AIR QUALITY RESEARCH PROGRAM

Texas Commission on Environmental Quality
Contract Number 582-10-94300
Awarded to The University of Texas at Austin

Quarterly Report

September 1, 2011 through November 30, 2011

Submitted to

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Texas Air Quality Research Program

Quarterly Progress Report

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Overview

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.

On April 30, 2010, the Texas Commission on Environmental Quality (TCEQ) contracted with the University of Texas at Austin to administer the AQRP. For the 2010-2011 biennium, the AQRP has approximately $4.9 million in funding available. Following discussions with the TCEQ and an Independent Technical Advisory Committee (ITAC) concerning research priorities, the AQRP released a call for proposals in May, 2010. Forty-five proposals, requesting $12.9 million in research funding were received by the due date of June 25, 2010. These proposals were reviewed by the ITAC for technical merit, and by the TCEQ for relevancy to the State's air quality research needs. The results of these reviews were forwarded to the AQRP's Advisory Council, which made final funding decisions in late August, 2010. Successful proposers were notified, and subcontracts were initiated. The subcontracting involved two phases. First, a sub-agreement was established with each institution specifying terms and conditions. Second, once a sub-agreement was in place and a project Work Plan was approved, a Task Order was issued authorizing work to commence. As of November 30, 2011, work on all projects was completed. Draft final reports are currently in the final stages of review. A description of project activities is described in this progress report.

In June 2011, the TCEQ renewed the AQRP for the 2012-2013 biennium. Funding for this period has yet to be awarded.

Background

Section 387.010 of HB 1796 (81st Legislative Session), directs the Texas Commission on Environmental Quality (TCEQ, Commission) to establish the Texas Air Quality Research Program (AQRP).

> Sec. 387.010. AIR QUALITY RESEARCH. (a) The commission shall contract with a nonprofit organization or institution of higher education to establish and administer a program to support research related to air quality.
>
> (b) The board of directors of a nonprofit organization establishing and administering the research program related to air quality under this section may not have more than 11 members, must include two persons with relevant scientific expertise to be nominated by the commission, and may not include more than four county judges selected from counties in the Houston-Galveston-Brazoria and Dallas-Fort Worth nonattainment areas. The two persons with relevant scientific expertise to be nominated by the commission may be employees or officers of the commission, provided that they do not participate in funding decisions affecting the granting of funds by the commission to a nonprofit organization on whose board they serve.
>
> (c) The commission shall provide oversight as appropriate for grants provided under the program established under this section.
>
> (d) A nonprofit organization or institution of higher education shall submit to the commission for approval a budget for the disposition of funds granted under the program established under this section.
>
> (e) A nonprofit organization or institution of higher education shall be reimbursed for costs incurred in establishing and administering the research program related to air quality under this section. Reimbursable administrative costs of a nonprofit organization or institution of higher education may not exceed 10 percent of the program budget.
>
> (f) A nonprofit organization that receives grants from the commission under this section is subject to Chapters 551 and 552, Government Code.

The University of Texas at Austin was selected by the TCEQ to administer the program. A contract for the administration of the AQRP was established between the TCEQ and the University of Texas at Austin on April 30, 2010. Consistent with the provisions in HB 1796, up to 10% of the available funding is to be used for program administration; the remainder (90%) of the available funding is to be used for research projects, individual project management activities, and meeting expenses associated with an Independent Technical Advisory Committee (ITAC).

Research Project Cycle

The research Program is being implemented through an 8 step cycle. The steps in the cycle are described from project concept generation to final project evaluation for a single project cycle. During the first quarter of AQRP operation, steps 1-5 were completed for the first project cycle. During the second quarter, sub-agreements for most projects were established and Task Orders began to be initiated (step 6 and parts of step 7). In the third quarter, the final sub-agreements were executed and Task Orders were initiated for the majority of the projects. In the fourth quarter, Task Orders were finalized for the remaining Projects and work was in progress on every Project. During the fifth quarter, work progressed on all projects, including the DFW Field Study. On August 31, 2011, six (6) projects were completed and the remaining projects were issued a 90-day contract extension. By November 30, 2011, the remaining projects were completed and reports were under final review.

1.) The project cycle is initiated by developing (in year 1) or updating (in subsequent years) the strategic research priorities. The AQRP Director, in consultation with the ITAC, and the TCEQ developed initial research priorities; the research priorities were released along with the initial Request for Proposals in May, 2010. An initial Strategic Plan was released in July, 2010. The Request for Proposals and the Strategic Plan are available at http://aqrp.ceer.utexas.edu/

2.) Project proposals relevant to the research priorities are solicited. The initial Request for Proposals was released on May 25, 2010. Proposals were due by June 25, 2010. Forty-five proposals, requesting $12.9 million in funding, were received by the deadline.

3.) The Independent Technical Advisory Committee (ITAC) performs a scientific and technical evaluation of the proposals. For the initial round of proposals, the ITAC reviewed the proposals in conference calls and in a meeting held in Austin, Texas. The reviews were completed on July 22, 2010. Twelve proposals were highly recommended for funding; twelve proposals were recommended for funding, and 21 proposals were not recommended for funding.

4.) The project proposals and ITAC recommendations are forwarded to the TCEQ. The TCEQ evaluates the project recommendations from the ITAC and comments on the relevancy of the projects to the State's air quality research needs. For the first round of proposals, the TCEQ rated, as highly recommended, the same 12 research projects that were highly recommended by the ITAC. The TCEQ also recommended for funding the same 12 proposals that the ITAC recommended, however, the rank ordering of these 12 recommended proposals differed between the two groups.

5.) The recommendations from the ITAC and the TCEQ are presented to the Council for their approval. The Council also provides comments on the strategic research priorities. For the first group of proposals, the Council approved for funding all of the projects that were highly recommended by both the ITAC and TCEQ (12 projects). In addition, the Council approved for funding several projects in the recommended category, which were highly ranked within the recommended category by both the ITAC and TCEQ.

6.) All Investigators are notified of the status of their proposals, either funded, not funded, or not funded at this time, but being held for possible reconsideration if funding becomes available.

7.) Funded projects are assigned a Project Manager at UT-Austin and a Project Liaison at TCEQ. The project manager at UT-Austin is responsible for ensuring that project objectives are achieved in a timely manner and that effective communication is maintained among investigators involved in multi-institution projects. The Project Manager has responsibility for documenting progress toward project measures of success for each project. The Project Manager works with the researchers, and the TCEQ to create an approved work plan for the project. The Project Manager also works with the researchers, TCEQ and the Program's Quality Assurance officer to develop an approved QAPP for each project. The Project Manager reviews monthly, annual and final reports from the researchers and works with the researchers to address deficiencies. All respondents to the RFP have been notified of their award status. A Project Manager has been assigned to all projects and they have made initial contact with their PIs. TCEQ has assigned a TCEQ Project Liaison to each project.

8.) The AQRP Director and the Project Manager for each project describes progress on the project in the ITAC and Council meetings dedicated to on-going project review. Six projects have been completed, having met project objectives, as of August 31. All projects were reviewed by the ITAC at a Data Workshop held in Austin on September 27 and 28, 2011.

9.) The project findings will be communicated through multiple mechanisms. Final reports will be posted to the Program web site; research briefings will be developed for the public and air quality decision makers; an annual research conference/data workshop will be held.

Program Timeline, May 1, 2010-August 31, 2011

May 2010: Finalize membership in Council and ITAC; solicit project proposals

June 2010: Proposals due; send proposals to ITAC for review.

July 2010: ITAC conducts review and ranking of proposals; TCEQ to review immediately after ITAC ratings are complete, Council to meet to approve projects immediately after TCEQ work is complete.

August 2010: Council to meet to approve projects immediately after TCEQ work is complete.

September 2010 – February 2011: Issue contracts and Task Orders for approved projects

September 2010-April 2011: Project reports and deliverables completed on an on-going basis

September 2010: Program quarterly report due to TCEQ

December 2010: Program quarterly report due to TCEQ

March 2010: Program quarterly report due to TCEQ

April 2011: Project progress report to ITAC and TCEQ; strategic plan review.

May 2011: Project progress reports to Council; strategic plan review. Program quarterly report due to TCEQ.

May 2011-November 2011: Projects continue with ITAC, TCEQ, and Council input; project reports and deliverables completed on an on-going basis

August 2011-November 2011: Project completion; Project final report completed. Contract Extensions granted, if needed.

September 27 and 28, 2011: AQRP Data Workshop

November 30, 2011: Project completion date for all extended projects.

RESEARCH PROJECTS

During the sixth quarter of operation, Program Administration focused on payment of monthly invoices for active projects, reporting activities, and planning and execution of the Data Workshop. Project Managers worked with the Principal Investigators (PIs) to complete project activities as specified in the Work Plans. As of November 30, 2011, all Projects are complete. Project Managers and TCEQ Liaisons are in the final stages of reviewing the Final Reports.

On September 27 and 28, 2011, the AQRP hosted a Data Workshop and ITAC meeting at The University of Texas at Austin's Pickle Research Campus. During the first day and a half, a representative from each project presented a report on project results and recommendations. The ITAC meeting was held during the last half of the second day. Topics of discussion included the upcoming NASA Discovery AQ project, procedures for possible future requests for proposals (RFPs), and the possible development of a State of the Science document to provide background information for establishing future research priorities.

A detailed summary of each of the projects approved for funding and their status follows. :

Project 10-006 **STATUS: Active – February 16, 2011**

Completed - November 30, 2011

Quantification of Industrial Emissions of VOCs, NO_2 and SO_2 by SOF and Mobile DOAS

Chalmers University – Johan Mellqvist
University of Houston – Bernhard Rappenglüeck
AQRP Project Manager – Dave Sullivan
TCEQ Project Liaison – John Jolly

Funded Amount: $484,662
($262,179 Chalmers, $222,483 UH)

Executive Summary:

In a collaboration between the University of Houston and the Chalmers University of Technology in Gothenburg/Sweden, a measurement study was conducted to help to locate and quantify industrial emissions of VOCs (alkanes, alkenes and other species), NO_2 and SO_2 utilizing the Solar Occultation Flux (SOF) and the mobile Differential Optical Absorption Spectroscopy (DOAS) methods. During part of the campaign, a mobile extractive Fourier Transform Infrared Spectroscopy (meFTIR) was also used. These methods allow estimates of pollutant concentrations in a column of air from a point on the ground. This study followed up on previous measurements in 2006 and 2009 to obtain a trend analysis for selected sites, and was also extended to new areas and improve the understanding of short and long term pollutant variability. Thus, the study objectives are relevant for the AQRP priority research area about emissions, emphasizing the need to improve the uncertainty of industrial gas emissions (VOC, NO_x) that lead to the formation of tropospheric ozone. The measurements were conducted from a van with a specially equipped sunroof to be able to conduct SOF measurements. The availability of such a platform will be valuable for future SOF studies. During the project, complementary wind measurements were conducted using GPS radiosondes and from a 10 meter portable mast that was acquired within the project. To complement the path measurements taken by the SOF, DOAS, and meFTIR, canister samples were taken downwind of the sites and analyzed afterwards using gas chromatography. In this way, emissions estimates for VOCs were derived. The study areas included locations in Houston (Houston Ship Channel, Mont Belvieu, Texas City, Chocolate Bayou, Freeport and Sweeny), Dallas - Fort Worth (DFW), Longview, Beaumont and Port Arthur. The measurements in the DFW area were carried out to augment other measurements taken by AQRP projects that are part of the DFW Field Campaign.

Project update:

During the period Sep 1, 2011 through Nov 30, 2011, data from a campaign carried out between April and June has been analyzed and quality assured. The data includes industrial emission data from Southeastern Texas measured using the Solar Occultation Flux (SOF) and mobile DOAS methods. To obtain gas fluxes, the measured data are combined with meteorological measurements obtained from balloon soundings, wind masts and wind radars when available.

The targeted industries correspond to conglomerates of refineries and petrochemical industries in the Houston ship channel (HSC), Mt Belvieu. Texas City, Port Arthur, Beaumont and Longview. From the above mentioned areas it was possible to estimate the fugitive emissions of VOCs (alkanes and alkenes) and emission of SO_2, NO_2 and in some cases formaldehyde. In addition, by

using a thermal FTIR we have carried out special alkene studies on approximately 10 flares to improve our understanding on how much of the emissions are caused by flaring. As part of the campaign, mobile extractive FTIR measurements, canister sampling and SOF measurements of alkanes were carried out in the Fort Worth area to investigate VOC emissions associated with natural gas production within the Barnett Shale. The measurements include source identification and in many cases quantification. A final draft report has been compiled by Oct 31.

Project 10-008 **STATUS: Active – October 21, 2010**

Completed - September 30, 2011

Factors Influencing Ozone-Precursor Response in Texas Attainment Modeling

Rice University – Daniel Cohan
ENVIRON International – Greg Yarwood
AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Jim Smith

Funded Amount: $178,796
($128,851 Rice, $49,945 ENVIRON)

Executive Summary:

"Factors Influencing Ozone-Precursor Response in Texas Attainment Modeling," investigated the influence of input uncertainties on model predictions of pollutant responsiveness to emission controls. Models used to inform air quality decision-making are known to be uncertain, but they are usually applied deterministically with what are thought to be the best available model formulations and inputs. This project characterized how various alternate choices for model formulations (structural uncertainty) and input parameters (parametric uncertainty) influence predictions of ozone-precursor response in Texas State Implementation Plan (SIP) modeling episodes. Both Bayesian and non-Bayesian approaches were applied to compute probabilistic representations of the sensitivity of ozone to changes in precursor emissions.

Base case modeling was taken from TCEQ's CAMx simulations of ozone during two month-long episodes in 2006. Structural scenarios were then developed by applying alternate options for the biogenic emissions model, the deposition scheme, the chemical mechanism, the global model for deriving boundary conditions, and satellite-based photolysis rates. Screening analysis of the impacts of these options on ozone concentrations and sensitivities led to a focus on scenarios involving alternate choices for biogenic emissions model and chemical mechanism. The base model achieved very low bias during the June 2006 episode (NMB = -1.0% relative to ozone monitors in the 12-km domain), so the structural scenarios provide plausible alternatives but could not dramatically improve model performance.

For parametric uncertainties, screening analysis identified the specific emission rates, reaction rate constants, and boundary conditions that most influence ozone concentrations and their sensitivities to nitrogen oxide (NO_x) and volatile organic compound (VOC) emissions. Some parameters such as ozone boundary conditions were found to impact concentrations far more strongly than sensitivities, whereas the converse was true for some other parameters such as anthropogenic VOC emissions.

Bayesian Monte Carlo analysis was then applied to weight the relative likelihood of alternate structural and parametric scenarios, based on model performance in simulating observed concentrations within the Dallas-Fort Worth (DFW) region during the June 2006 episode. Multiple metrics were used in the analysis. Metric 1 evaluated model performance on high-ozone days at three DFW monitors, while Metric 2 considered average 8-hour ozone concentrations across all DFW monitors on each episode day. A non-Bayesian metric for

assigning weights based on standard model performance statistics (Metric 3) was also developed and was applied to produce alternative weightings of the Monte Carlo scenarios.

The Bayesian and non-Bayesian analyses generated probabilistic representations of ozone responses to changes in precursor emissions and of model input parameters. All of the results confirmed the findings of the base model that 8-hour ozone in the DFW region during the June 2006 episode was predominately NO_x-limited. However, the three metrics yielded conflicting shifts in the probability distributions of ozone sensitivities. For example, results from Metric 1 tended to increase the predicted sensitivity of ozone to NO_x, whereas Metric 2 indicated slightly greater sensitivity to VOC than originally modeled. Non-Bayesian Metric 3 yielded a slight shift toward greater sensitivity to VOCs, but retained the primarily NO_x-limited conditions of the base model. Further work is needed to refine the metrics and incorporate consideration of other measurements beyond ozone for evaluating model performance. Nevertheless, the project has demonstrated how probabilistic analyses via an ensemble approach can supplement deterministic estimates of ozone response and characterize the uncertainty of those results.

Project 10-009 **STATUS: Active – September 8, 2010**

Completed - November 30, 2011

Additional Flare Test Days for TCEQ Comprehensive Flare Study

University of Texas at Austin – Vincent Torres

AQRP Project Manager – Cyril Durrenberger
TCEQ Project Liaison – Russell Nettles

Funded Amount: $591,332

Executive Summary:

Task 1 - In May 2009, the TCEQ contracted with The University of Texas at Austin (UT Austin) to conduct the Comprehensive Flare Study Project (Tracking Number 2010-04) (TCEQ, 2009). In August 2010, the Air Quality Research Program (TCEQ Grant No. 582-10-94300) provided supplemental funding for this project. The purpose of this project was to conduct field tests to measure flare emissions and 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 primary study objectives for this project in order of decreasing priority are:

- Assess the potential impact of vent gas flow rate turndown on flare CE and VOC DRE;
- Assess the potential impact of steam/air assist on flare CE and VOC DRE at various operating conditions, including low vent gas flow rates;
- Determine whether flares operating over the range of requirements stated in 40 Code of Federal Regulations (CFR) § 60.18 achieve the assumed hydrocarbon DRE of 98 percent at varying waste gas flow rate turndown, assist ratios and waste stream heat content; and
- Identify and quantify the hydrocarbon species in flare plumes currently visualized with passive infrared cameras.

