

# **AIR QUALITY RESEARCH PROGRAM**

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

**Quarterly Report  
June 1, 2011 through August 31, 2011**

**Submitted to**

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**September 3, 2011**

## **Texas Air Quality Research Program**

### **Quarterly Progress Report**

**September 3, 2011**

#### **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. 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 determined.

## Background

Section 387.010 of HB 1796 (81<sup>st</sup> 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.

- 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 AQRD 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 will be reviewed by the ITAC at a meeting to be held in Austin in September, 2011. The AQRD Director will ensure that any comments made by the ITAC in the September, 2011 meeting are responded to in the final project deliverables of the remaining active projects.
- 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 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 & 28, 2011: AQRP Data Workshop

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

## **RESEARCH PROJECTS**

During the fifth quarter of operation, Program Administration focused on payment of monthly invoices for active projects and reporting activities. Project Managers worked with the Principal Investigators (PIs) to complete project activities as specified in the Work Plans. As of August 31, 2011, Projects 10-008, 10-021, 10-024, 10-045, 10-DFW, and 11-DFW are complete. Each of these projects, with the exception of 10-021, 10-DFW, and 11-DFW, has been granted a 30-day Contract Extension to allow the participants to travel to UT-Austin to attend the AQRP Workshop on September 27 and 28, 2011. All remaining projects have been granted a 90-day Contract Extension to allow additional time to complete data analysis and the final report.

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

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**Project 10-006**

**STATUS: Active – February 16, 2011**

**End Date Extended to November 30, 2011**

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***Quantification of Industrial Emissions of VOCs, NO<sub>2</sub> and SO<sub>2</sub> by SOF and Mobile DOAS***

Chalmers University – Johan Mellqvist

AQRP Project Manager – Dave Sullivan

University of Houston – Bernhard Rappenglück

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 will be conducted which will help to locate and quantify industrial emissions of VOCs (alkanes, alkenes and other species), NO<sub>2</sub> and SO<sub>2</sub> 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) will also be used. These methods allow estimates of pollutant concentrations in a column of air from a point on the ground. This study will follow up previous measurements in 2006 and 2009 to obtain a trend analysis for selected sites, but also will be 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<sub>x</sub>) that lead to the formation of tropospheric ozone. The measurements will be 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 will be conducted using GPS radiosondes and from a 10 meter portable mast that will be acquired within the project. To complement the path measurements taken by the SOF, DOAS, and meFTIR, canister samples will be taken downwind of the sites and analyzed afterwards using gas chromatography. In this way, emissions estimates for VOCs will be derived. The study areas will include 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 priorities for the measurement areas outside Houston will be discussed with TCEQ and the AQRP project manager prior to the measurements.

The measurement campaign will take place largely in April and May 2011. The measurements in the DFW area will be carried out to augment other measurements taken by AQRP projects that are part of the DFW Field Campaign. The SOF measurements will be conducted 1 month earlier than the other DFW projects in order to get more sunshine hours and have better chances of cooler temperatures which will optimize SOF measurements, and for other logistical reasons.

The overall measurements in this project will be carried out in the same manner as in previous studies in the Houston area during 2006 and 2009, but a few qualitative studies will be conducted in addition, measuring CO and formaldehyde (HCHO) in parallel with VOCs. We also plan to perform thermal emission measurements with FTIR, targeting flares as a source of emissions.



**Project Update:**

During the period March 1, 2011 through May 31, 2011, a 7 week field campaign has been carried out in north eastern Texas during which industrial emissions of VOCs, formaldehyde, NO<sub>2</sub> and SO<sub>2</sub> has been measured using the Solar Occultation Flux (SOF) and mobile DOAS methods. During the period June 1 to August 22, less intense measurements were carried out until June 20 when the equipment was sent back to Sweden. The data have then been analyzed and this will be reported in the comprehensive report that will be finalized August 31.

The targeted industries correspond to conglomerates of refineries and petrochemical industries in the Houston ship channel, 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<sub>2</sub>, NO<sub>2</sub> 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 includes source identification and in many cases quantification.

