SHARP 2009 in Houston, Texas, *Journal of Geophysical Research-Atmospheres*, 118, 5770-5780, doi:10.1002/jgrd.50342.

10-042

Heo, G., McDonald-Buller, E.C., Carter, W.P.L., Yarwood, G., Whitten, G.Z. and Allen, D.T. "Modeling Ozone Formation from Alkene Reactions using the Carbon Bond Chemical Mechanism, *Atmospheric Environment*, 59, 141-150, DOI: 10.1016/j.atmosenv.2012.05.042 (2012).

Heo, G. Y. Kimura, E. McDonald-Buller, D. T. Allen, G. Yarwood, G. Z. Whitten Evaluation of a New Toluene Mechanism For Carbon Bond 05 Using Environmental Chamber Data and Ambient Data, Air and Waste Management Association Annual Meeting, Paper #154, Detroit, June 2009

In preparation for Atmospheric Environment: *Environmental chamber experiments to evaluate NOx removal and recycling represented in atmospheric mechanisms for air quality modeling*
Gookyoung Heo, William Carter, Greg Yarwood, Gary Z. Whitten, David T. Allen

In preparation for Atmospheric Environment: *Evaluation of mechanisms for modeling ozone formation from isoprene in SAPRC-07 and CB6 using environmental chamber data with low initial NOx*
Gookyoung Heo, William Carter, Greg Yarwood

10-045

Olga Pikelnaya, James H. Flynn, Catalina Tsai, and Jochen Stutz (2013), Imaging DOAS detection of primary formaldehyde and sulfur dioxide emissions from petrochemical flares, *Journal of Geophysical Research*, [Volume 118, Issue 15](#), pages 8716–8728, 16 August 2013, DOI: 10.1002/jgrd.50643

The following papers were published in *Industrial & Engineering Chemistry Research* Special Issue on Industrial Flaring. The paper edition of this special edition came out in Fall 2012.

W. Berk Knighton, Scott C. Herndon, Ezra C. Wood, Edward C. Fortner, Timothy B. Onasch, Joda Wormhoudt, Charles E. Kolb, Ben H. Lee, Miguel Zavala, Luisa Molina, and Marvin Jones. "Detecting Fugitive Emissions of 1,3-Butadiene and Styrene from a Petrochemical Facility: An Application of a Mobile Laboratory and a Modified Proton Transfer Reaction Mass Spectrometer," *Industrial & Engineering Chemistry Research* 2012 51 (39), 12706-12711

Ezra C. Wood, Scott C. Herndon, Ed C. Fortner, Timothy B. Onasch, Joda Wormhoudt, Charles E. Kolb, W. Berk Knighton, Ben H. Lee, Miguel Zavala, Luisa Molina, and Marvin Jones. "Combustion and Destruction/Removal Efficiencies of In-Use Chemical Flares in the

Greater Houston Area,” *Industrial & Engineering Chemistry Research* 2012 51 (39), 12685-12696

Pikelnaya, O., J. H. Flynn, C. Tsai, and J. Stutz (2013), Imaging DOAS detection of primary formaldehyde and sulfur dioxide emissions from petrochemical flares, *J. Geophys. Res. Atmos.*, 118,8716–8728, doi:[10.1002/jgrd.50643](https://doi.org/10.1002/jgrd.50643).

This project has also resulted in the following publications:

Olga Pikelnaya, Jochen Stutz, Scott Herndon, Ezra Wood, Oluwayemisi Oluwole, George Mount, Elena Spinei, William Vizuete, Evan Couzo, “*Formaldehyde and Olefin from Large Industrial Sources (FLAIR) in Houston, TX – Campaign Overview*”, in preparation for *Journal of Geophysical Research*

Olga Pikelnaya, Scott Herndon, Ezra Wood, and Jochen Stutz, “*Observations of emissions from ships in the Houston Ship Channel during 2009 FLAIR campaign*,” under development.

FY12-13

12-006

Journal Papers:

Gookyoung Heo, Peng Wang, Qi Ying, Ron Thomas, William P.L. Carter. Using chemically detailed emissions data to test assumptions used in developing chemical mechanisms: a case study for southeast Texas, USA. [To be submitted to *Atmospheric Environment* in Summer 2014]

Peng Wang, Gookyoung Heo, William P.L. Carter, Qi Ying. Comparison of a detailed and a lumped version of SAPRC-11 photochemical mechanism during a summer ozone episode. [To be submitted to *Atmospheric Environment* in Summer 2014]

Gookyoung Heo, Chia-Li Chen, Ping Tang, William P.L. Carter. Evaluation of mechanisms for major terminal and internal alkenes with environmental chamber data. [To be submitted to *Atmospheric Environment* in Summer 2014]

Gookyoung Heo, Shunsuke Nakao, William P.L. Carter. Evaluation of mechanisms for 1,3-butadiene with environmental chamber data. [To be submitted to *Atmospheric Environment* in Summer 2014]

Conference Paper:

Heo, G., Carter, W.P.L., Wang, P., Ying, Q., Thomas, R. (2013). Evaluating and improving atmospheric chemical mechanisms used for modeling ozone formation from alkenes. Presented at the 12th Annual CMAS Conference, Chapel Hill, NC, October 28-30, 2013.