The field tests were conducted in September 2010 on a steam-assisted flare (nominal 36-inch diameter, rated at 937,000 lbs/hr) and on an air-assisted flare (nominal 24-inch in diameter, rated at 144,000 lbs/hr) at the John Zink Company, LLC flare test facility in Tulsa, Oklahoma. The test plan consisted of a matrix of flare operating conditions designed to provide data that would be the basis to address as many of the study objectives as possible. This matrix of operating conditions included two low vent gas flow rates for the steam flare (937 and 2,342 lbs/hr) and two low LHVs (300 and 600 Btu/scf). For the air-assisted flare, 359 and 937 lbs/hr vent gas flow rates and the same two low LHVs used for the steam flare were used. The vent gas composition used was a 1:4 ratio of Tulsa Natural Gas to propylene diluted to achieve the desired LHV. Air and steam assist rates used varied from the amount used to achieve the incipient smoke point to an amount near the snuff point. All of the tests in this study were conducted under conditions that are in compliance with all criteria of 40 CFR § 60.18.

All operating parameters for the flare were measured and monitored during each test run. The CE and DRE of the flare for each test point were determined by continuously extracting a sample from the flared gas beyond the point in the plume where all combustion had ceased and then analyzing the sample at a rate of 1 Hz using a suite of analytical instruments operated by Aerodyne Research Incorporated. A carbon balance was performed on the constituents in the sample as compared to the constituents in the vent gas flow and the appropriate quantities were used to calculate DRE and CE. Two remote-sensing technologies were also employed in the study and have been compared to the extractive measurement results.

On March 9, approval was given to reallocate funds that did not have to be spent on stand-down days as a result of excellent weather conditions, to fund multivariate image analysis and computational fluid dynamics to develop a predictive model for flare performance using the data obtained in the flare tests to develop and evaluate the model. This task, referred to as Task 2 – Modeling of Flare Performance Using Multivariate Image Analysis and Computational Fluid Dynamics, builds on work of Dr. Tom Edgar's research group and expands their work to model a full-scale flare. The goal is to be able to use the model to assess the relative impact on combustion efficiency by operating variables such as vent gas flow, steam or air assist, flame temperature and the presence of certain volatile organic compounds. This model can also be used to better understand the performance data obtained in the flare tests and the effect of such parameters as wind, vent gas flow rate and composition, and air and steam assist at operating points that were not run in the tests.

Project Update:

Task 1, flare tests – This task was completed during the previous quarter. The Final Report for this task was submitted to the TCEQ on August 1, 2011.

Task 2 – The image analysis code was applied to the usable tests (those with a visible flame) for both the air-assisted and steam-assisted flares. Two separate training/validation schemes were examined. In scheme "A", half of all the images were used as a training set to train the model. This means that half of the images from every flare test (such as A1.1) were used for training. The other images were used to validate the model. In scheme "B", for each test, all the *other* cases were used to train the model, which was then applied to the remaining case. This scheme simulates the real-world application, wherein a series of different tests would be used to train the model, which would then be applied to an unknown case. The results are shown in Figures 1 through 4.

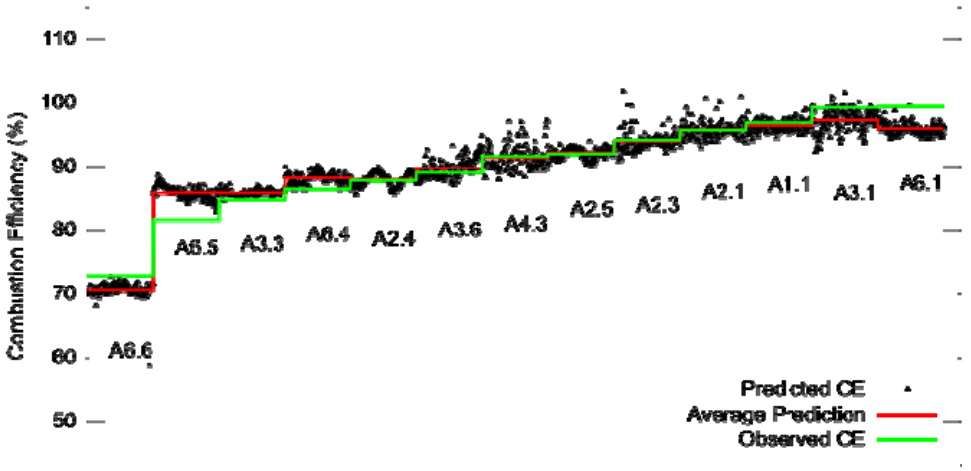

Figure 1: Predictions using the image analysis model on the air-assisted flare, with testing/validation scheme "A".

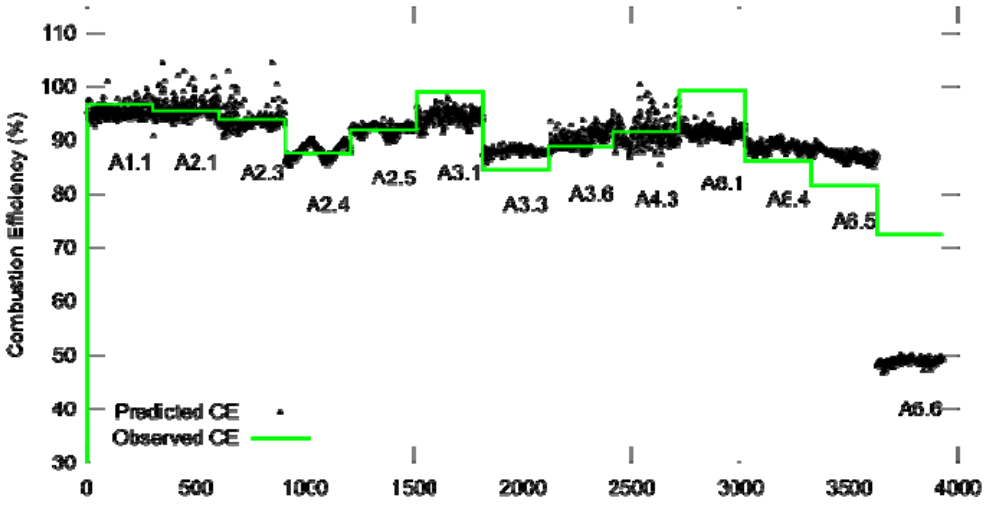

Figure 2: Predictions using the image analysis model on the air-assisted flare, with testing/validation scheme "B".

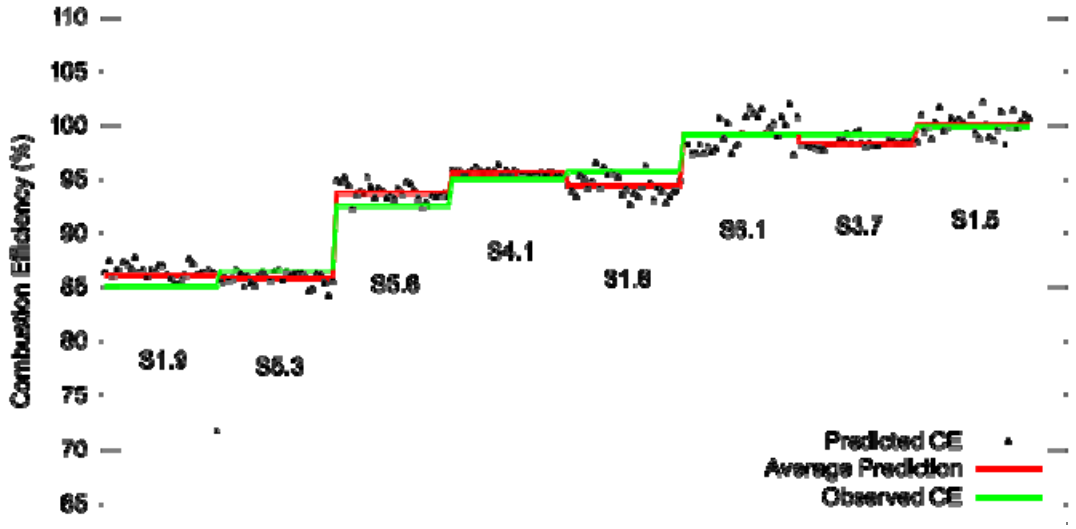

Figure 3: Predictions using the image analysis model on the steam-assisted flare, with testing/validation scheme "A".

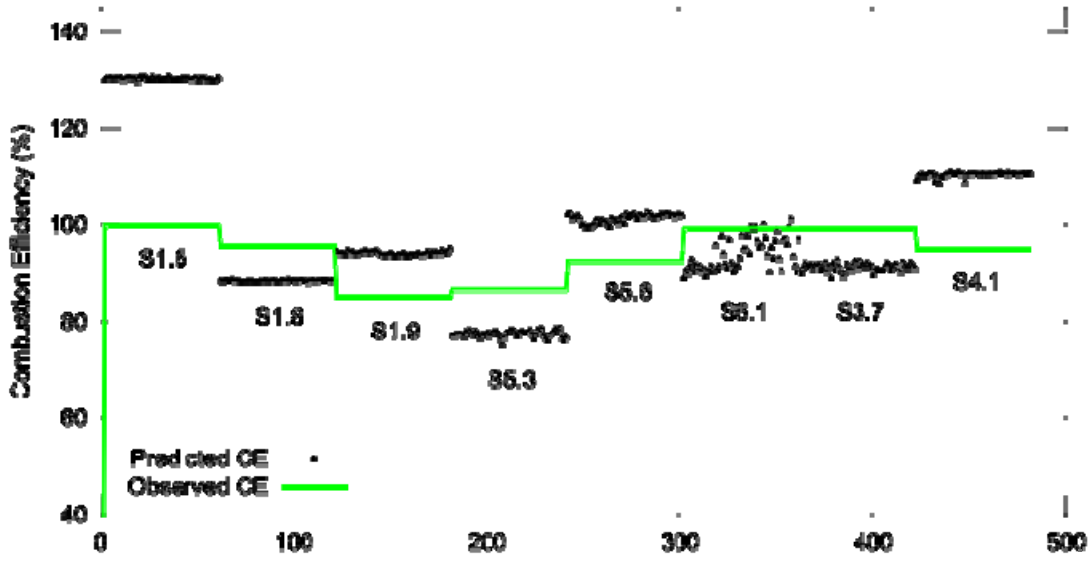

Figure 4: Predictions using the image analysis model on the steam-assisted flare, with testing/validation scheme "B". There were not enough usable tests for this approach to work with the steam-assisted flare.

When training/validation scheme “A” is used, the model accurately predicts the combustion efficiency for both the steam-assisted and air-assisted flare. What this means is that while the appearance of the flame varies over time, if the model is trained using some images from a given test, the other images will be similar enough (and distinct from the other tests) that the model will function properly. The different results when using scheme “B” (with respect to the accuracy of the model’s predictions) indicate that a wide range of conditions must be used to train the model in order for it to make accurate predictions about similar (but previously unseen) flares. In the case of the steam-assisted flare, there were not enough usable tests (8) to train the model such that it could make accurate predictions. For the air-assisted flare, there were 13 usable tests, which proved to be enough for the model to accurately predict the combustion efficiency of a flare that was not in the testing set.

Additional work was performed on computational modeling of the flare tests. The propylene-air combustion mechanism, which is included with Fluent, does not accurately predict the combustion efficiency values that were observed. Based on the burning speed of propylene, which is similar to that of propane, the propane combustion mechanism, which is included with Fluent, was selected as an alternative to the propylene mechanism. Hopefully the fact that the combustion of propane has been more widely studied and tested will lead to a more accurate combustion mechanism.

The CFD model was executed using the propane combustion mechanism in order to determine if it would accurately predict the combustion efficiency, or follow the same trends as the observed data with respect to changes in the operating conditions. No definitive conclusion has been reached yet.

The final report for Task 2 was prepared during this quarter.

Project 10-015 **STATUS: Active – March 4, 2011**

Completed - November 30, 2011

An Assessment of Nitryl Chloride Formation Chemistry and its Importance in Ozone Non-attainment areas in Texas

ENVIRON International – Greg Yarwood

AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Mark Estes

Funding Requested: $201,280

Executive Summary:
Results from the TexAQS 2006 field study in Houston showed that reactions at night between ozone (O_3), nitrogen oxides (NOx), hydrogen chloride (HCl) and particles (PM) give rise to nitryl chloride ($ClNO_2$). This finding is confirmed by other studies and is significant because $ClNO_2$ undergoes rapid photolysis in the morning and can influence photochemistry and O_3 formation at the start of the day. Sea salt PM is an important source of chloride in coastal regions but $ClNO_2$ also has been observed far from the ocean (in Boulder, Colorado) indicating that other sources of chloride can give rise to $ClNO_2$ and that its influence on photochemistry may not be limited to coastal regions.

This study analyzed the ambient measurements made during TexAQS 2006, along with the other ambient measurement and laboratory chemistry studies pertinent to the Texas non-attainment areas, to provide the sound technical basis for the inclusion of this important chemistry in air quality models. This new chemistry has been included in the CAMx photochemical grid model that is used by the TCEQ for SIP modeling. The CAMx model was applied first using a national modeling database that includes all of the field study locations. The emission inventories for the national database were reviewed and expanded to include as many sources of chloride as possible, including sea salt, HCl, molecular Cl_2 and PM chloride. Performance of the national CAMx model was assessed to evaluate the chemistry included for $ClNO_2$ and the completeness of the chloride emission inventory.

Project Update:
Analysis of Sources of Reactive Chlorine and Aerosol Soluble Chloride

Two thermodynamic equilibrium models (ISORROPIA and E-AIM) were applied to aerosol measurement data at the Pasadena site during CalNex 2010. The prediction of gas phase HCl and aerosol phase chloride with both models is really quite good when the measured sodium concentrations are included. This is shown in Figure 1 for a three day period at the end of the CalNex Pasadena campaign.

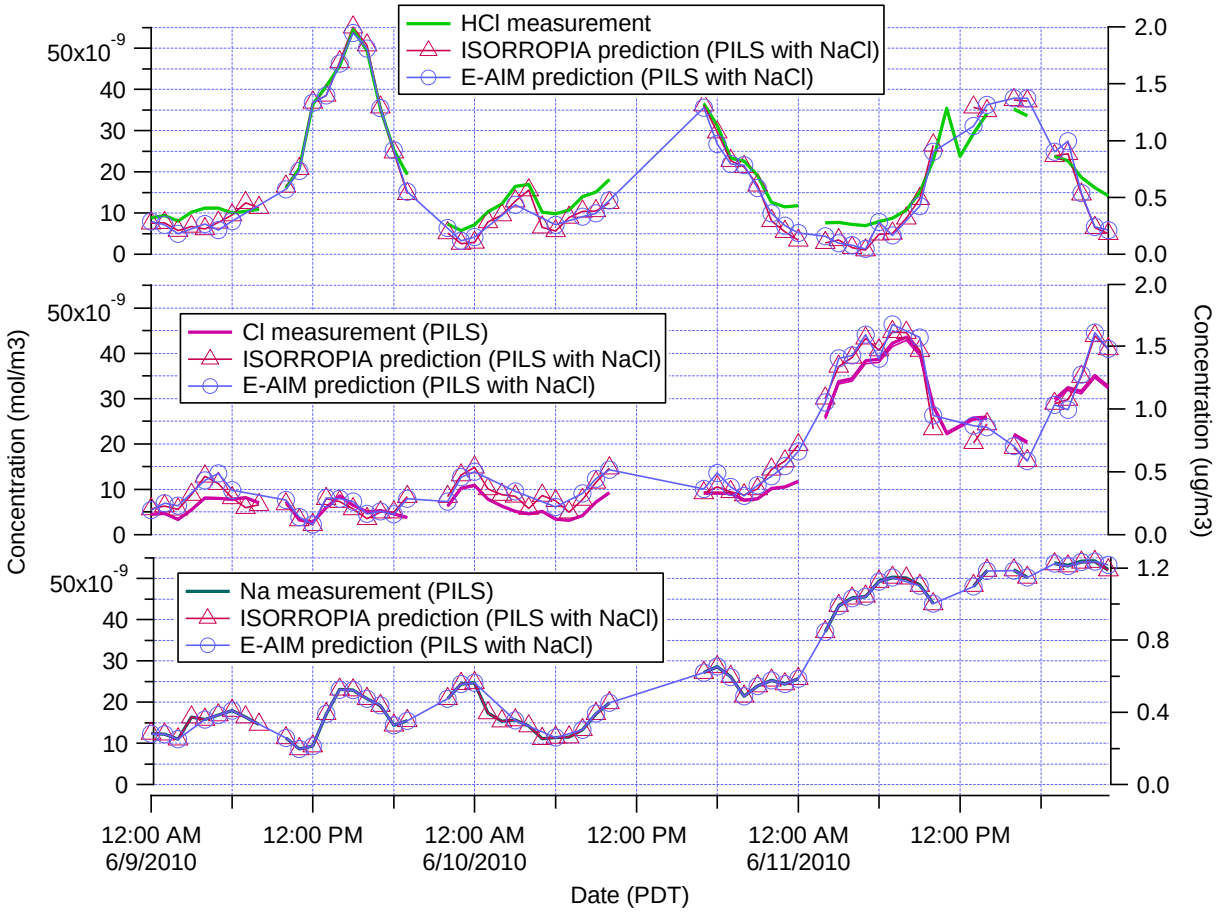

Figure 1. Comparison of measured and model HCl and aerosol chloride for the CalNex Pasadena data. The data are from the NOAA laboratory (HCl) and R. Weber at Georgia Tech. The figure is courtesy of Trevor Vandenboer and Jennifer Murphy, University of Toronto.