**Preliminary results**

In the sites surveyed with SOF and mobile DOAS before, i.e. HSC, Mt Belvieu and Texas City we have measured emissions of alkanes, alkenes, SO<sub>2</sub>, NO<sub>2</sub> and formaldehyde. The general emission patterns are the same, but compared to 2006 and 2009 there are differences

The Beaumont and Port Arthur area was surveyed for the first time with SOF in this campaign. Alkane emissions as summed from seven individual plant areas is slightly more than half of the alkane emissions measured from the Houston Ship Channel area 2011. In terms of alkenes, four plants in the Beaumont Port Arthur area contributed but no major propene emissions were observed. One site was found to emit butadiene. A major alkene source was found in Longview, also surveyed for the first time with SOF.

In the Fort Worth study we find that the largest continuous sources are the treatment facilities and the large compressor stations emitting mostly methane but also ethane (2-5% by mass) and other species such as propane and ethene. Another source is well pads emitting several orders of magnitude less than the treatment facilities but due to the large amount of well pads, this constitutes a major source.

**Project progress**

There were no delays in the project for the reporting period and the work has been carried out according to the scope of work. An extension has been granted until end of November 2011, to work further with data analysis and QA/QC issues. We anticipate that the project will follow the scope of work and that all allocated funds will be used.

***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:**

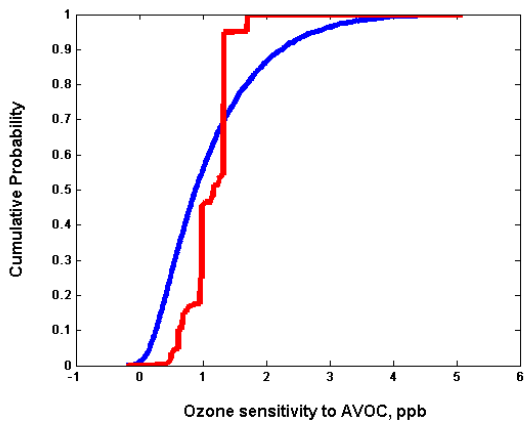
This project aims to characterize how various model inputs and formulations influence predictions of ozone-precursor response in Texas ozone attainment modeling episodes. Bayesian inference is being used to consider model performance for alternate structural and parametric scenarios to develop probabilistic representations of ozone response to emissions. The expected outcomes of this research are to improve understanding of how various factors (anthropogenic and biogenic emission rates, chemical mechanisms, photolysis rates, boundary conditions, and dry deposition schemes) influence ozone response predictions; to help prioritize future improvements to Texas SIP modeling; and to demonstrate how probabilistic analyses via an ensemble approach can supplement deterministic estimates of ozone response.

**Project Update:**

This project has used TCEQ's CAMx air quality modeling episodes for the year 2006 as a starting point, and developed an ensemble of structural and parametric perturbations to that modeling to explore the uncertainty in results. Work in earlier periods assembled the various structural cases, representing alternate assumptions for chemical mechanism, biogenic emissions model, and deposition scheme; and parametric cases, representing uncertainty in emission rates, reaction rate constants, and boundary conditions. After screening analysis to identify the cases that most influence predictions of ozone concentrations and their sensitivities to emissions, work in the latest quarter conducted Bayesian analysis to adjust model results based on the uncertainties and performance against observed concentrations. A Reduced Form Model (RFM) based on Taylor expansion of sensitivity coefficients was used to characterize O<sub>3</sub> concentration and responsiveness to NO<sub>x</sub> and VOC emissions from the Dallas-Fort Worth region. Observed O<sub>3</sub> concentrations at monitors within DFW were then be used to perform Bayesian Monte Carlo analysis for alternate observational metrics in order to determine the relative likelihood of each model case based on the model performance. The resulting "weightings" or "likelihoods" are used to generate probabilistic distributions of ozone sensitivity to emission reductions from the Dallas-Fort Worth region, and of the actual values of the originally assumed model inputs. The figure below shows an example of how the original estimates of ozone sensitivity to VOC (blue) may be adjusted when Bayesian weights are applied (red).