12-012

Conference presentations:

C. Faxon, J. Bean, L. Hildebrandt Ruiz. Evidence of atmospheric chlorine chemistry in Conroe, TX: Regional implications. American Chemical Society Southwest Regional Meeting, November 2013, Waco, TX.

J. Bean, C. Faxon, L. Hildebrandt Ruiz. Atmospheric processing of pollutants in the Houston Region: First insights from DISCOVER-AQ. American Chemical Society Southwest Regional Meeting, November 2013, Waco, TX.

L. Hildebrandt Ruiz, J. Bean, G. Yarwood, B. Koo, U. Nopmongcol. Formation and Gas-Particle Partitioning of Organic Nitrates: Influence on Ozone Production. American Association for Aerosol Research Annual Meeting, October 2013, Portland, OR.

Planned publications:

C. Faxon, J. Bean and L. Hildebrandt Ruiz. Preliminary title "Significant Inland Concentrations of ClNO₂ Detected in Conroe TX during DISCOVER-AQ 2013". Submission planned for August 2014.

J. Bean, C. Faxon and L. Hildebrandt Ruiz. Manuscript summarizing particle-phase measurements from DISCOVER-AQ. Submission planned for late 2014.

13-016

Gary Morris presented a poster entitled "Tropospheric Ozone Pollution Project (TOPP) Overview: A Context for DISCOVER-AQ Houston 2013" at the DISCOVER-AQ Science Team Meeting on February 27, 2014.

13-022

A. Bui, Y.J. Leong, N. Sanchez, H.W. Wallace, and R. Griffin, Distribution, influential factors, and sources of aerosol liquid water during the DISCOVER-AQ 2013 campaign in Houston, TX, *American Association for Aerosol Research Annual Meeting*, Minneapolis, MN, October 2015. (poster)

Y.J. Leong, N. Sanchez, H.W. Wallace, B. Karakurt Cevik, J. Flynn, Y. Han, P. Massoli, C. Floerchinger, E. Fortner, S. Herndon, B. Lefer, and R. Griffin, Overview of surface measurements of submicron particulate matter in the greater Houston area during the DISCOVER-AQ 2013 field campaign, *American Association for Aerosol Research Annual Meeting*, Minneapolis, MN, October 2015.

B. Lefer, J. Flynn, L. Judd, X. Ren, M. Estes, and R. Griffin, The spatial and temporal variability of ozone in the Houston metropolitan area during DISCOVER-AQ and its relation to meteorological conditions, *American Geophysical Union Winter Meeting*, San Francisco, CA, December 2014.

R. Sheesley, T. Barrett, S. Yoon, A. Clark, L. Hildebrandt-Ruiz, R. Griffin, B. Karakurt Cevik, R. Long, R. Duvall, and S. Usenko, Spatial trends in surface-based carbonaceous aerosol, including organic, water-soluble, and elemental carbon, during DISCOVER-AQ in Houston, TX, *American Geophysical Union Winter Meeting*, San Francisco, CA, December 2014. (poster)

H.W. Wallace, Y.J. Leong, B.K. Cevik, M.G. Camp, J.H. Flynn, B.L. Lefer, and R.J. Griffin, Characterization of nocturnal aerosol formation in Houston during DISCOVER-AQ, *American Association for Aerosol Research Annual Meeting*, Orlando, FL, October 2014.

R. Ferrare, J. Crawford, R. Griffin, C. Hostetler, B. Anderson, B. Holben, R. Hoff, A. Beyersdorf, and L. Ziemba, DISCOVER-AQ investigation of aerosol impacts on air quality over Houston, *American Association for Aerosol Research Annual Meeting*, Orlando, FL, October 2014.