A major effect of the inclusion of Alkali metal cations (and alkaline earth cations when present) is to increase the pH of the particles. The modeled pH is often 0.3 pH units higher when Na^+ was included. Moreover, pH predicted from the particle-into-liquid sampler (PiLS) data, with or without Na^+ included, was always higher than that predicted from AMS data, sometimes by more than 0.5 pH units.

Gas-aerosol partitioning of chloride predicted by ISORROPIA showed that at high relative humidity (RH), substantial amount of Cl^-, more than 50% of the total, remain in the particle phase even at the lowest pH (pH 3.2). This result is essentially in agreement with the box model results from the CalNex aircraft measurements, in which the highest $ClNO_2$ formation was observed at the highest RH. Thus high RH (>85%) has the dual effect of not only increasing N_2O_5 uptake, but also increasing the concentration of particle chloride, for a given amount of total chloride.

Modeling of Reactive Chlorine and Hydrogen Chloride

The CAMx modeling results showed that HCl and particle chloride (PCl) were significantly underestimated while HNO_3 was overestimated at the Pasadena site, which indicates additional chloride sources that were missing in the current model simulations. We conducted a series of sensitivity simulations to test hypotheses attempting to explain the discrepancies between the model results and observations.

First, we tested whether simply increasing chlorine emissions would improve the model performance. We repeated the base case simulation with domain-wide chlorine (Cl_2, HCl and HOCl) emissions increased by a factor of 10. Episode mean hourly concentrations of $ClNO_2$, HCl, PCl and total chloride (HCl+PCl) from this test run are shown in Figure 2 (red lines). It increased $ClNO_2$ but not to the observed level. Also, the model predicted too much HCl at night and failed to reproduce daytime HCl peak. The fraction of total chloride predicted to be in the particle phase was still much lower than observations.

The second hypothesis suggests that additional chloride might be supplied from sea salts deposited on the surface by acid displacement following HNO_3 deposition. To test this hypothesis, we modified the CAMx dry deposition module so that HCl is released from the ground when HNO_3 is deposited.

$HNO_3 + NaCl \rightarrow NaNO_3 + HCl$

We assume that there exist sufficient sea salts deposited on the surface to fully react with every mole of HNO_3 deposited. This would serve as an upper-limit case. The model results showed $ClNO_2$ level comparable to observations, but too much HCl (and total chloride) throughout the average day while predicting too low PCl (green lines in Figure 2).

The third hypothesis argues that the model overestimates dry deposition velocity of HCl. CAMx, by default, sets surface resistance for dry deposition of strong acids (e.g., HNO_3, HCl) to zero. To test this hypothesis, we modified the model so that dry deposition of HCl was calculated without setting the surface resistance to zero. Blue lines in Figure 2 present the model results from this test. Modeled $ClNO_2$ concentrations significantly increased (to the level higher than the 10x chlorine emissions case, but still lower than observations). The model still overpredicts HCl at night and underpredicts during daylight. However, it gets total chloride (HCl+PCl) right at night.

Lastly, we tested another possibility of additional chloride sources. We hypothesized that coarse sea salt particles would react in the same way as fine sea salt particles (in the original CAMx CF aerosol scheme, coarse sea salt particles are treated as inert species). This resulted in big increases in $ClNO_2$ concentrations as well as total chloride, leading to significant overprediction of these species (purple lines in Figure 2). Overprediction of total chloride might have been aggravated due to too shallow nighttime boundary layer predicted by the meteorological model. However, the model showed diurnal variation of HCl similar to observations (peak around noon), which suggests that reacting a fraction of the coarse chloride may provide a better result. It should be noted that the CAMx aerosol module includes the CMU aerosol scheme which provides multiple approaches to modeling coarse mode aerosol components: equilibrium,

dynamic and hybrid (combination of equilibrium and dynamic approaches) methods. The latest CMAQ model also can model coarse mode aerosol components using an approach similar to the CAMx hybrid method.

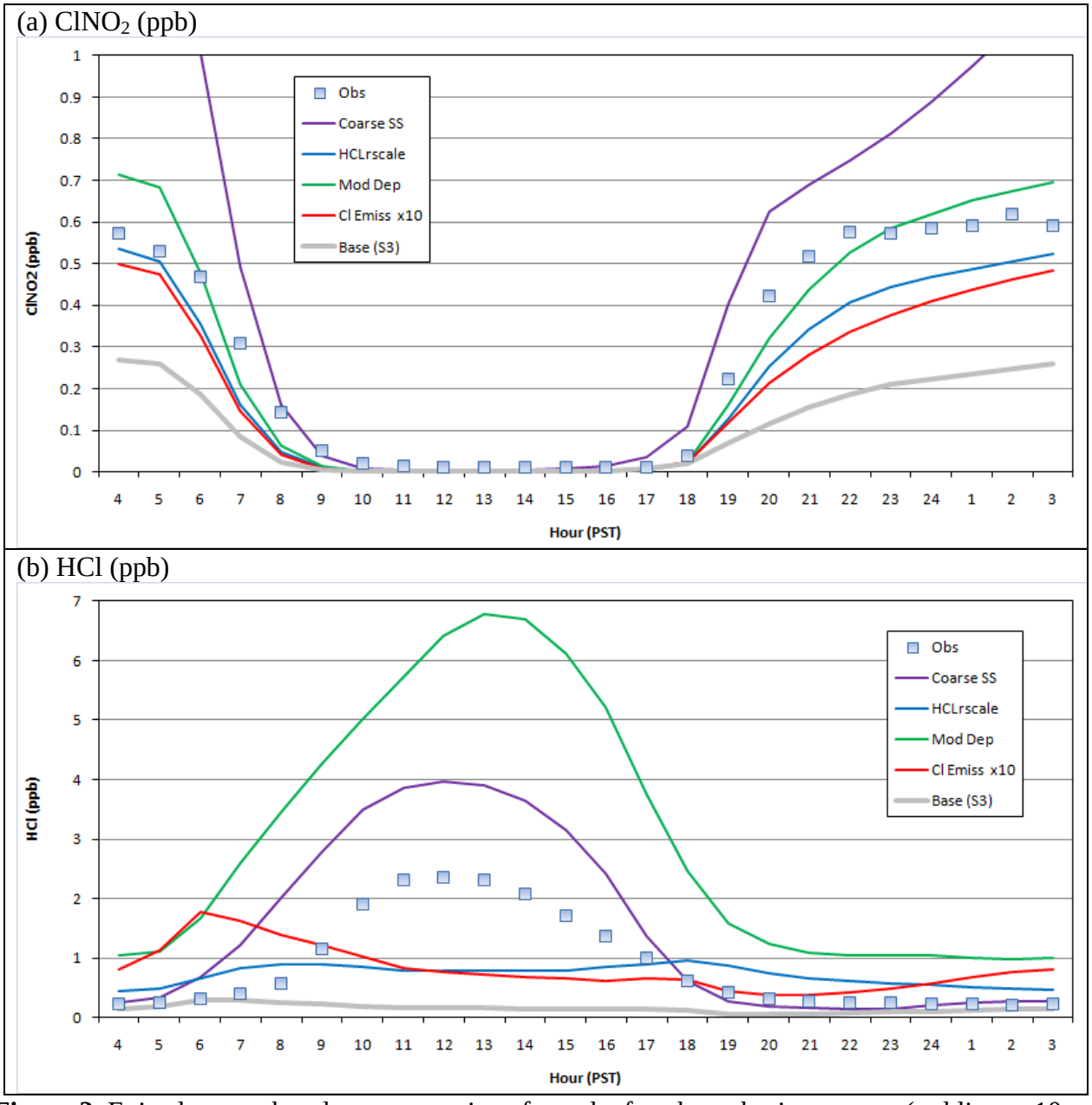

Figure 2. Episode mean hourly concentrations from the four hypothesis test runs (red lines - 10x chlorine emissions; green lines - acid displacement of deposited sea salt by HNO_3 deposition; blue lines - HCl dry deposition without zero surface resistance assumption; purple lines - reactive coarse sea salt particles) along with those from the base case (gray lines) and observations (squares) at the Pasadena site.

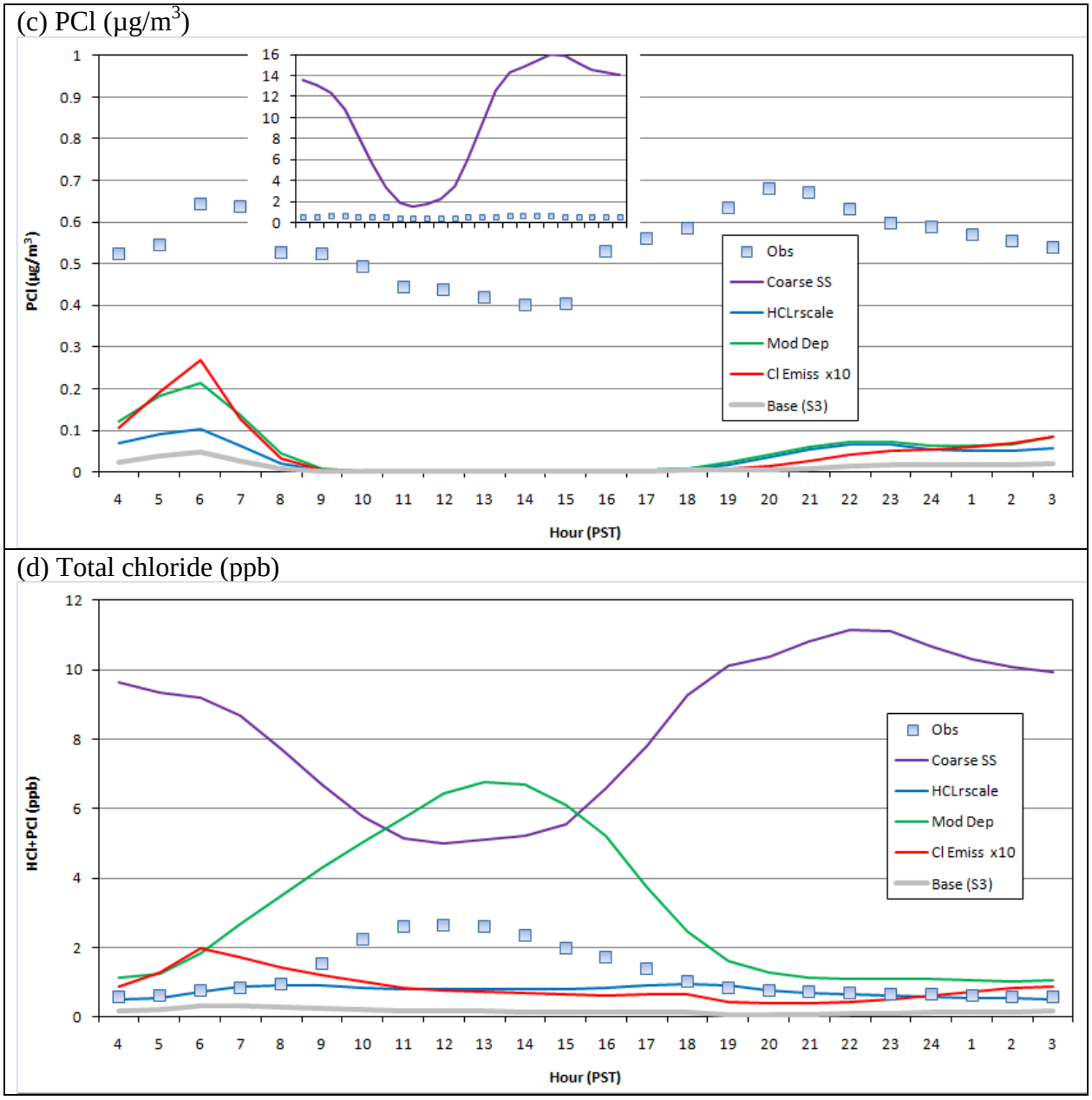

Figure 2. Episode mean hourly concentrations from the four hypothesis test runs (red lines - 10x chlorine emissions; green lines - acid displacement of deposited sea salt by HNO_3 deposition; blue lines - HCl dry deposition without zero surface resistance assumption; purple lines - reactive coarse sea salt particles) along with those from the base case (gray lines) and observations (squares) at the Pasadena site (continued).

Project 10-020 **STATUS: Active – March 5, 2011**

Completed - November 30, 2011

NO_x Reactions and Transport in Nighttime Plumes and Impact on Next-Day Ozone

ENVIRON International – Greg Yarwood

AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Dick Karp

Funding Requested: $202,498

Executive Summary:
Understanding atmospheric chemical transformations and pollutant transport are critical to assessing the impacts of emissions sources on formation of ozone (O_3). Chemical transformations of nitrogen oxides (NOx) emissions that occur at night will influence their availability to participate in next day O_3 formation. The objective of this project was to utilize data for NOx plumes collected at night by the NOAA P-3 aircraft during the second Texas Air Quality Study in 2006 (TexAQS 2006). The data were analyzed to assess the chemical transformations and plume dispersion that occurred for NOx plumes in Texas under nighttime conditions. Heterogeneous chemistry occurring in nighttime NOx plumes is subject to uncertainties that can be addressed using TexAQS 2006 data. Results from the data analysis will be compared with a detailed plume model (SCICHEM) and the chemical reactions occurring under night time plume conditions may be revised. Model improvements developed in SCICHEM will be transferred to the CAMx model used by TCEQ for SIP modeling. CAMx simulations with SIP modeling episodes developed by TCEQ will be used to evaluate the impact of model improvements on downwind O_3 impacts. Study results will directly address current uncertainties in heterogeneous chemistry of NOx plumes. They will also address the potential for nighttime transport of NO_x from concentrated point source emissions and the subsequent effect on regional ozone in Texas.

Project Update:
This project has four tasks:

Task 1 – Analysis of vertical profiles observed at night by the P-3 aircraft

Task 2 – Plume modeling using SCICHEM and impacts analysis using CAMx

Task 3 – Analysis of chemistry and mixing in NOx plumes from large point sources

Task 4 – Final Report

During this quarter, efforts were primarily focused on Tasks 1 and 4.

Task 1: Analysis of vertical profiles observed at night by the P-3 aircraft

Nighttime chemistry of NO_x, VOC, ozone and aerosol is important to regional air quality, but is difficult to characterize because it occurs within a stratified boundary layer structure. In this component of the AQRP study, NOAA analyzed nighttime vertical profiles measured by the WP-3D aircraft during missed approaches, takeoffs and landings at airfields in and around the Houston, TX urban area. Nocturnal boundary layer (NBL) depths varied between 100 – 400 m, with overlying residual layer depths of 0.8 – 1.5 km. Pollutants were highly concentrated within the NBL, but ozone was never titrated to zero by surface level NO_x emissions. As a result, nighttime oxidative and heterogeneous chemistry was active, with nitrate (NO_3) radical production rates frequently in excess of 1 ppbv hr^{-1}, up to a maximum of 2.7 ppbv hr^{-1} within the NBL. Net VOC oxidation rates due to NO_3 and O_3 varied between 0.1 – 1 ppbv hr^{-1}, with surface level emissions of anthropogenic alkenes making a large contribution. Biogenic VOCs, isoprene and monoterpenes, were frequently observed at modest levels within the NBL, and underwent rapid oxidation (0.2 – 1 ppbv hr^{-1}), mainly by NO_3. This oxidation may have been a source of secondary organic aerosol, although observed aerosol enhancements within the NBL likely had a large contribution from primary emissions. Nighttime NO_x loss through N_2O_5 heterogeneous uptake was likely modest. A relatively small uptake coefficient determined from a previous analysis of the residual layer, $\gamma(N_2O_5) = 0.003$, was consistent with the vertically resolved data in the NBL.

A detailed paper on these findings has been prepared and is currently under internal review at NOAA. Submission to a peer-reviewed journal (Atmospheric Environment, Journal of Geophysical Research or Atmospheric Chemistry and Physics) is anticipated within calendar year 2011.

Task 2: Plume modeling using SCICHEM and impacts analysis using CAMx

The CAMx modeling analysis of next-day ozone impacts from the Oklaunion power plant emissions on October 10, 2006 was completed and described in the draft final report submitted on October 31, 2011 (see Task 4). NO_x emission control scenarios for the Oklaunion plant were investigated with two configurations of CAMx: with and without Plume in Grid (PiG). The PiG simulation provided a more realistic response of ozone impacts to emission reductions than the grid-only simulation. The findings from the analysis resulted in improvements to the CAMx PiG formulation in CAMx Version 5.40, released in October 2011. Specifically, the PiG puff growth rates were modified to ignore growth contributions from horizontal and vertical shear during stable/nighttime conditions. Shear effects remain during neutral/unstable/daytime conditions. The minimum limits on vertical diffusivity, turbulent flux moments, and nighttime planetary boundary layer (PBL) depths were reduced. With these improvements, PiG puff behavior will change potentially significantly at night and above the boundary layer, usually leading to longer lifetimes before dumping to the grid.