One of the challenges identified in the current work is that results can vary sharply depending on the metric used to evaluate model performance. Thus, researchers from this project are exploring a range of potential metrics, as well as non-Bayesian methods that may provide alternative

approaches for weighting the model cases. Ensemble statistics will be used to assess the performance of the resulting weightings.



**Figure.** Cumulative distribution functions for ozone sensitivity to DFW anthropogenic VOC emissions, averaged over all days of the episode at the Denton monitor. The blue curve assumes all 4000 of the Monte Carlo model ensemble cases are equally likely, and the red curve applies Bayesian weights based on model performance in predicting ozone concentrations in the DFW region.

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**Project 10-009**

**STATUS: Active – September 8, 2010**

**End Date Extended to November 30, 2011**

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***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.

*Task 2 – Modeling of Flare Performance Using Multivariate Image Analysis and Computational Fluid Dynamics:* 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 this task to use multivariate image analysis and computational fluid dynamics to develop a predictive model for flare performance using the data obtained in Task 1 to develop and evaluate the model. This task will build on work of Dr. Tom Edgar’s research group and expand 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 will also be used to better understand the performance data obtained in Task 1 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 Task 1.

This modeling approach will use feature variables extracted from the spectral information of the flare images on the video recordings from the tests to improve the predictive capability of the computational fluid dynamics model, which will be developed using first principles to model the full-scale flares used in the Task 1 tests. This model will predict flare performance, i.e., combustion efficiency and destruction and removal efficiency, while at the same time predict emissions produced at various operational conditions.

**Project Update:**

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

*Task 2.1* – 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.

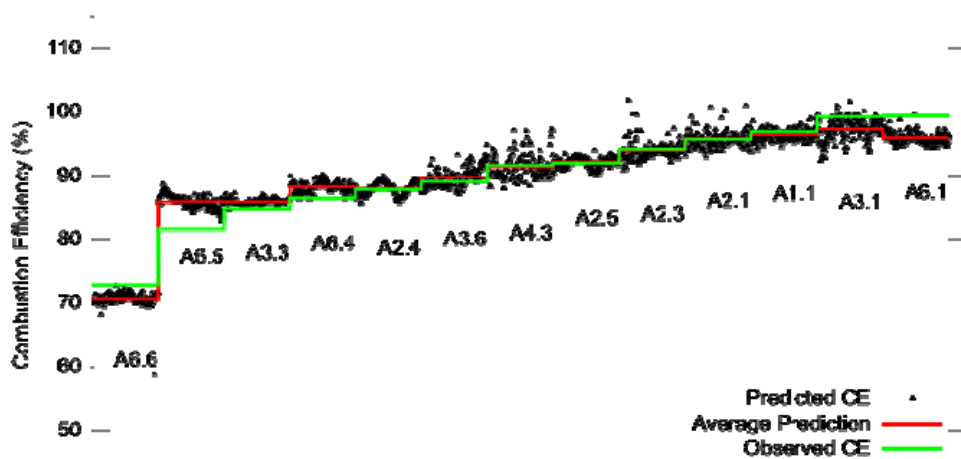


Figure 1: Predictions using the image analysis model on the air-assisted flare, with testing/validation scheme “A”.