H.W. Wallace, Y.J. Leong, B.K. Cevik, M.G. Camp, J.H. Flynn, B.L. Lefer, and R.J. Griffin, Characterization of nocturnal aerosol formation in Houston during DISCOVER-AQ, *International Global Atmospheric Chemistry Quadrennial Meeting*, Natal, Brazil, September 2014. (poster)

H.W. Wallace, Y.J. Leong, B. Lefer, B.K. Cevik, J.H. Flynn, R.W. Talbot, P.L. Laine, B.C. Sive, X. Lan, D. Anderson, Y. Zhou, M. Camp, and R.J. Griffin, Characterization of aerosol organic nitrate in the outflow from Houston, TX, during the DISCOVER-AQ campaign, *American Chemical Society Annual Meeting*, San Francisco, CA, August 2014.

Y.J. Leong, H.W. Wallace, B. Lefer, B.K. Cevik, J.H. Flynn, R.W. Talbot, P.L. Laine, B.C. Sive, X. Lan, D. Anderson, Y. Zhou, M. Camp, R.J. Griffin, Chemical characterization of submicron aerosol emissions in the greater Houston area using an aerosol mass spectrometer on a mobile platform, *American Geophysical Union Winter Meeting*, San Francisco, CA, December 2013. (poster)

13-024

NASA AQUEST meeting at Rice University in Houston, TX (Jan. 14-16, 2014), where Xinrong Ren gave a talk titled: "Measurements of trace gases at the Manvel Croix and Galveston sites during DISCOVER-AQ."

NASA DISCOVER-AQ science meeting at NASA Langley in Hampton, VA, where Winston Luke gave a talk titled: "NOAA/Air Resources Laboratory Surface Observations at Galveston and Manvel-Croix: Summary and Comparison with Aircraft Data."

A paper is in preparation with the intent to submit to Atmospheric Chemistry and Physics within about 3 months.

12-028

Implementation and Refinement of a Surface Model for HONO formation in a 3-D Chemical Transport Model. Prakash Karamchandani¹, Chris Emery¹, Greg Yarwood¹, Barry Lefer², Jochen Stutz³, Evan Couzo⁴, and William Vizuete⁵. (¹ENVIRON, ²University of Houston, ³University of California-Los Angeles, ⁴Massachusetts Institute of Technology, and ⁵University of North Carolina.)

Impacts of heterogeneous HONO formation on radical sources and ozone chemistry in Houston, Texas. Evan Couzo¹, Barry Lefer², Jochen Stutz³, Greg Yarwood⁴, Prakash Karamchandani⁴, Barron Henderson⁵, and William Vizuete¹. (¹University of North Carolina (now at MIT), ²University of Houston, ³University of California-Los Angeles, ⁴ENVIRON, ⁵University of Florida.)

12-032

Poster at the American Geophysical Union national meeting (Dec 2013) *Initial characterization of surface-based carbonaceous aerosol during DISCOVER-AQ in Houston, TX* Rebecca J. Sheesley, Tate E. Barrett, Subin Yoon, Adelaide Clark and Sascha Usenko

Poster at the DISCOVER-AQ Science Working Group meeting (Feb 2014) *Initial characterization of surface-based carbonaceous aerosol during DISCOVER-AQ in Houston, TX* Rebecca J. Sheesley, Tate E. Barrett, Subin Yoon, Adelaide Clark and Sascha Usenko

Manuscript in preparation. Submission planned to Atmospheric Environment in summer 2014. Draft title: "*Initial characterization of surface-based carbonaceous aerosol during DISCOVER-AQ in Houston, TX.*"

12-TN1

Presentation:

"A regional chemical reanalysis prototype" Pius Lee , Greg Carmichael, Tianfeng Chai, Rick Saylor, Li Pan, Hyuncheol Kim, Daniel Tong, and Ariel Stein

Poster:

"Preliminary analyses of flight measurements and CMAQ simulation during Southeast Nexus (SENEX) field experiment" Li Pan, Pius Lee , Hyun Cheol Kim, Daniel Tong ,Rick Saylor and Tianfeng Chai

Publication:

Pius Lee, Fantine Ngan, Hang Lei, Barry Baker, Bright Dornblaser, Gary McGauhey, and Daniel Tong. An Application for Improving Air Quality: a Houston Case Study, Earthzine 2014 [available at: http://www.earthzine.org/2014/03/29/an-application-for-improving-air-quality-a-houston-case-study/?shareadraft=baba698217_53330c8eab882]

12-TN2

The project team presented at the Community Modeling and Analysis System (CMAS) Conference in October 2013.

Presentations:

"HCHO and NO₂ column comparisons between OMI, GOME-2 and CMAQ during 2013 SENEX campaign (21 slides)" Hyun Cheol Kim, Li Pan, Pius Lee, Rick Saylor, and Daniel Tong

Posters:

Fine-scale comparison of GOME-2, OMI and CMAQ NO₂ columns over Southern California in 2008" Hyun Cheol Kim, Sang-Mi Lee, Fong Ngan, and Pius Lee