Task 3: Analysis of chemistry and mixing in NOx plumes from large point sources

A draft manuscript detailing was submitted to a peer-reviewed journal (Journal of Geophysical Research) on September 29, 2011. A copy of the submitted paper was provided to TCEQ and AQRP. A copy of the final manuscript will also be provided to TCEQ and AQRP. In addition, the work has produced a detailed plume model that will be provided to TCEQ following quality control and final paper submission.

Task 4: Final report

The final draft report was submitted on October 31, 2011 and the Final Report will be submitted by November 30, 2011 after receiving comments from TCEQ and AQRP.

Project 10-021 **STATUS: Active – October 11, 2010**

Completed - August 31, 2011

Dry Deposition of Ozone to Built Environment Surfaces

University of Texas at Austin – Richard Corsi

AQRP Project Manager – Gary McGaughey
TCEQ Project Liaison – Jim Smith

Funding Awarded: $248,786

Executive Summary:
Photochemical grid models, such as the Comprehensive Air Quality Model with extensions (CAMx) that is used by the State of Texas, have a central role in the design of emission control strategies for attainment demonstrations and air quality planning. Dry deposition is an important physical removal mechanism for ozone in Texas. Consequently, it is critical that related model algorithms be as accurate as possible in order to reduce uncertainties in predictions that will be used to implement ozone reduction strategies. Currently, national default values for dry deposition resistances are used in CAMx. Improvements in the dry deposition algorithms in CAMx are particularly important given the rapidly changing nature of urban landscapes, including increases in built environment surfaces (BES) such as roofing, building façades, and roadways, and changes in urban vegetative cover. In this study we assessed whether built environment surfaces can appreciably affect the dry deposition of ozone in urban settings. The research included two major phases. Phase 1 involved extensive experiments to determine the reactivity, or inversely the surface resistance, of large built environment surface materials with ozone. Phase 2 involved applications of CAMx with a more refined urban deposition calculation to account for variations in built environment surfaces and updated surface resistances.

Experiments to determine surface resistances involved eighteen different materials. Materials were placed in electro-polished stainless-steel chambers and exposed to ozone in a laboratory setting. Built environment surface materials were also placed outdoors and allowed to weather in order to explore temporal changes in surface resistances.

Geospatial data were collected for three broad types of built environment surfaces in areas classified as urban in Travis County, including the transportation network, residential properties, and commercial and tax-exempt properties. Among the primary data sources utilized for the project were the Texas Department of Transportation's (TxDOT's) Pavement Management Information System (PMIS), the City of Austin's 2003 ArcGIS transportation and building footprint files, the Travis County Appraisal District (TCAD) database, Google Earth, and field surveys conducted by our team. These data were matched with surface resistances for fresh and weathered materials, respectively, determined from the experiments to obtain new estimates of dry deposition velocities and ozone concentrations using CAMx.

Major findings from the experimental phase of the study are listed below:

1. Initial (Day 0) surface resistances associated with ozone removal to test materials ranged over a factor of 30, from a low (most reactive) of 150 seconds/meter (s/m) for limestone to a high (least reactive) of 4,300 s/m for painted concrete.

2. Painted materials (brick, concrete, Hardie Board, wood siding) had initial surface resistances that were approximately an order of magnitude greater than most unpainted materials.

3. Other than limestone, unpainted materials exhibited a relatively narrow range (370 to 670 s/m) of initial surface resistances.

4. Weathering of test materials for two months on the top of an office building generally led to an increase in surface resistance to ozone removal. This was true for all materials except for limestone, one concrete specimen, and painted brick; each of these exhibited a slight reduction in surface resistance after two months of weathering.

Major findings from the characterization of the built environment and air quality modeling are listed below:

5. Improved characterization of the urban environment resulted in decreases in predicted daily maximum 8-hour average ozone concentrations of 0.2 to 1.3 ppb in the Austin area relative to a 2007 CAMx Base Case.

6. The maximum decreases in predicted 8-hour ozone concentrations regardless of time of day or grid cell location across the Austin area ranged from 1.2 to 1.6 ppb.

7. The results indicated the large contribution of vegetation in comparison to built surfaces to the dry deposition of ozone, suggesting the need for better characterization of urban vegetation and future changes due to urban growth and building practices.

8. Decreases in 8-hour average ozone concentrations could primarily be attributed to urban vegetation with the built environment moderating the impacts of ozone removal by dry deposition in Travis County.

9. The framework for characterizing the urban built environment and experimental results for material surface resistances are applicable to other regions of Texas.

Project 10-022 **STATUS: Active – February 16, 2011**

Completed - November 30, 2011

Development of Speciated Industrial Flare Emission Inventories for Air Quality Modeling in Texas

Lamar University – Daniel Chen

AQRP Project Manager – Vincent Torres
TCEQ Project Liaison – Jim MacKay

Funding Limited to: $150,000

Executive Summary:
Current methodologies for calculating VOC emissions from flaring activities generally apply a simple mass reduction to the VOC species sent to the flare. While it is assumed that a flare operating under its designed conditions and in compliance with 40 CFR 60.18 may achieve 98% destruction/removal efficiency (DRE), a flare operating outside of these parameters may have a DRE much lower than 98%. Basic combustion chemistry demonstrates that many intermediate VOC species may be formed by the combustion process.

In this project, computational fluid dynamics (CFD) methods based on CHEMKIN-CFD and FLUENT are used to model low-Btu, low- flow rate propylene/Tulsa Natural Gas/nitrogen flare tests conducted during September, 2010 in the John Zink test facility, Tulsa, Oklahoma. The flare test campaign was the focus of the TCEQ Comprehensive Flare Study Project (PGA No. 582-8-862-45-FY09-04) and AQRP Project 10-009 in which plume measurements using both remote sensing and direct extraction were carried out to determine flare efficiencies and emissions of regulated and photo chemically important pollution species for air-assist and steam-assist flares under open-air conditions. This project (1) primarily used CFD modeling as a predicting tool for the Tulsa flare performance tests (2) further compared the CFD modeling with the flare performance data and speciated volatile organic compound (VOC) concentrations. This modeling tool has the potential to help TCEQ's on-going evaluation on flare emissions and to serve as a basis for a future State Implementation Plan (SIP) revision.

The 50-species mechanism is reduced from the combined GRI and USC mechanisms with the goal of allowing NOx formation and handling light hydrocarbon combustion. This Lamar mechanism has been validated against methane, ethylene, and propylene experimental data.

Lamar University (LU) acquired the operating, design, and meteorological data of the flare test campaign from The University of Texas (UT) and conducted CFD modeling and prediction. The test data, were compared with the model results. The test data include Combustion Efficiency (CE), Destruction & Removal Efficiencies (DRE) and monitored CO/CO_2, NO, NO_2, methane, acetylene, ethylene, propylene, formaldehyde, acetaldehyde, and acetone concentrations. Cases were modeled for the effect of varying steam flow and heating value for the steam-assist flare and the effect of varying air flow and heating value for the air-assist flare.

Project Update:
Task Order was received on March 17, 2011 to start the CFD flare modeling project. Further, Lamar University presented 2 base cases (1 for air-assisted flare and 1 for steam-assisted flare) to serve as the starting point for CFD modeling.

New 50-species mechanism with NO_2 was developed and shown to be in good agreement with the full mechanism. Both Probability Density Function (PDF) and Eddy Dissipation Concept (EDC) turbulence-chemistry interaction approaches were adopted to run Tulsa flare test cases. Six air-assisted flare test cases and one steam-assisted flare test case have been run and compared with the measured DRE/CE data. In general, the EDC model under- predicts DRE by 6% to 19% with an average of 11%. It under- predicts CE by 12% to 39% with an average of 23%. The potential causes may be the low flow rates, low heating values, high air/steam assists, complexity of geometry, placement of the pilots, and choice of turbulence intensity.

When the DRE and CE data of CFD simulation (using PDF approach) is compared with the high BTU experimental results for the air assisted flare, it can be observed that the CFD results closely matches the experimental results. Even though the PDF approach was verified with University of Alberta wind tunnel data and was shown in good agreement for the steam-assisted case; the more simplistic PDF model tends to over-predict flare efficiencies than the measured ones. Nearly complete combustion (over 99% DRE and CE) was seen when using the non-premixed combustion model. As a result, the PDF model appears to predict little intermediate species and radicals like formaldehyde, OH, NO etc.

Project 10-024 **STATUS: Active – February 16, 2011**

Completed - September 30, 2011

Surface Measurements and One-Dimensional Modeling Related to Ozone Formation in the Suburban Dallas-Fort Worth Area

Rice University – Robert Griffin
University of Houston – Barry Lefer
University of New Hampshire – Jack Dibb
University of Michigan – Allison Steiner
NCAR – Withdrawn

AQRP Project Manager – Vincent Torres
TCEQ Project Liaison – Doug Boyer

Funding Requested: $458,957
($225,662 Rice, $98,134 Houston, $70,747 New Hampshire $64,414 Michigan)

Executive Summary:
In the Dallas-Fort Worth (DFW) area, the most prevalent local emission sources of NO_x and VOCs are automobiles and other motor vehicles and a number of large point sources, specifically electric power plants and cement kilns. However, it is theorized that the dramatic increase in both the number of natural gas wells and the production of natural gas in the DFW region are contributing to additional VOC and NO_x sources, leading to the hypothesis that there is a relationship between O_3 levels and natural gas activities. A team from Rice University, the University of Houston (UH), and the University of New Hampshire (UNH) are investigating this hypothesis through performance of an air quality sampling campaign and subsequent data analyses.

The Rice, UH, and UNH team installed several additional pieces of air quality monitoring equipment at the Eagle Mountain Lake Texas Commission on Environmental Quality monitoring site for a one-month period from May 30 to June 30, 2011. Eagle Mountain Lake is located approximately 40 kilometers to the northwest of downtown Forth Worth. This location was chosen for several reasons: a wealth of natural gas activity, wind that predominantly blows from the direction of the DFW metropolitan area, and monitoring that has noted high levels of O_3 in the northwest corner of the DFW region. The timing of the campaign was selected to optimize likely O_3 formation (due to favorable meteorological conditions), staff availability, and duration of the project.

Relevant measurements included not only the concentrations of O_3, NO_x, and VOCs but also values for other relevant chemical and physical variables, including meteorological parameters. In addition, a group from the University of Michigan conducted computational modeling used in conjunction with the data generated from these measurements to determine the VOC emissions, atmospheric reactions, and meteorological conditions that lead to O_3 formation in the DFW region.

The first round of data analyses indicate that the air quality at the Eagle Mountain Lake site is determined by being a receptor of aged and processed air from the DFW metropolitan area.

However, there are strong indications that intermittent local sources influence air quality at the site.

Project 10-029 **STATUS: Active – December 1, 2010**

Completed - November 30, 2011

Wind Modeling Improvements with the Ensemble Kalman Filter

Texas A&M University – John Nielsen-Gammon

AQRP Project Manager – Gary McGaughey
TCEQ Project Liaison – Bright Dornblaser

Funding Awarded: $80,108

Executive Summary:
Meteorological models provide essential inputs to photochemical models that are used to simulate and study the formation and transport of air pollutants such as ozone. The appropriate treatment of vertical mixing in the lower atmosphere is a crucial component of meteorological and air quality models. Models use various schemes to simulate the vertical changes in heat, momentum, and other constituents within the lower portion of the atmosphere. Errors and uncertainties associated with these schemes remain one of the primary sources of inaccuracies in model predictions.

The purpose of this project was to improve meteorological analyses and forecasts, particularly of low-level winds and vertical diffusion, using a technique known as the Ensemble Kalman Filter (EnKF) data assimilation system. EnKF provides a methodology, using a combination of independent sources of observed and model-predicted information, to reduce errors in the model state resulting in an improved meteorological simulation. Previous work with a single case study demonstrated improvements in both analyses and forecasts using an initial version of EnKF.

This meteorological research is directed toward the modeling priority area of the AQRP Strategic Plan. It specifically addresses the need for better use of data assimilation for more accurate modeling of individual ozone episodes and improvements in the physical representation of processes within the models. It also indirectly addresses all other modeling aspects of the AQRP Strategic Plan, because improved representation of winds and transport will allow more accurate conclusions to be drawn in all modeling studies involving meteorology, including but not limited to TCEQ attainment demonstrations.

This project utilized the WRF (Weather Research and Forecast) mesoscale meteorological model and the Asymmetrical Convection Model, version 2 (ACM2) vertical mixing scheme. The final results include software modifications for use in WRF along with the appropriate documentation.

Project Update:
The project was initiated in late February. The four goals associated with the project were (1) reproduction of results, delivery of software, documentation, and references; (2) parameter estimation on additional ozone episodes; (3) variations of parameter estimation setup; and (4) non-assimilation runs with altered parameters.

The previous parameter estimation work on which this project was based was conducted using versions of the meteorological model (WRF) that were two to three years old. In addition to transitioning the software to a new computer system, the Ensemble Kalman Filter software and workflow was upgraded to utilize the current version of WRF (version 3.3, released in April 2011). This porting process caused the remaining part of the first goal to evolve into a comparison of results from the earlier modeling system with results from the current, up-to-date modeling system.

Project 10-032 **STATUS: Active - February 9, 2011**
Completed - November 30, 2011

SHARP Data Analysis: Radical Budget and Ozone Production

University of Houston – Barry Lefer
UCLA – Jochen Stutz
University of New Hampshire -

AQRP Project Manager – Cindy Murphy
TCEQ Project Liaison – John Jolly

Requested Funding: $248,652
($176,314 UH, $23,054 New Hampshire, $49,284 UCLA)

Executive Summary:
The chemistry of atmospheric radicals, especially the hydroxyl radical (OH) and hydroperoxyl radical (HO_2), together called HO_x, is deeply involved in the formation of secondary pollutants ozone and fine particles. Radical precursors, such as nitrous acid (HONO) and formaldehyde (HCHO), significantly affect the HO_x budget in urban environments such as Houston. These chemical processes connect surface emissions, both human and natural, to local and regional pollution, and climate change. This project evaluated the radical budget and ozone production using the data collected during the Study of Houston Atmospheric Radical Precursors (SHARP) on the campus of the University of Houston in the spring of 2009.

This project used statistical methods to analyze the observations related to ozone formation, and also usied numeric zero-dimensional models with five different chemical mechanisms to simulate the oxidation processes during the study. Using the model results, the radical budget was calculated and the sensitivity of ozone production to oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) were analyzed. The model results allow the comparison of the observed OH reactivity and ozone production rate to the model calculations. The models used in this project have been previously used for similar studies (Shuang et al., 2010; Flynn et al., 2010; Bais et al., 2003, Wong and Stutz, 2010).

The primary objectives of this project included:

- Identify the variation of measured HO_x and HO_2/OH with NO_x and VOCs and compare to the model prediction.
- Quantify OH reactivity and compare observed and calculated OH reactivity to examine any missing OH sink species.
- Examine the significance of nighttime OH and determine the importance of both the reaction of O_3 + alkenes and NO_3 chemistry as nighttime OH sources.
- Compare and contrast the HO_x levels in Houston to those in Mexico, Nashville and New York City.

- Investigate the instantaneous O_3 production and deviations of the NO_x photostationary state due to clouds and aerosols. This analysis will also include comparison of observed and calculated $HO_2 + RO_2$ mixing ratios and net O_3 production.
- Study the sensitivity of O_3 production to NO_x and VOCs.
- Investigate the potential of HONO as a daytime precursor of OH.
- Evaluate the role of nitryl chloride ($ClNO_2$) as an early morning radical source and its' contribution to ozone production.
- Investigate the processes creating strong correlations between HNO_3 and gas phase chloride, and their implications for coupled Cl and NOx chemistry in Houston.

Project Update:
In the past quarter, the PI team has been working on the following tasks:

1) Performed extensive 0-D modeling (Task 3) using the RACM (Regional Atmospheric Chemistry Mechanism) Version 2, CB05 (Carbon Bond 2005), LaRC (Langley Research Center, J. Olson & J. Crawford), SAPRC07 (W. Carter), and MCM (Master Chemical Mechanism, University of Leeds) chemical mechanisms. Previous modeling efforts for this project were only using the RACM and LaRC mechanisms.

2) For Objective 5, calculating the impact of clouds and aerosols on ozone production, the UH team recomputed the instantaneous ozone production and loss rates using the LaRC photochemical box model with the newest SHARP data merge with speciated VOCs for both measured and modeled photolysis frequencies. These new results are in the process of being analyzed.

3) For Objective 7, Evaluating potential of HONO as a daytime precursor of OH, UCLA has finalized the 1D model calculations of daytime HONO. These results have been summarized in a manuscript that will be submitted to ACPD shortly. In addition, results from the finalized 1D model calculations confirm that the surface is the main source of daytime HONO, with a likely contribution of a formation process involving aerosols.

4) For Objective 9, Processes creating correlations between HNO_3 and gas phase chloride, and their implications for coupled Cl and NO_x chemistry in Houston, UMiami worked on and tested a revised RACM chemical mechanism with additional halogen reactions to better understand these processes.

5) Prepare for and present preliminary project results at the AQRP Data Workshop in Austin, TX on the 27th and 28th of September, 2011.

One of the project's primary goals was to compare measured OH and HO_2 mixing ratios to those calculated by a 0-D steady-state photochemical box model. A second primary objective was an intercomparison of OH and HO_2 mixing ratios predicted by the photochemical box model using five different chemical mechanisms (RACMv2, CBO5, LaRC, SAPRC07, and MCM). The

primary differences between these chemical mechanisms are the various ways they simulate the chemistry involving volatile organic compounds (see Table 1).