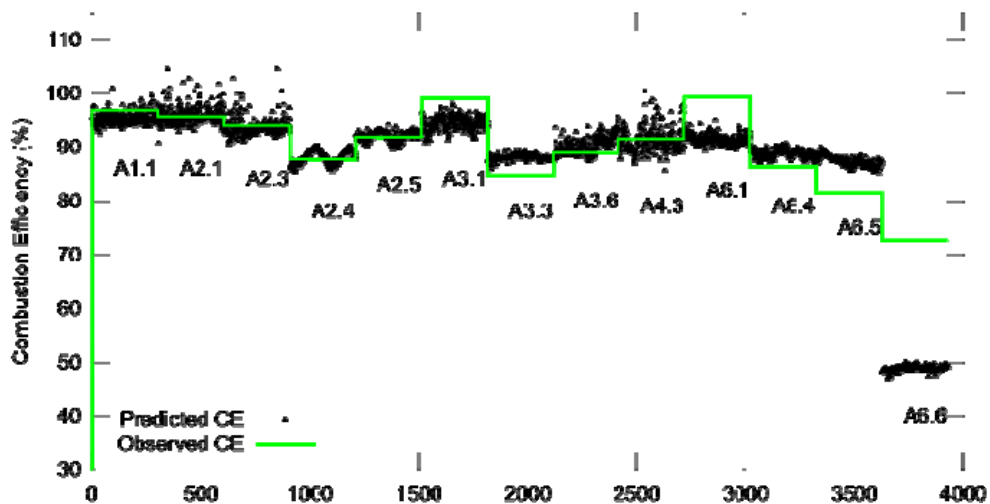


Figure 2: Predictions using the image analysis model on the air-assisted flare, with testing/validation scheme “B”.

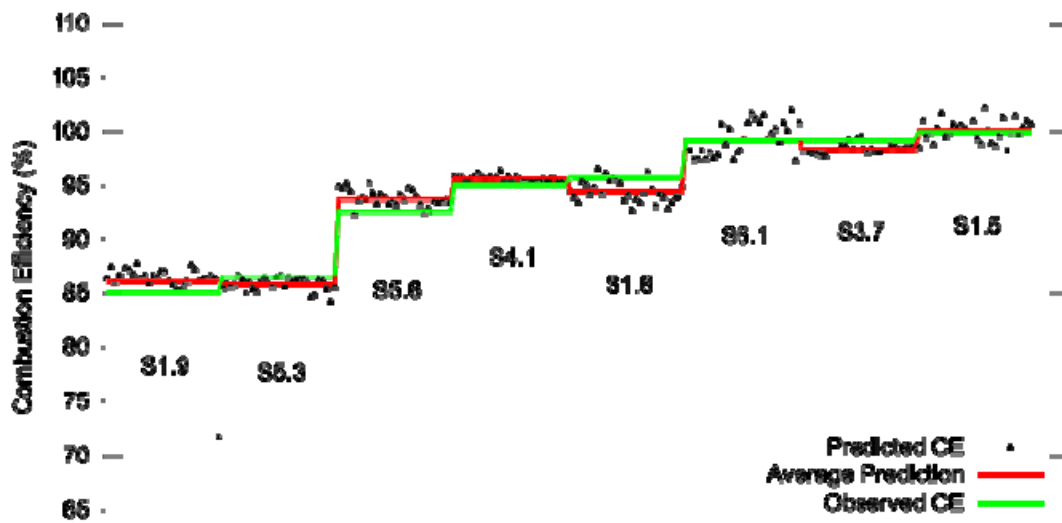


Figure 3: Predictions using the image analysis model on the steam-assisted flare, with testing/validation scheme “A”.

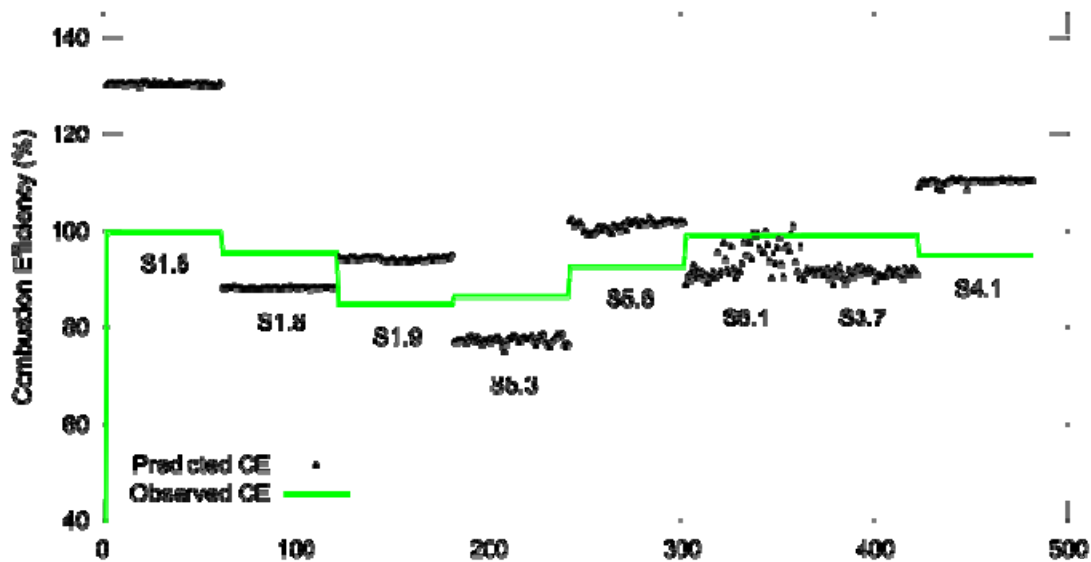


Figure 4: Predictions using the image analysis model on the steam-assisted flare, with testing/validation scheme “B”. There were not enough usable tests for this approach to work with the steam-assisted flare.

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.

When using image analysis with testing/validation scheme “B” (see Preliminary Analysis for an explanation), which more accurately simulates the conditions that would be present in an actual application of this method, a wide range of training data are required to build a robust model. For the steam-assisted flare, only 7 tests showed a visible flame, which was not sufficient to make an accurate model. For the air-assisted flare, however, 13 of the tests showed a visible flame, and the wider range of training data resulted in an accurate model.

Task 2.2: 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 propylene-air combustion mechanism, which is included with Fluent, does not accurately predict the combustion efficiency values that were observed. The current solution that is being examined is to use the propane-air combustion rates, which are included in Fluent. This approach is based on the fact that propane combustion has been studied more widely than has propylene combustion, and the fact that burning rate data for propylene are very similar to those for propane.

The lack of an accurate propylene combustion mechanism continues to hinder the CFD model. An alternative, which involves using the propane combustion rate from Fluent in place of the propylene mechanism, is currently being examined.



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

ENVIRON International – Greg Yarwood

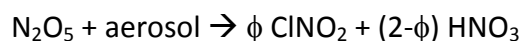
AQRP Project Manager – Elena McDonald-Buller  
TCEQ Project Liaison – Mark Estes**Funding Requested:** \$201,280**Executive Summary:**

Results from the TexAQS 2006 field study in Houston showed that reactions at night between ozone (O<sub>3</sub>), nitrogen oxides (NO<sub>x</sub>), hydrogen chloride (HCl) and particles (PM) give rise to nitryl chloride (ClNO<sub>2</sub>). This finding is confirmed by other studies and is significant because ClNO<sub>2</sub> undergoes rapid photolysis in the morning and can influence photochemistry and O<sub>3</sub> formation at the start of the day. Sea salt PM is an important source of chloride in coastal regions but ClNO<sub>2</sub> also has been observed far from the ocean (in Boulder, Colorado) indicating that other sources of chloride can give rise to ClNO<sub>2</sub> and that its influence on photochemistry may not be limited to coastal regions.

This study will analyze 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 will be included in the CAMx photochemical grid model that is used by the TCEQ for SIP modeling. The CAMx model will be applied first using a national modeling database that includes all of the field study locations. The emission inventories for the national database will be reviewed and expanded to include as many sources of chloride as possible, including sea salt, HCl, molecular Cl<sub>2</sub> and PM chloride. Performance of the national CAMx model will be assessed to evaluate the chemistry included for ClNO<sub>2</sub> and the completeness of the chloride emission inventory.