Surprisingly, both the simple/parameterized and high explicit hydrocarbon mechanisms produced similar levels of OH and HO_2. In general, all five models reproduced observed OH and HO_2 fairly well. The CB05 mechanism produced slightly more O_x than the others. During the daytime, all the models forecasted OH levels that were higher than the measurements (Figure 1). In contrast, the measured HO_2 was always higher than what was predicted by the various models. Consequently, the measured HO_2/OH ratio was significantly higher than the ratio forecasted by all the models. Interestingly, there was low but non-zero OH measured at night, this was not captured by any of these models.

Using a pseudo steady state approach (see Equations 1 and 2), it is possible to further analyze the HONO formation rate and solve for $P_{unknown}$.

$$d[HONO]dt = P_{unknown} + k_2[NO][OH] - jHONO[HONO] - k_3[HONO][OH] + emission = 0 \quad (1)$$

$$P_{unknown} = jHONO[HONO] + k_3[HONO][OH] - k_2[NO][OH] - emission \quad (2)$$

The result of this calculation for the unknown HONO production rate, $P_{unknown}$, is shown in Figure 2 for two days during SHARP (April 21st and May 18th, 2009). In this figure, $P_{unknown}$ is also compared to other known daytime HONO sources. The unknown HONO source dominates throughout both of these days. $P_{unknown}$ shows a clear diurnal variation with somewhat higher HONO formation rates in the morning. This asymmetry may be explained by the dependence of $P_{unknown}$ on NO_2, or another gas that is well correlated with NO_2.

Table 1. Summary of the number and types of reactions and number and types of species in the five different chemical mechanisms tested in this project.

Mechanism	**RACM2**	**CB05**	**LaRC**	**SAPRC07**	**MCMv3.1**
Lumped?	Y	Y	Y	Y	N
# of RXN	356	156	279	291	13,568
Photolysis	33	23	35	34	~2,600
Inorganic	35	44	31	55	36
Organic	288	89	185	202	~11,000
# of species	117	58	106	109	4,647
Stable inorganics	16	14	16	16	16
Short-lived inorganics	5	5	5	9	5
Stable organics	54	30	57	42	3,644
Short-lived organics	42	9	28	42	982

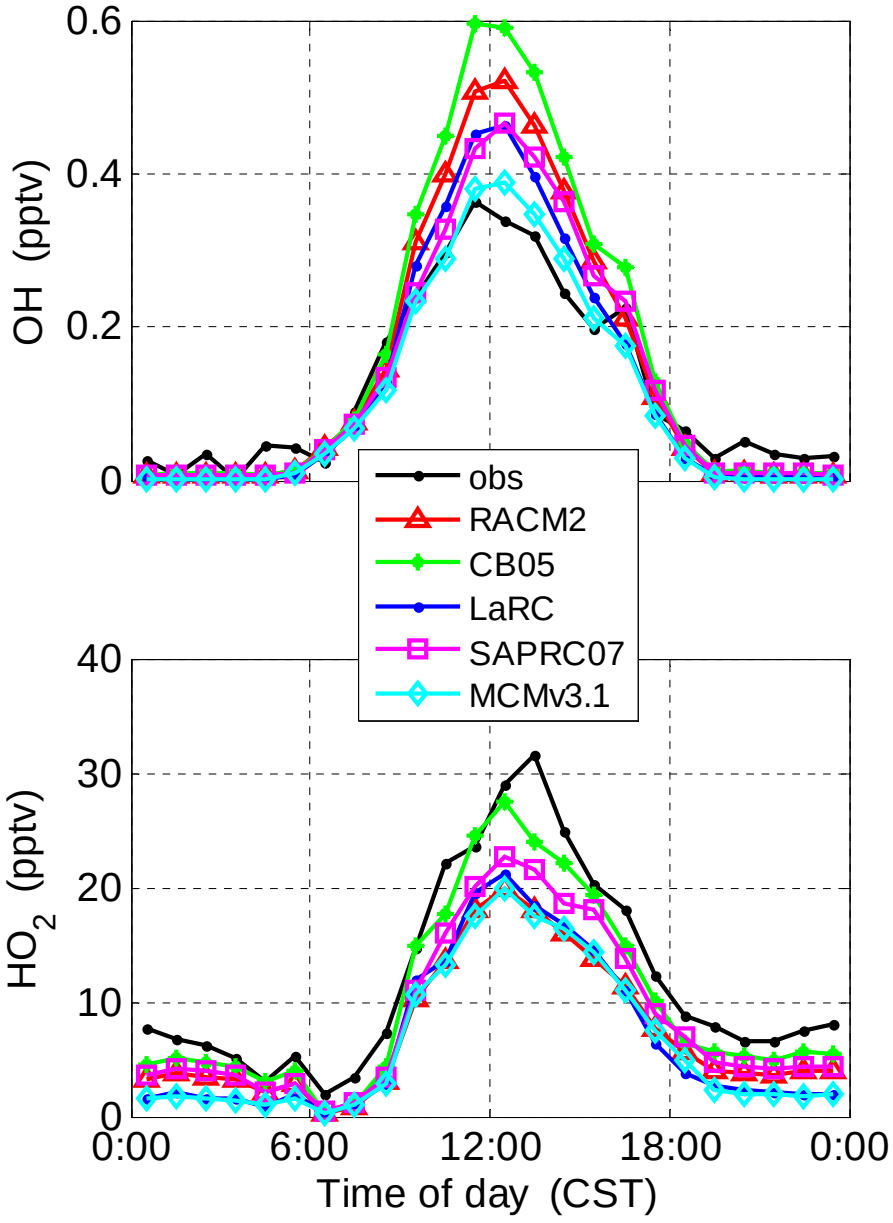

Figure 1. Average diel cycles for OH and HO_2 during SHARP, comparing Penn State measurements a 0-D photochemical box model using different chemical mechanisms.

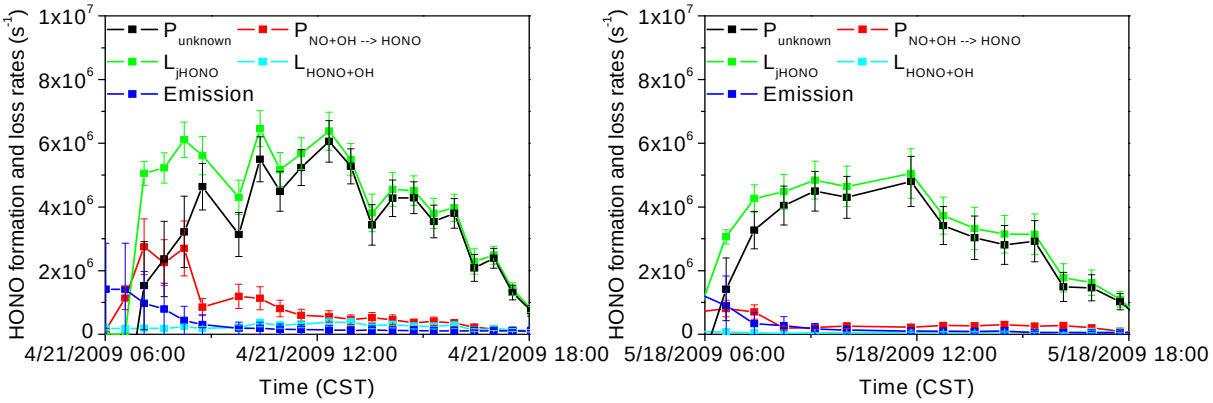

Figure 2. Timeseries of HONO formation and removal rates at the lower height interval on April 21, 2009 (left) and May 18, 2009 (right). Please note that errors were propagated from the statistical uncertainties in the observations.

Project 10-034 **STATUS: Active – February 2, 2011**

Completed - November 30, 2011

Dallas Measurements of Ozone Production

University of Houston – Barry Lefer

AQRP Project Manager – Dave Sullivan
TCEQ Project Liaison – Doug Boyer

Requested Funding: $195,054

Executive Summary:
The understanding of photochemical ozone production in the Dallas – Fort Worth (DFW) Metroplex is still incomplete (AQRP, 2010). Central to gaining a better understanding of the DFW ozone issue is providing chemical measurements that can directly be compared to the SIP chemical transport models. Measurements of the ozone production rates would quickly and significantly help constrain the degree to which the TCEQ chemical transport models are performing in a realistic way and improve the understanding of how these models can be employed for policy recommendations. Direct measurements of the ozone production rate can be used to determine not only if the measured ozone is similar to the forecasted but if the ozone measured at a site was produced locally or transported from somewhere else. As the NAAQS for ozone decreases the distinction between transported (or background) ozone and locally produced ozone is critical. To help provide the measurements to reduce the uncertainty in our understanding of the conditions contributing to photochemical ozone in the Dallas area, two of the new Pennsylvania State University Measurements of Ozone Production Sensors (MOPS) were deployed to continuously measure ozone production rates in the DFW region, beginning with the TCEQ Eagle Mountain Lake site (CAMS 75), and then at additional locations.

The data show the temporal and spatial variability of *in situ* net ozone production rates in the DFW area, as well as potential NO_x sensitivity. The data enable determination of the fraction of the ozone is produced locally compared to the transported or background ozone. Coupling this data with speciated auto-GC data and other measurements (i.e. meteorological, ozone, NO, NO_x, etc.) from the TCEQ CAMS sites where the instruments were located will help determine how ozone production changes with varying air composition.

Project Update:
Task 3 was to deploy two MOPS instruments for an extended period of time in the DFW area. During this quarter (Sept-Nov 2011) the MOPS instruments have been working consistently, including reliable operation of the zeroing cover. The MOPS PI team is currently evaluating the MOPS data collected the two sites (Eagle Mountain Lake and Fort Worth Northwest) from approximately August 15th to October 21st, 2011.

The MOPS team presented preliminary results and a project update to the AQRP Independent Technical Advisory Committee at the AQRP Data Workshop in Austin, Texas on Tuesday, September 27, 2011. This preliminary analysis indicates that the 2nd generation MOPS

instruments developed for this project are working reliably. During the first 11 days that have been analyzed (September 11th to 22nd, 2011) thus far for the MOPS sensor at the Fort Worth Northwest site, the measured daily peak net O_3 production varied from a low of approximately 10 ppbv/hour to values greater than 60 ppbv/hr (see Figure 3). Also shown in Figure 3, the net ozone production was greater than 40 ppbv on three days (September 12th, 20th, and 21st). The peak measured ozone production rates typically occurred in the early morning and resulted in the highest ambient ozone mixing ratios later that afternoon. Interestingly, the highest ozone days were the mornings with the highest NO levels. During this time period the smaller net ozone production peaks are seen for days with lower NO (and O_3) mixing ratios.

The preliminary net $P(O_3)$ data shown in Figure 3 has been smoothed with a 3hr filter. This smoothing may be able to be shortened as a better temperature correction method is developed. The $P(O_3)$ signal has had a first order correction for temperature differences between the zero (closed cover) and sample (open cover) instrument modes (Figure 2). At times the temperature correction is equivalent to the calculated net $P(O_3)$ (ie., ~0-40 ppbv/hr). Even with this preliminary temperature correction a temperature drift is still evident. The MOPS team anticipates that post-mission lab testing and instrument characterization currently underway will enable a better correction and new design that is less sensitive to sensor thermal drift.

At the Ft. Worth Northwest site (C13), the ozone production rate can be accumulated during each day to give the cumulative ozone production for each day (Figure 4). The preliminary conclusion is that much more ozone is produced at this site than is observed, sometimes by as much as a factor of six. If the preliminary $P(O_3)$ measurements are proven to be accurate by the laboratory tests, this observation suggests that the Ft. Worth Meacham site is in the midst of an ozone production region and that much of the ozone produced there is exported elsewhere. This analysis will be extended to all days for which the ozone production measurements are found to be good.

Figure 1. MOPS instruments installed and operating at the Fort Worth Northwest (left) and Eagle Mountain Lake (right) CAMS sites. These sites have collected multiple weeks of ozone production data that is currently being evaluated.

Figure 2. MOPS zeroing cover closed (left) and MOPS zeroing cover in the open position (right). The cycling of this UV absorbing cover every 10 minutes has proven to be the best way to achieve an effective instrument "zero".

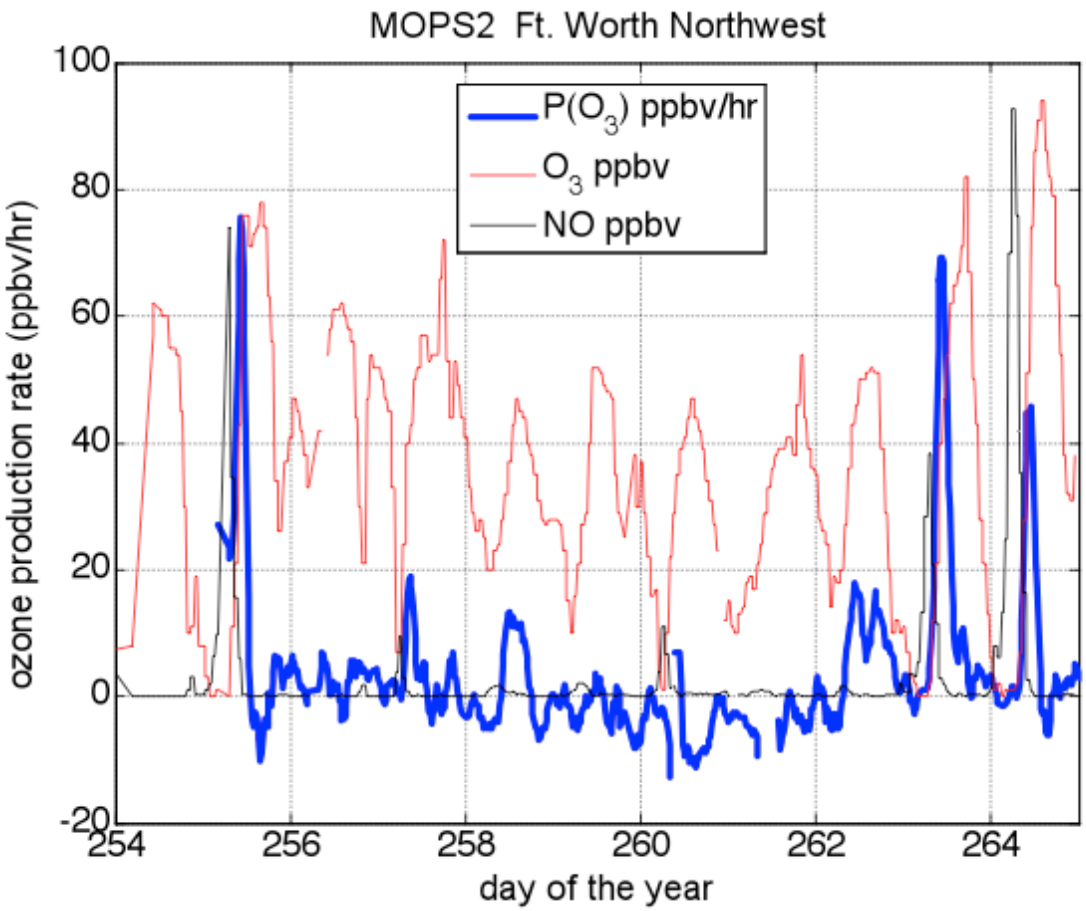

Figure 3. Preliminary results from the MOPS instrument at the Fort Worth Northwest site (CAMS 13) at Meacham Field. The net ozone production (measured by the MOPS instrument is shown in blue in units of ppbv per hour for period of September 11th (DOY 254) to September 22th (DOY 265). Also shown are ambient O_3 (red trace) and NO (black trace) mixing ratios measured by the co-located CAMS instruments.

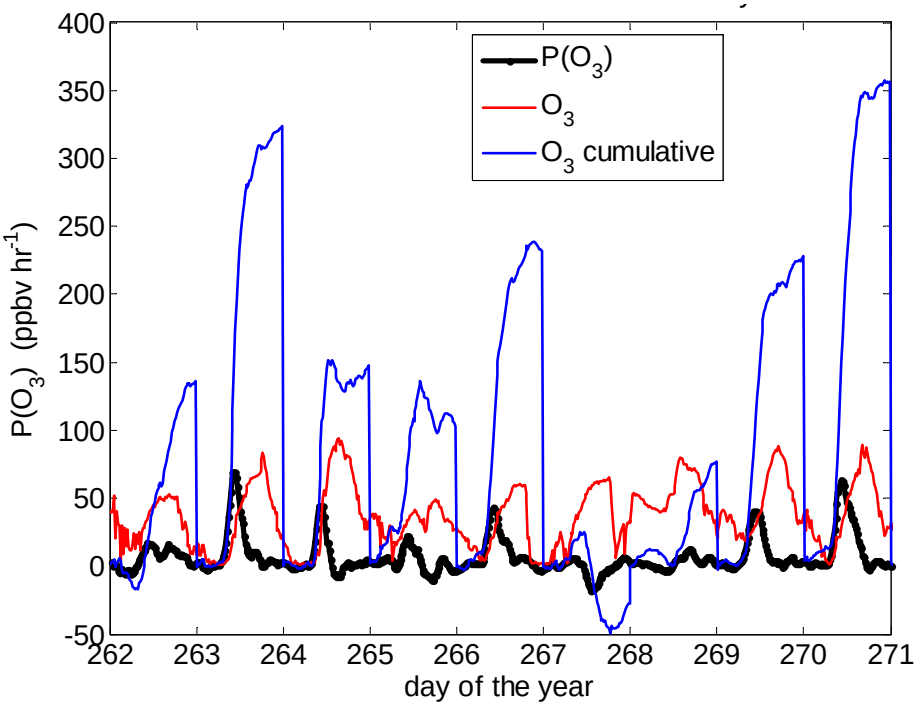

Figure 4. Preliminary ozone production at Ft. Worth Northwest (C13) from September 19-28, 2011. The ozone production rate (black), ozone (red), and cumulative ozone produced during each day (blue) indicate days with different levels of ozone production.