**Project Update:****Task 1. Assessment of Nitryl Chloride (ClNO<sub>2</sub>) Formation in Urban Areas**

The SHARP 2009 effort involved approximately 10 days of intensive measurements, of which there are 2 days of ClNO<sub>2</sub> measurements that were over 100 pptv and have concurrent N<sub>2</sub>O<sub>5</sub> measurements. We applied a box model that simulates formation of ClNO<sub>2</sub> from N<sub>2</sub>O<sub>5</sub> to determine the net N<sub>2</sub>O<sub>5</sub> uptake coefficients ( $\gamma$ ) and effective ClNO<sub>2</sub> yields ( $\phi$ ) from the measurement data:



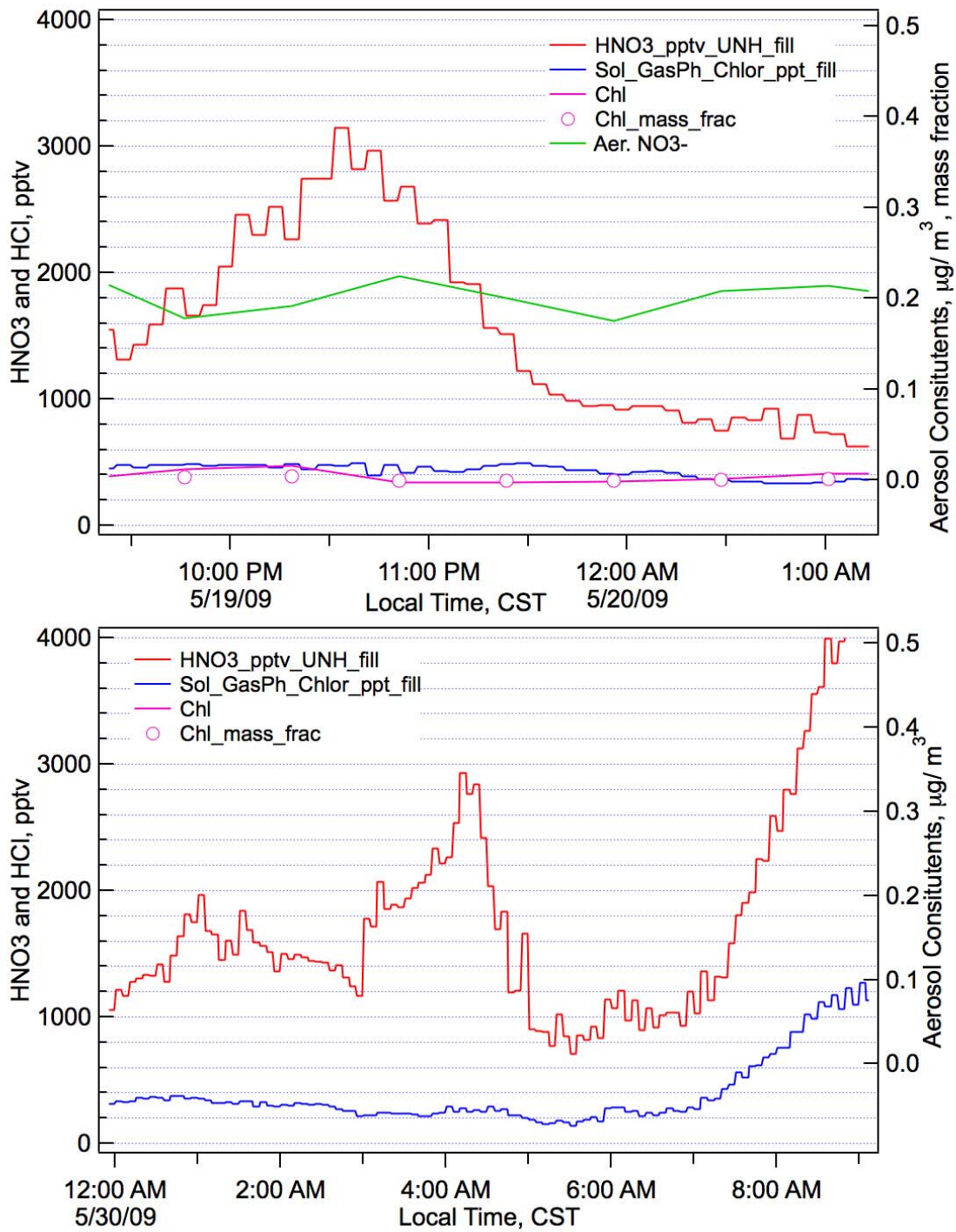
The pseudo first-order rate coefficient for the heterogeneous decay of  $\text{N}_2\text{O}_5$  is a function of  $\lambda$  as well as total aerosol surface area and mean molecular speed of  $\text{N}_2\text{O}_5$ . The values of  $\gamma$  and  $\phi$  were determined by data fitting. The two nights that were analyzed were 5/19/2009 and 5/29/2009.