Project 10-042 **STATUS: Active – October 8, 2010**

Completed - November 30, 2011

Environmental Chamber Experiments to Evaluate NOx Sinks and Recycling in Atmospheric Chemical Mechanisms

ENVIRON International – Greg Yarwood

AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Mark Estes

Funded Amount: $237,481

Executive Summary:
Formation of ground level ozone requires both NOx and VOCs. When VOCs undergo chemical reactions in the atmosphere they can reduce the availability of NOx by converting it to un-reactive compounds which we call NOx-sinks. However, some of these "NOx-sink" compounds can react further in the atmosphere and may return the NOx to an active form, which we refer to as NOx-sources. The chemical reactions of VOCs with NOx can be characterized by environmental chamber experiments which expose controlled amounts of VOC and NOx to light and measure the products (e.g., ozone) that are formed. This project will carry out new environmental chamber experiments to characterize NOx sinks and sources for VOCs that are poorly understood. At the same time, we will search for chamber experiments performed in Europe that have not been utilized in the US for developing chemical mechanisms. The data obtained will be used to improve the chemical reaction mechanisms that are used in the TCEQ's State Implementation Plan (SIP) ozone modeling and control strategy development.

Project Update:
This project has four tasks:

Task 1 – Assessment of Available Data and Experimental Design

Task 2 – Conduct Environmental Chamber Experiments

Task 3 – Mechanism Improvements

Task 4 – Final Report

During this quarter, work was undertaken for Tasks 3 and 4.

Mechanism Improvements
The TCEQ is using the CB6 mechanism for State Implementation Plan (SIP) modeling and mechanism improvements will benefit the reliability of SIP planning. The new experiments conducted at the University of California at Riverside (UCR) for Task 2 of this project, combined with experiments retrieved from the European EUPHORE chamber for Task 1 of this project, were used to improve the Carbon Bond 6 (CB6) mechanism. The revised mechanism is called CB6r1.

Potential updates for CB6r1 were identified in several ways:

- New information that had become available for some reactions, e.g., the OH + NO_2 rate constant, was reviewed and evaluated.

- The CB6 mechanism was reviewed and several corrections were made.

- The performance of CB6 in simulating EUPHORE experiments with several aromatic degradation products (i.e., 2-butenedial, 4-oxo-2-pentenal, o-cresol) was evaluated and mechanism changes were developed to improve consistency between mechanism predictions and experiments. The EUPHORE experiments are particularly useful because they reported concentrations for several species including HCHO, glyoxal and HNO_3.

- The performance of CB6 in simulating NOx-sink and NOx-source experiments was evaluated and mechanism updates were implemented to improve performance of CB6r1. These updates affected the chemical mechanisms for aromatic hydrocarbons and their degradation products and isoprene and its degradation products.

Mechanism Evaluation

The CB6r1 mechanism was evaluated using data and procedures used previously to evaluate CB6. Chamber experiments in which mixtures of VOC and NOx were irradiated to form ozone were simulated using both CB6r1 and CB6. The performance of CB6 and CB6r1 in simulating the maximum ozone (MaxO3) for 339 chamber experiments is shown graphically in Figure 1. Other performance metrics also were evaluated but are not included in this progress report. Mean model errors were calculated as {(modeled - experimental)/experimental} and expressed as a percentage. Experiments included both single compounds (CO, FORM, MEOH, etc.) and surrogate mixtures of VOCs (Surg-NA etc.) The VOC composition for surrogate mixture experiments is as follows: Surg-NA mixtures are incomplete surrogate mixtures without toluene, xylene or formaldehyde; Surg-Inc (Surg-incomplete) mixtures are incomplete surrogate mixtures containing at least one of toluene or xylene; Surg-Full mixtures are full surrogate mixtures that contain at least 8 different VOCs (n-butane, n-octane, ethene, propene, trans-2-butene, toluene,

m-xylene, formaldehyde) with NOx.

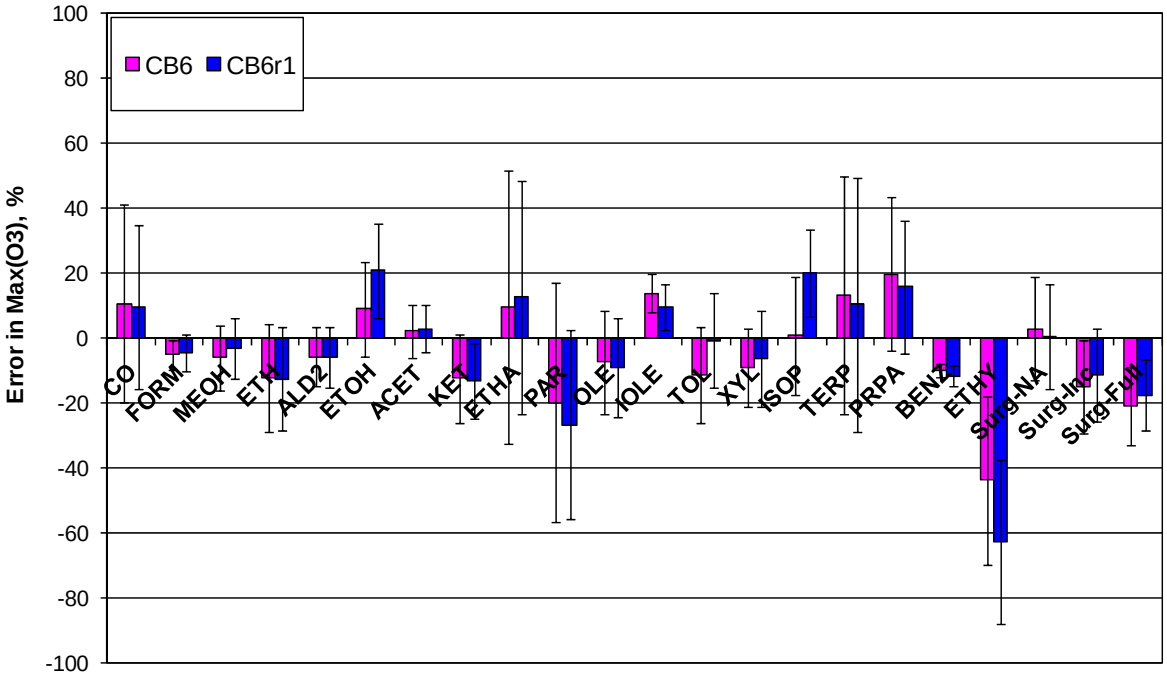

Figure 1. CB6 and CB6r1 model errors (%) for Max(O_3).

The mechanism changes from CB6 to CB6r1 were mainly for the aromatic hydrocarbons (TOL, XYL and BENZ), isoprene (ISOP) and organic nitrates (NTR and CRON). For the aromatics TOL and XYL, CB6r1 improved the model performance. CB6r1 also improved performance for surrogate mixtures that included aromatics (Surg-Inc and Surg-Full) although a tendency to under predict ozone production remains. For BENZ, CB6 tended to under predict ozone formation and CB6r1 degraded this performance. For ISOP, CB6 already performed very well and CB6r1 degraded performance by over predicting ozone production although the performance for NOx crossover time improved. However, we attach limited weight to these isoprene evaluation results from only 6 experiments at moderately high initial NOx and note that CB6r1 performed well in simulating experiments with low initial NOx that were performed in Task 3 of this project.

There were changes in model performance for other species such as alcohols, alkanes, alkenes and ethyne. The changes for alcohols, alkanes and alkanes are attributed to correcting two errors in CB6 for the products of (1) the reaction of XO2 and XO2N with RO2 and (2) photolysis of ALDX as discussed above. The performance of CB6r1 for PAR was poorer than CB6 but there are only 5 experiments for PAR (using n-butane and 2,3-dimethyl butane) and both CB6r1 and CB6 performed very well for mixtures of alkanes with alkenes (Surg-NA). Model performance for ethyne (ETHY) was degraded by changes to glyoxal chemistry, however the main uncertainty for ethyne (and glyoxal) is considered to be the quantum yields for glyoxal photolysis.

The changes in model performance with CB6r1 that are expected to be most important for photochemical modeling are (1) improved performance for ozone production from toluene and xylenes; (2) changes in ozone production from isoprene that improved performance at low initial NOx but degraded performance at higher initial NOx. Changing the products of the OH reaction of alkyl nitrates (NTR) to produce NO_2 is expected to increase ozone production regionally and may be an important change, although the CB6r1 model performance evaluation is unable to assess this.

Reporting

The final draft report was submitted for review and comment and the Final Report will be submitted after receiving comments from TCEQ and AQRP.

Project 10-044 **STATUS: Active – March 25, 2011**

Completed - November 30, 2011

Airborne Measurements to Investigate Ozone Production and Transport in the Dallas-Fort Worth (DFW) Area during the 2011 Ozone Season

University of Houston – Maxwell Shauck

AQRP Project Manager – Gary McGaughey
TCEQ Project Liaison – Erik Gribbin

Funding Requested: $279,642

Executive Summary:
The University of Houston (UH) aircraft-based Air Quality Monitoring Team conducted an airborne measurements investigation in the Dallas Fort Worth (DFW) area during the 2011 ozone season. The measurement campaign was conducted during summer 2011 using the twin-engine Piper Aztec aircraft. The constituents and mechanics of ozone formation and transport of ozone and ozone precursor compounds are the primary measurements of interest for this effort. The aircraft airborne sampling data can be used as a complement to ground based monitoring to better understand the atmospheric chemistry, meteorology, and transport of pollutants of interest in and around the DFW area.

Information obtained using an instrumented aircraft enables investigators to better understand the mechanisms associated with the transport of precursors and their contribution to ozone formation under various meteorological conditions. This and other similar aircraft have been used in previous projects in Texas to obtain this type of information. The aircraft has a full complement of instrumentation and is extensively modified for the purpose of air quality characterization.

Project Update:
The aircraft team, having deployed to the field at the end of May, planned to be fully operative at the beginning of June. However, technical problems were experienced in the first weeks of the study. A replacement of the data acquisition system during the pre-deployment phase had required an upgrade of the PC operating system. This change resulted in compatibility issues that required software and hardware upgrades and further testing while in the field. Issues with the AIMMS and RAD instruments were also encountered and resolved during this time. Additionally, the low level flight altitude of 200 and 500 ft. Above Ground Level (AGL) placed a heavier than normal burden on the engine cooling capacity causing engine overheating and resulting in the termination of the first flights. Experiments with different engine power settings and airspeeds resulted in sustainable engine operating temperatures. Science flights were successfully completed beginning the third week of June.

Between June 21st and June 30th, four science flights were completed. A total of 42.1 hours were flown in the AZTEC aircraft during the month of June.

On July 2nd the last science flight was flown. On July 3rd a pressure altitude calibration flight was flown and on July 5th the aircraft was flown back to Brazoria County Airport. During the month of July a total of 7.9 hours were flown.

The instrumentation and the equipment were transported back to the University of Houston. The decommissioning of the aircraft was initiated as well as the data validation and reporting.

As an example of the ongoing data revision work, a description of the June 28h flight and related graphs are herein included:

June 28TH Flight

Barnett Shale Flight: The aircraft took off from KPWG airport at 11:30 CST, made three downwind traverses and seven upwind traverses covering the area shown in Figure 1, recording 4.8 hours of data. The aircraft made flight tracks similar to the ones performed on June 22nd, with the exception of a longer east-west transect south of the DFW area which allowed a more comprehensive study of the background air mass conditions coming into the DFW area. Also similar to June 22nd, the synoptic wind flow was from the south and wind speeds were approximately 8 miles per hour. The aircraft flew 5.1 hours of flight time covering approximately 714 statute miles. The flight terminated at Decatur to refuel and then returned to KPWG to prepare for the following day's flight.

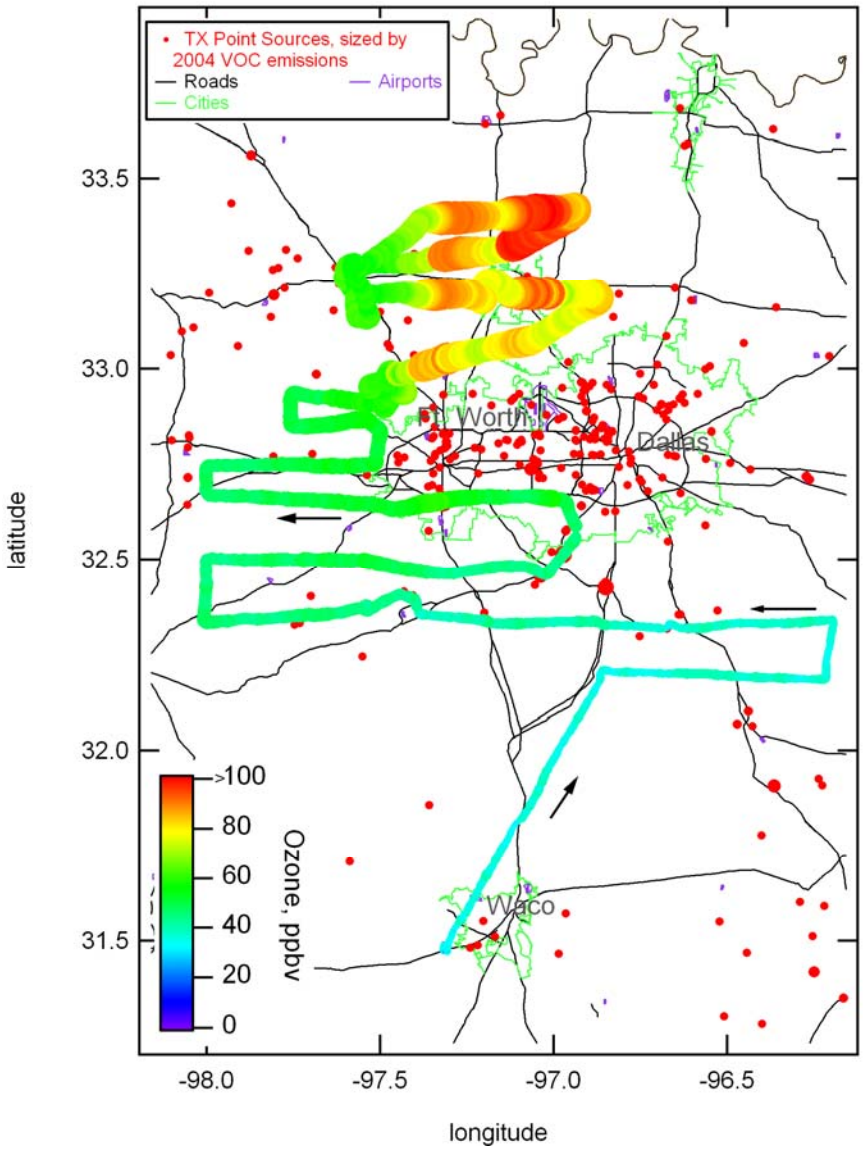

Figure 1 Ozone measurements along the flight track on June 28, 2011. The red dots plotted are VOC emission sources and are sized based on emissions. Arrows indicate flight direction