(a) 5/19/2009 – The box model analysis using measurements from this night yields a  $\text{ClNO}_2$  efficiency of roughly 3.3%, and a net uptake coefficient of 0.052, assuming an aerosol surface area of  $200 \text{ um}^2/\text{cm}^3$ . However,  $\text{NO}_2$  calculated by the box model was about a factor of 3 lower than the observations. One reason for this could be that the site (rooftop of Moody Tower near downtown Houston), even though above ground, is impacted by urban  $\text{NO}_x$  sources that continue throughout the night. A source of  $\text{NO}_2$  was added to the box model by adding a slow first order reaction that forms  $\text{NO}_2$  from a large reservoir. This effectively yields a constant source of  $\text{NO}_2$  that can be adjusted by slight adjustment of the rate constant. In practice, this source is in the range of a few ppbv/hr, which seems like a reasonable number, and effectively maintains the ambient  $\text{NO}_2$  mixing ratio close to the measured values. With 2 ppbv/hr of the added  $\text{NO}_2$  emissions, the model result that gives the best simulation of the May 19 period indicates a slightly lower  $\text{ClNO}_2$  formation efficiency (2.5%) and a higher  $\text{N}_2\text{O}_5$  uptake coefficient, 0.1. The  $\text{NO}_2$  source brings the model  $\text{NO}_2$  closer to that measured.

(b) 5/29/2009 – The second period of interest in the SHARP 2009 dataset occurred on May 29. In this case the highest  $\text{ClNO}_2$  occurred later in the night, almost 8 hours after sunset. The  $\text{ClNO}_2$  efficiencies implied by the box model results were low (0.5-1%) and the  $\text{N}_2\text{O}_5$  uptake coefficients were quite high (0.04 to 0.1) for the two cases (the straight model and  $\text{NO}_2$  source case). As above, an  $\text{NO}_2$  source (emission rate of 4 ppbv/hr in this case) gave a better fit to the  $\text{NO}_2$  ambient measurements.

## **Task 2. Analysis of Sources of Reactive Chlorine and Aerosol Soluble Chloride**

The SHARP 2009 project had measurements of soluble gas-phase chloride (thought to be  $\text{HCl}$ ) and sub-micron volatile aerosol chloride, and those are shown in Figure 1 for the two periods that were analyzed by the box model, although AMS measurements were only available for the first period (5/19/2009). Those measurements show that there were only modest amount of aerosol chloride present, consistent with a low  $\text{N}_2\text{O}_5$  to  $\text{ClNO}_2$  conversion efficiency. The model results showed substantial  $\text{HNO}_3$  formation, exceeding what was observed either as gas phase  $\text{HNO}_3$  or particle  $\text{NO}_3^-$ , as shown in Figure 1. This  $\text{HNO}_3$  is inevitable given the  $\text{N}_2\text{O}_5$  production rates and relatively low concentrations of  $\text{N}_2\text{O}_5$  that were observed.