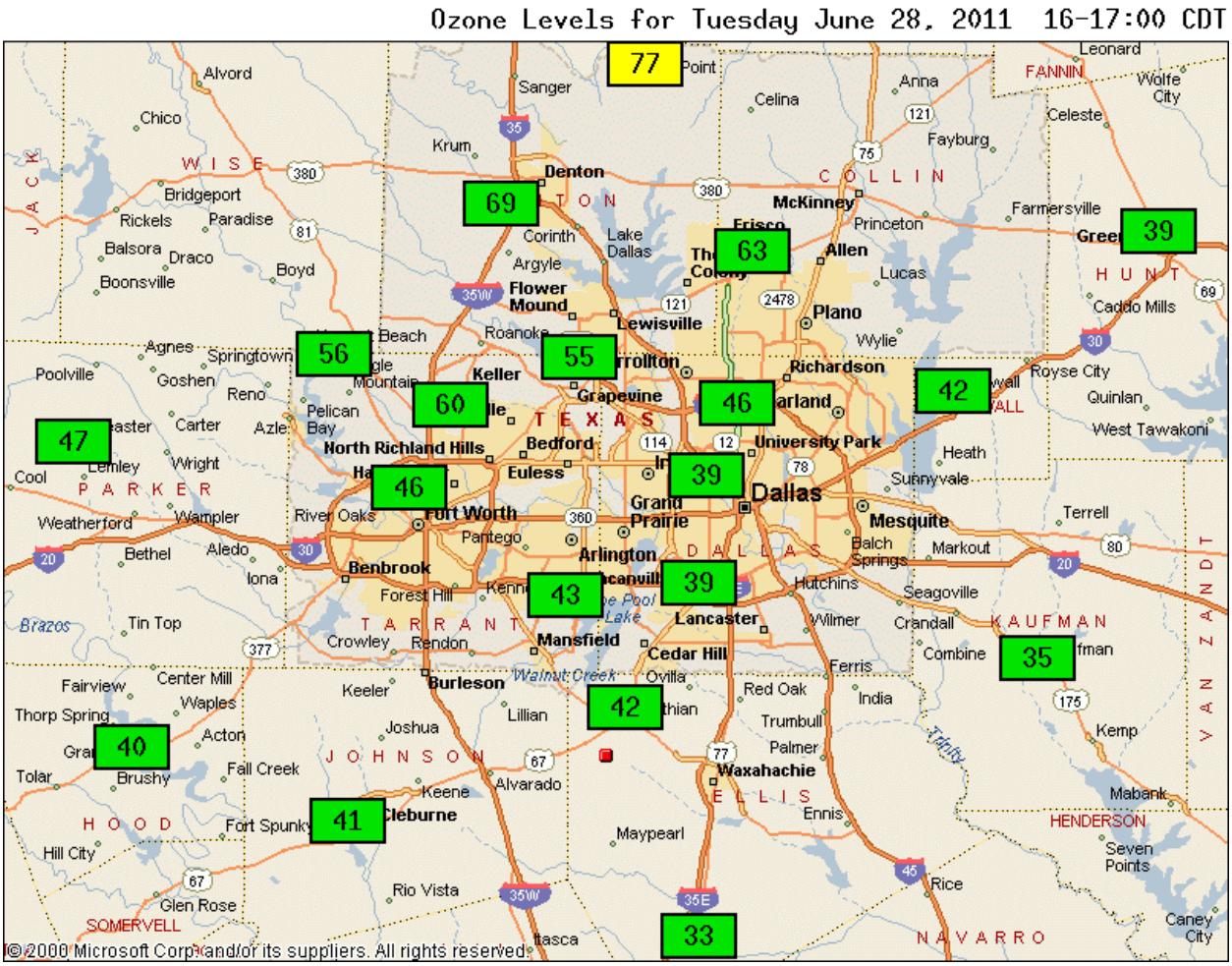

Figure 2 Spatial distribution of ozone in the DFW area on June 28, 2011, 15-17:00 CST (source TCEQ website)

Figure 2 shows the spatial distribution of surface ozone during the afternoon on that day. The hourly surface ozone levels on June 28th reached 69-77 ppbv between 15-16:00 CST in the north of the DWF area. South of the DFW Metroplex low values in the 30-40 ppbv range were observed. This general spatial distribution is also reflected in the airborne ozone measurements as shown in Figure 1. However, while the aircraft measurements confirm low ozone values in the range of 30-40 ppbv south of the Barnett Shale and DFW (altitude around 150-350 m agl; 11-13:00 CST), airborne ozone maximum values in the north of DFW reached values of 80 ppbv to almost 100 ppbv (altitude between 250-450 m agl; 15-16:00 CST). Thus these values were slightly higher than those measured on surface locations during the same time period.

Figure 3 shows that NOy levels largely correlate with ozone throughout the flight tracking with increasing values from the south to the north of the DFW Metroplex. It only shows a few excursions on the southern edge of the DFW area.

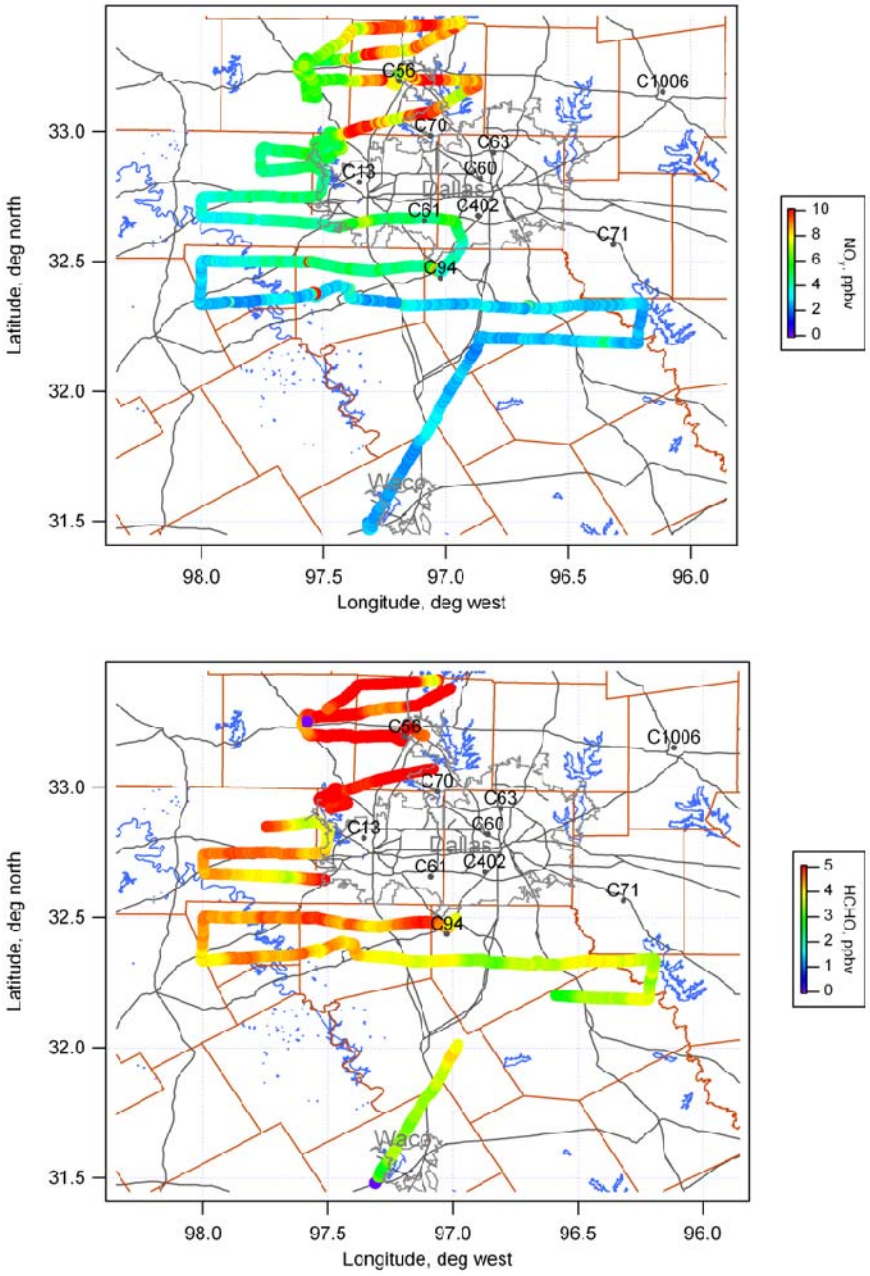

Figure 3 NOy (upper plot) and HCHO (lower plot) measurements along the flight track on June 28, 2011

Also, HCHO shows a continuous increase along the south-north gradient over the DFW Metroplex (see Figure 3) and largely correlates with ozone. However, its increase is not as strong as for ozone. While HCHO south of the DFW Metroplex exhibits ranges between 3-4 pbbv, maximum values north of DFW hardly surpass 6 ppbv. Thus north of DFW, HCHO values reached almost double the values observed south of DFW, while ozone values increased by a factor of 3. In the Barnett Shale region HCHO tends to correlate with RAD (see Figure 4), while on the northern edge of the DFW Metroplex this relationship tends to weaken and shows better coincidence with ozone.

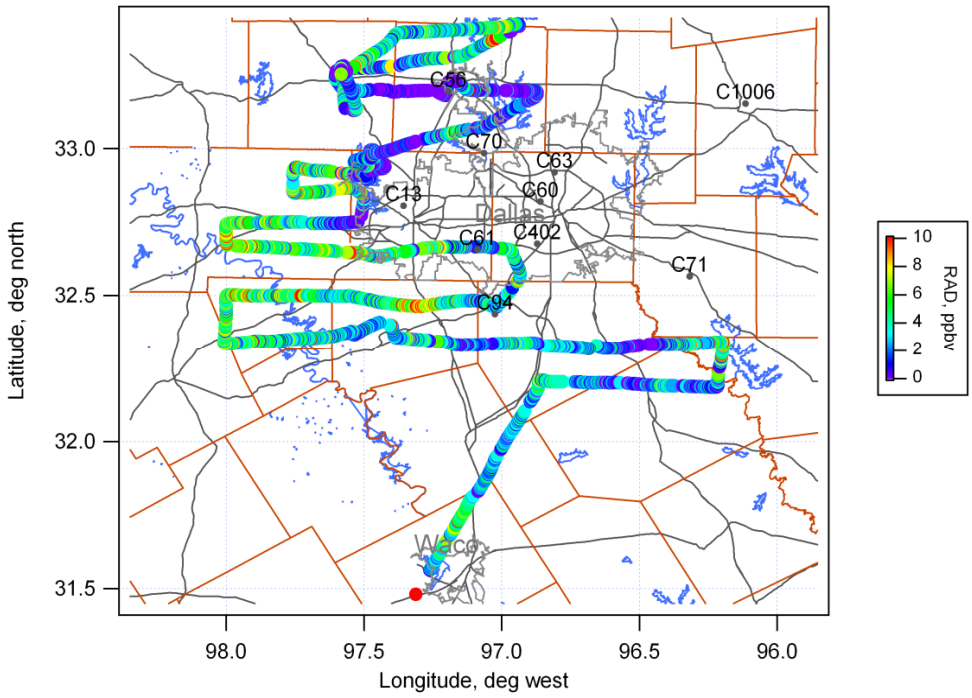

Figure 4. RAD measurements along the flight track on June 28, 2011

An estimate of any funds that might be returned as a release of claims from the researcher:

No funds are estimated to be returned.

Project 10-045 **STATUS: Active - January 22, 2011**

Completed - September 30, 2011

Quantification of Hydrocarbon, NOx, and SO2 emissions from Petrochemical Facilities in Houston: Interpretation of the 2009 FLAIR dataset

UCLA – Jochen Stutz
UNC - Chapel Hill – William Vizuete
Aerodyne – Scott Herndon
Washington State University – George Mount

AQRP Project Manager – Cindy Murphy
TCEQ Project Liaison – Marvin Jones

Funding Awarded: $398,042
($149,773 UCLA, $33,281 UNC, $164,988 Aerodyne, $50,000 Washington State)

Executive Summary:

In the spring of 2009 a multi-institutional and multi-platform field experiment to understand and classify industrial sources of ozone-forming chemicals took place in Houston, TX. During the "Formaldehyde and Olefin from Large Industrial Sources" (FLAIR) project the Aerodyne Research Inc. (ARI) mobile laboratory performed in-situ measurements of VOCs, NO_x and HCHO. At the same time an Imaging Differential Optical Absorption Spectrometer (I-DOAS) developed by the University of California Los Angeles (UCLA) sampled flares and other individual sources for emissions of HCHO, SO_2 and NO_2. Two Multi-Axis Differential Optical Absorption Spectrometers (MAX-DOAS) operated by UCLA and Washington State University (WSU) sampled air masses upwind and downwind of a large petrochemical complex to determine facility-wide emissions of HCHO and NO_2. As a result of all these efforts, a unique observational dataset of VOCs, HCHO, and NO_x observations was created.

Findings from this project interpret this observational data-set with the goal of determining emission rates of ozone precursors, such as VOCs, HCHO, SO_2, and NO_2, for the specific times and locations of the observation. The project was a collaborative effort between the University of California Los Angeles (UCLA), Aerodyne Research Inc. (ARI), Washington State University (WSU), and the University of North Carolina Chapel Hill (UNC).

In general we found that HCHO is not directly emitted by un-ignited flare stacks, while burning flares clearly emit HCHO at the flare tip. This is based on observations of flares in the Houston area from the different measurement platforms. Direct HCHO emission rates of burning flares observed during FLAIR varied between 0.3-2.5 kg/h. Direct emissions of HCHO from burning flares are currently not considered in emission inventories. We also observed emissions of SO_2 (up to 2-5kg/h) and NO_2 (up to 0.3 kg/hr) from certain flares, but many other burning flares did not emit these compounds above the average detection limit of 0.7 kg/hr for SO_2 and 0.1 kg/hr for NO_2.

The destruction removal efficiency, DRE, and combustion efficiencies, CE, from in-use flares were also quantified using ground-based in situ measurements. Uncertainty in knowledge of the

vent gas leads to uncertainties in the DRE but not the CE values. A range of DRE and CE values were observed for in-use flares – ranging from 0 (unlit) to 0.7 (steaming) to 0.999 (presumably operating as intended).

One of the surprises in the FLAIR data was the observation of a large source of HCHO in the Texas City refinery complex. This source was observed from all platforms in this project as well as from the SOF van from Chalmers University, Sweden. The estimates of the strength of this source of 18 ± 5 kg/h during one of the events on May 13, 2009 agreed remarkably well between the different platforms. Our analysis suggests that this is a direct primary source of HCHO. Analysis of the HCHO/SO_2 ratio revealed that during most of the time this source(s) co-emitted both species with ratios of 0.06 (MAX-DOAS) or 0.07-0.16 (in-situ), with an in-situ average of 0.12. However, all systems also found HCHO emission that showed no correlation with SO_2. We conclude that separate HCHO and SO_2 sources are co-located within ~300 ft and that emissions of HCHO and SO_2 are either not simultaneous, or that sometimes there is another strong unrelated HCHO source. Area averaged HCHO fluxes were also determined. A facility-averaged HCHO flux of ~45 kg/h was determined. Using the reported SO_2 fluxes and the average HCHO/SO_2 ratio the flux of HCHO co-emitted with SO_2 is 20 - 25 kg/h, in good agreement with the other observations.

Analysis of the emission inventory in Texas City, as well as triangulation and wind field analysis revealed that the most likely source of HCHO is a FCCU regeneration unit. The 2006 ozone non-acid rain inventory reports 2.6 kg/h of HCHO emissions from this FCCU unit. The 2006 base case CAMx model emission inventories shows that the area around this unit emits 3.3 – 4.3 kg/h of formaldehyde-like compounds (designated in inventory as FORM). All reported HCHO emission rates are considerably smaller than those found in our observations. It is not clear at this point if units of this type in other refineries would also emit HCHO.

Average SO_2 fluxes from Texas City industrial complex during FLAIR were determined to be 510 kg/h, with average flux from the eastern part of the facility of 360 kg/h. For 2006, the non-acid rain data base lists the SO_2 emission for the FCCU unit, which is by far the largest SO_2 source in Texas City, located east to the WSU MAX-DOAS instrument, as 453 kg/h. The observed flux and the emission inventory agree well. The average NO_2 flux from the Texas City industrial complex was determined to be ~100 kg/h.

Ethylene and propylene chemical plants did not show direct emissions of HCHO, but HCHO was observed both downwind and above these facilities. This HCHO is most likely of secondary nature, i.e. it is chemically formed from the oxidation of hydrocarbons emitted at the facilities.

An important finding was that emissions of highly reactive VOCs are important for ozone production because they serve as the “fuel” for ozone production, and also because their reaction with O_3 increases the flux of OH radicals through the radical cycling. These factors result in enhanced rates of HRVOC oxidation and ozone formation in freshly emitted HRVOC plumes. This finding is supported by an analysis of the impact of the ozonolysis of HRVOCs in freshly emitted plumes (from flares and/or fugitive emissions) showing a great enhancement of the radical production rates. Even during the night this can lead to production rates approaching typical daytime values of 0.3 to 1.5 ppt/s. The total OH loss rate in a fresh alkene plume was calculated as 47 s^{-1}, mostly due to high concentrations of ethylene and propylene.

Using the Aerodyne Inverse Modeling System (AIMS), we have computed emission rates from data obtained at Mt. Belvieu (ethene and propene), Texas City (benzene), Ship Channel (butadiene) and the Texas City Courthouse (SO_2). Computed ethene and propene emission rates significantly exceed the levels reported in emission inventories (by over 2 orders of magnitude in some cases) and support the values of Mellqvist et al (2010) that were derived from the Solar Occultation Flux (SOF) method. Computed benzene emission rates in Texas City were also found to be much greater than the inventory values, with episodes of up to two to three orders of magnitude higher. Computed butadiene emission rates in the Ship Channel area were found to vary widely over time and were in some cases over four times the reported inventory rates. Inverse modeling of the Texas City courthouse in-situ observations yielded SO_2 emission rates between 100-500 kg/h, confirming the observations by the other FLAIR participants and matching the reported inventory values. While not the main purpose of this project, observations of ship plumes were also analyzed. This analysis revealed that the NO_2/NO_X emission ratio in the observed vessels in the Houston ship channel was between 6% and 12%. The thus far unreported $HONO/NO_X$ emission ratio of ships was between 0.7% and 1.4%, similar to that observed for diesel vehicles.

Project 10-DFW & 11-DFW **STATUS: Active - February 1, 2011**

Completed - August 31, 2011

Dallas – Fort Worth Field Study

UT-Austin – Vincent Torres

AQRP Project Manager – Jim Thomas
TCEQ Project Liaison – Raj Nadkarni

Funding Awarded: $88,809
($37,857 10-DFW (FY 10 Funds) $50,952 11-DFW (FY 11 Funds))

Executive Summary:
Due to the fact that there were 4 projects dealing with issues in the DFW area the AQRP wanted to actively promote integration of the measurements and ensure the projects worked cohesively. In cooperation with TCEQ Field Operations and TCEQ Region 4, the DFW Field Study Committee was formed.

The Committee consisted of the AQRP Project Management (David Allen, Jim Thomas, and Maria Stanzione), the PIs of each of the projects being performed in the DFW area (Johan Mellqvist, Robert Griffin, Barry Lefer and Maxwell Shauck), the AQRP Project Managers for those projects (David Sullivan, Vincent Torres, and Gary McGaughey), the TCEQ Project Liaisons for those projects (John Jolly, Doug Boyer, and Erik Gribbin), TCEQ management representing the Chief Engineer, the Air Quality Division, Field Operations, and Region 4 (Mark Estes, Keith Sheedy, Raj Nadkarni, Ejaz Baig, Patricia De La Cruz, and Alyssa Taylor), and other interested parties (Kuruvilla John and John Nielson-Gammon).

Project Update:
Observations and data collection at the DFW Site at Eagle Mountain Lake began on May 30, 2011 and ended on June 30, 2011. Regular conference calls were held throughout the month to facilitate operations at the Site.

All projects completed their activities and vacated the Site by July 2, 2011. The following week work began to decommission the Site and restore it to pre-operations conditions. As of July 31, 2011, all activities were complete and the Texas Adjutant General's Office, the property manager, was notified that we no longer were utilizing the Site.

Financial Status Report

Initial funding for fiscal year 2010 was established at $2,732,071.00. In late May 2010 an amendment was issued increasing the budget by $40,000. Funding for fiscal year 2011 was established at $2,106,071, for a total project award of $4,878,142. These funds were distributed across several different reporting categories as required under the contract with TCEQ. The reporting categories are:

Program Administration – limited to 10% of the overall funding
This category includes all staffing, materials and supplies, and equipment needed to administer the overall AQRP. It also includes the costs for the Council meetings.

ITAC
These funds are to cover the costs, largely travel expenses, for the ITAC meetings.

Project Management – limited to 8.5% of the funds allocated for Research Projects
Each research project will be assigned a Project Manager to ensure that project objectives are achieved in a timely manner and that effective communication is maintained among investigators in multi-institution projects. These funds are to support the staffing and performance of project management.

Research Projects / Contractual
These are the funds available to support the research projects that are selected for funding.

Program Administration

Program Administration includes salaries and fringe benefits for those overseeing the program as a whole, as well as, materials and supplies, travel, equipment, and other expenses. This category allows indirect costs in the amount of 10% of salaries and wages.

During the reporting period seven staff members were involved in the administration of the AQRP. Dr. David Allen, Principal Investigator and AQRP Director, is responsible for the overall administration of the AQRP. James Thomas, AQRP Manager, is responsible for assisting Dr. Allen in the program administration. Ms. Maria Stanzione, AQRP Grant Manager, with assistance from Rachael Bushn, Melanie Allbritton, and Susan McCoy assisted with program organization and financial management. This included assisting with the contracting process, invoice review and payment, and other invoicing functions. Mr. Denzil Smith is responsible for the AQRP Web Page development and for data management.

Table 1: AQRP Administration Budget

Administration Budget (includes Council Expenses)

Budget Category		FY10	FY11	Total	Expenses	Pending Expenses	Remaining Balance
Personnel/Salary		$199,252	$164,437	$363,689	$319,917.85	$23,177.21	$20,593.94
Fringe Benefits		$37,682	$29,726	$67,408	$55,754.90	$3,092.54	$8,560.56
Travel		$347	$0	$347	$346.85		$0.15
Supplies		$20,000	$0	$20,000	$13,712.25	$1,331.58	$4,956.17
Equipment		$0	$0	$0			$0
Other			$0	$0			$0
Total Direct Costs		$257,281	$194,163	$451,444	$389,731.85	$27,601.33	$34,110.82
Authorized Indirect Costs		$19,926	$16,445	$36,371	$30,463.21		$5,907.79
10% of Salaries and Wages							
Total Costs		**$277,207**	**$210,608**	**$487,815**	**$420,195.06**	**$27,601.33**	**$40,018.61**
Fringe Rate		22%	22%		18%		

Fringe benefits for the Administration of the AQRP were initially budgeted to be 22% of salaries and wages across the term of the project. It should be noted that this is an estimate, and actual fringe benefit expenses will be reported for each month. The fringe benefit amount and percentage will fluctuate each month depending on the individuals being paid from the account, their salary, their FTE percentage, the selected benefit package, and other variables. For example, the amount of fringe benefits will be greater for a person with family medical insurance versus a person with individual medical insurance. At the end of the project, the overall total of fringe benefit expensed is expected to be at or below 22% of the total salaries and wages. Actual fringe benefit expenses for the months of September and October are included in the spreadsheet above. November fringe benefit expenses have not posted as of the writing of this report.

Supplies and materials expenditures included monthly telecom charges, postage, office supplies, annual phone expenses, a laptop computer, and monitor.

Indirect costs for the months of September and October are included in Table 1. November indirect costs have not posted as of the writing of this report.

As discussed in previous Quarterly Reports, the AQRP Administration requested and received permission to utilize the FY 10 funds during FY 11. This is for all classes of funds including Administration, ITAC, Project Management, and Contractual. The intent is to fully expend (or

encumber, in the case of the contractual funds) the FY 10 funds, and then begin spending the FY 11 funds.

In June 2011, UT-Austin received a Contract Extension for the AQRP. This extension will continue the program through the end of the 2012/2013 biennium, and will allow the AQRP to utilize the FY 10 funds through April 30, 2012, and the FY 11 funds through April 30, 2013.

The AQRP also requested and was granted a rebudget of the FY 10 and 11 Administration and Project Management funds, to better reflect the expenditures of this portion of the program.

ITAC

An ITAC meeting was held on the afternoon of September 28, 2011, in conjunction with the Data Workshop. Travel expenses were paid for ITAC members to attend the meeting. (ITAC members who were involved in research projects with travel funds, had expenses paid from project funds, as part of their participation in the Data Workshop.) The meeting was held in the Commons Learning Center on the J.J. Pickle Campus of The University of Texas at Austin. Expenses for the meeting room, A/V equipment and a working lunch for the ITAC members were paid on the ITAC account.

Table 2: ITAC Budget

ITAC Budget

Budget Category		FY10 Budget	FY11 Budget	Total Budget	Expenses	Pending Expenses	Remaining Balance
Personnel/Salary							
Fringe Benefits							
Travel		$16,500	$16,600	$33,100	$15,275.40	$726.00	$17,098.60
Supplies		$2,364	$2,800	$5,164	$1,033.34		$4,130.66
Equipment							
Other							
Contractual							
Total Direct Costs		$18,864	$19,400	$38,264	$16,308.74	$726.00	$21,229,26
Authorized Indirect Costs							
10% of Salaries and Wages							
Total Costs		**$18,864**	**$19,400**	**$38,264**	**$16,308.74**	**$726.00**	**$21,229,26**

Project Management

Project Managers (PMs) have been assigned to each of the research projects. During the period from September 1, 2011 through November 30, 2011, PMs have worked with PIs to accomplish project goals and ensure that all reporting requirements are met. In November, the primary focus was on the review of the draft final reports.

As none of the Research Projects were approved for funding until the end of FY 10, as with the Project Administration funds, the intent is to utilize the FY 10 and FY 11 funds during FY 11 to cover costs associated with project management. As with the Administration funds, the contract extension will allow the AQRP to utilize the FY 10 funds through April 30, 2012, and the FY 11 funds through April 30, 2013. All FY 10 funds are expected to be fully expended by the deadline. Development of the State of the Science document should utilize any remaining FY 11 funds.

Table 3: Project Management Budget

Project Management Budget

Budget Category		FY10 Budget	FY11 Budget	Total Budget	Expenses	Pending Expenses	Remaining Balance
Personnel/Salary		$145,566	$90,348	$235,914	$199,985.13	$12,838.48	$23,090.39
Fringe Benefits		$29,099	$16,564	$45,663	$34,722.25	$1,772.47	$9,168.28
Travel		$0	$0	$0	$0		$0
Supplies		$778	$260	$1,038	$1,037.49		$0.51
Equipment							
Other							
Contractual							
Total Direct Costs		$175,443	$107,172	$282,615	$235,744.87	$14,610.95	$32,259.18
Authorized Indirect Costs		$14,557	$10,792	$25,349	$17,800.06		$7,548.94
10% of Salaries and Wages							
Total Costs		**$190,000**	**$117,964**	**$307,964**	**$253,544,93**	**$14,610.95**	**$39,808.12**

Research Projects

As of November 30, 2011, all projects were complete and draft final reports were in the final review stages. Table 4 on the following 2 pages illustrates the funding awarded to each project and the total expenses reported on each project as of November 30, 2011. Please note that this reflects expenses that have posted to the UT-Austin accounting system as of November 30, 2011. There may be additional expenses pending that will not post until the following month.

Several of the Task Orders have had all spending completed, and they have turned in final invoices. At this point in time, it is anticipated that there will be approximately $40,000 in unspent project funds.

Table 4: Contractual Expenses

Contractual Expenses

FY 10 Contractual Funding		**$2,286,000**		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
10-008	Rice University	$128,851	$126,622	$2,229
10-008	Environ International	$49,945	$49,945	$0
10-009	UT-Austin	$591,332	$591,307	$25
10-021	UT-Austin	$248,786	$248,786	$0
10-022	Lamar University	$150,000	$124,654	$25,346
10-032	University of Houston	$176,314	$117,304	$59,010
10-032	University of New Hampshire	$23,054	$18,693	$4,361
10-032	UCLA	$49,284	$46,652	$2,632
10-034	University of Houston	$195,054	$139,880	$55,174
10-042	Environ International	$237,481	$232,497	$4,984
10-045	UCLA	$149,773	$142,358	$7,415
10-045	UNC - Chapel Hill	$33,281	$33,281	$0
10-045	Aerodyne Research Inc.	$164,988	$164,988	$0
10-045	Washington State University	$50,000	$50,000	$0
10-DFW	UT-Austin	$37,857	$37,688	$169
FY 10 Total Contractual Funding Awarded		$2,286,000		
FY 10 Contractual Funding Remaining to be Awarded		$0		
FY 10 Contractual Funds Expended to Date*			$2,124,655	
FY 10 Contractual Funds Remaining to be Spent				$161,345

FY 11 Contractual Funding		**$1,736,063**		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
10-006	Chalmers University of Tech	$262,179	$255,989	$6,190
10-006	University of Houston	$222,483	$203,891	$18,592
10-015	Environ International	$201,280	$195,337	$5,943
10-020	Environ International	$202,498	$202,493	$5
10-024	Rice University	$225,662	$223,770	$1,892
10-024	University of New Hampshire	$70,747	$70,720	$27
10-024	University of Michigan	$64,414	$60,598	$3,816
10-024	University of Houston	$98,134	$88,914	$9,220
10-029	Texas A&M University	$80,108	$78,147	$1,961
10-044	University of Houston	$279,642	$197,790	$81,852
11-DFW	UT-Austin	$50,952	$29,262	$21,690
FY 11 Total Contractual Funding Awarded		$1,758,099		
FY 11 Contractual Funding Remaining to be Awarded		-($22,036)		
FY 11 Contractual Funds Expended to Date*			$1,606,910	
FY 11 Contractual Funds Remaining to be Spent				$129,153
Total Contractual Funding		$4,022,063		
Total Contractual Funding Awarded		$4,044,099		
Total Contractual Funding Remaining to be Awarded		-($22,036)		
Total Contractual Funds Expended to Date*			$3,731,565	
Total Contractual Funds Remaining to be Spent				$290,498

*(Expenditures Reported as of August 31, 2011.)

Appendix

Financial Reports by Fiscal Year

(Expenditures reported as of November 30, 2011. Does not include all expenditures for the month of November 2011.)

Administration Budget (includes Council Expenses)

FY 2010

Budget Category		FY10 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$199,252	$195,028.64		$4,223.36
Fringe Benefits		$37,682	$36,849.42		$832.58
Travel		$347	$346.85		$0.15
Supplies		$20,000	$13,712.25	$1,331.58	$4,956.17
Equipment		$0			$0
Other					
Contractual					
Total Direct Costs		$257,281	$245,937.16	$1,331.58	$10,012.26
Authorized Indirect Costs		$19,926	$19,502.88		$423.12
10% of Salaries and Wages					
Total Costs		**$277,207**	**$265,440.04**	**$1,331.58**	**$10,435.38**

Administration Budget (includes Council Expenses)

FY 2011

Budget Category		FY11 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$164,437	$124,889.21	$23,177.21	$16,370.58
Fringe Benefits		$29,726	$18,905.48	$3,092.54	$7,727.98
Travel		$0			$0
Supplies		$0			$0
Equipment					
Other		$0			$0
Contractual					
Total Direct Costs		$194,163	$143,794.69	$26,269.75	$24,098.56
Authorized Indirect Costs		$16,445	$10,960.33		$5,484.67
10% of Salaries and Wages					
Total Costs		**$210,608**	**$154,755.02**	**$26,269.75**	**$29,583.23**

ITAC Budget

FY 2010

Budget Category		FY10 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary					
Fringe Benefits					
Travel		$16,500	$13,008.20	$726.00	$2,765.80
Supplies		$2,364	$1,033.34		$1,330.66
Equipment					
Other					
Total Direct Costs		$18,864	$14,041.54	$726.00	$4,096.46
Authorized Indirect Costs					
10% of Salaries and Wages					
Total Costs		**$18,864**	**$14,041.54**	**$726.00**	**$4,096.46**

ITAC Budget

FY 2011

Budget Category		FY11 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary					
Fringe Benefits					
Travel		$16,600	$2,267.20		$14,332.80
Supplies		$2,800			$2,800.00
Equipment					
Other					
Total Direct Costs		$19,400	$2,267.20		$17,132.80
Authorized Indirect Costs					
10% of Salaries and Wages					
Total Costs		**$19,400**	**$2,267.20**	**$0.00**	**$17,132.80**

Project Management Budget

FY 2010

Budget Category		FY10 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$145,566	$144,698.68		$867.32
Fringe Benefits		$29,099	$28,828.90		$270.10
Travel		$0	$0		$0
Supplies		$778	$777.49		$.51
Equipment					
Other					
Total Direct Costs		$175,443	$174,305.07	$0	$1,137.93
Authorized Indirect Costs		$14,557	$14,698.87		-$141.87
10% of Salaries and Wages					
Total Costs		**$190,000**	**$189,003.94**	**$0**	**$996.06**

Project Management Budget

FY 2011

Budget Category		FY11 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$90,348	$55,286.45	$12,838.48	$22,223.07
Fringe Benefits		$16,564	$5,893.35	$1,772.47	$8,898.18
Travel		$0			$0
Supplies		$260	$260.00		$0
Equipment					
Other					
Total Direct Costs		$107,172	$61,439.80	$14,610.95	$31,121.25
Authorized Indirect Costs		$10,792	$3,101.19		$7,690.81
10% of Salaries and Wages					
Total Costs		**$117,964**	**$64,540.99**	**$14,610.95**	**$38,812.06**

AQRP Budget

FY 2010

Budget Category		FY10 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$199,252	$195,028.64	$0.00	$4,223.36
Fringe Benefits		$37,682	$36,849.42	$0.00	$832.58
Travel		$347	$346.85	$0.00	$0.15
Supplies		$20,000	$13,712.25	$1,331.58	$4,956.17
Equipment		$0	$0.00	$0.00	$0.00
Other		$0	$0.00	$0.00	$0.00
Contractual		$2,286,000	$2,124,655.01	$0.00	$161,344.99
ITAC		$18,864	$14,041.54	$726.00	$4,096.46
Project Management		$190,000	$189,003.94	$0.00	$996.06
Total Direct Costs		$2,752,145	$2,573,637.65	$2,057.58	$176,449.77
Authorized Indirect Costs		$19,926	$19,502.88	$0.00	$423.12
10% of Salaries and Wages					
Total Costs		**$2,772,071**	**$2,593,140.53**	**$2,057.58**	**$176,872.89**

AQRP Budget

FY 2011

Budget Category		FY11 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$164,437	$124,889.21	$23,177.21	$16,370.58
Fringe Benefits		$29,726	$18,905.48	$3,092.54	$7,727.98
Travel		$0	$0.00	$0.00	$0
Supplies		$0	$0.00	$0.00	$0
Equipment		$0	$0.00	$0.00	$0
Other		$0	$0.00	$0.00	$0
Contractual		$1,758,099	$1,606,909.62	$0.00	$151,189.38
ITAC		$19,400	$2,267.20	$0.00	$17,132.80
Project Management		$117,964	$64,540.99	$14,610.95	$38,812.06
Total Direct Costs		$2,089,626	$1,817,512.50	$40,880.70	$231,232.80
Authorized Indirect Costs		$14,445	$10,960.33	$0.00	$5,484.67
10% of Salaries and Wages					
Total Costs		**$2,106,071**	**$1,828,472.83**	**$40,880.70**	**$236,717.47**