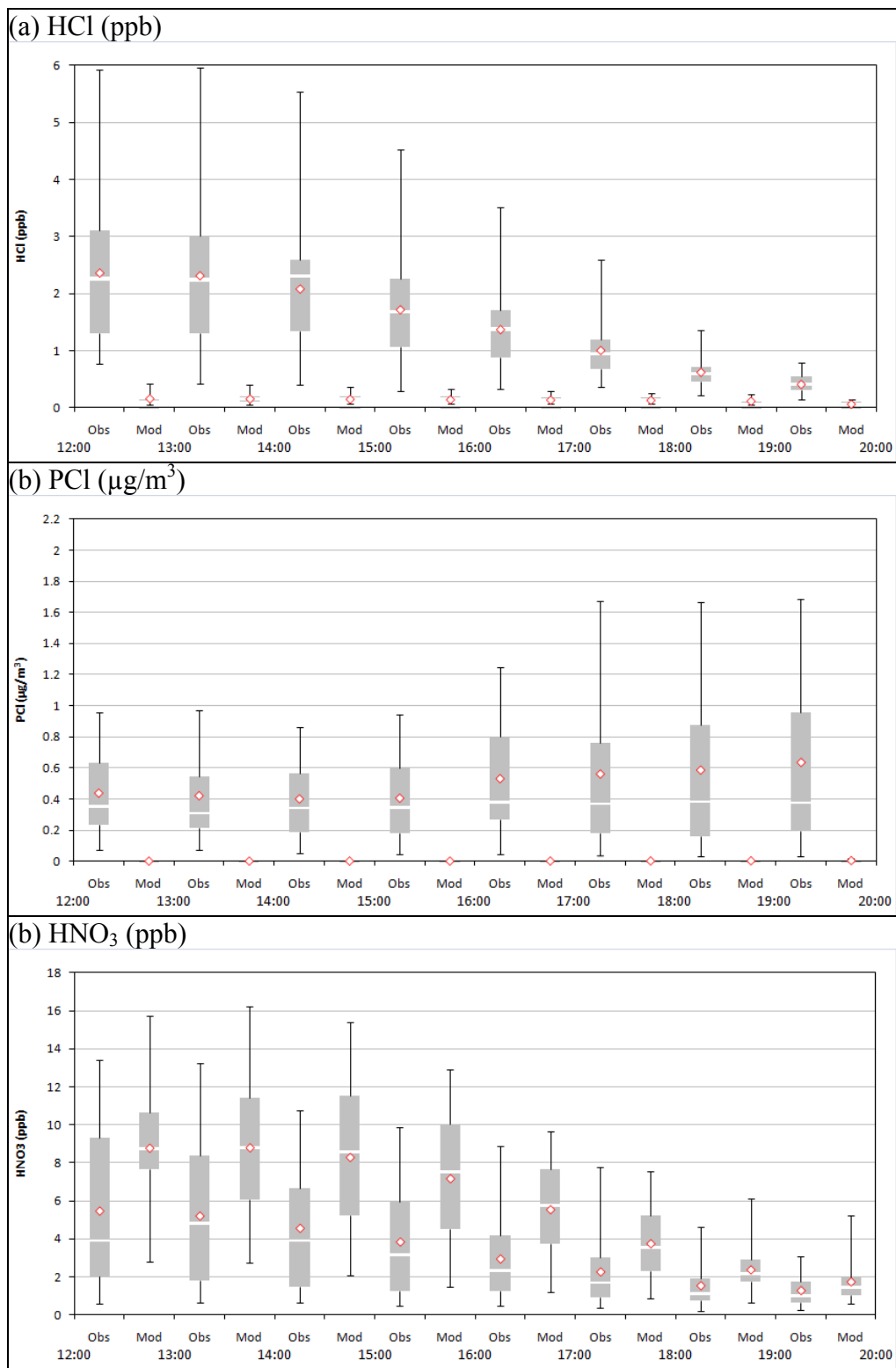
**Figure 1.** Measurements of HNO<sub>3</sub>, gas phase soluble chloride and particle NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> for Period 1 (top), and HNO<sub>3</sub> and gas phase soluble chloride for Period 2 (bottom).

### Task 3. Modeling of Reactive Chlorine and Hydrogen Chloride

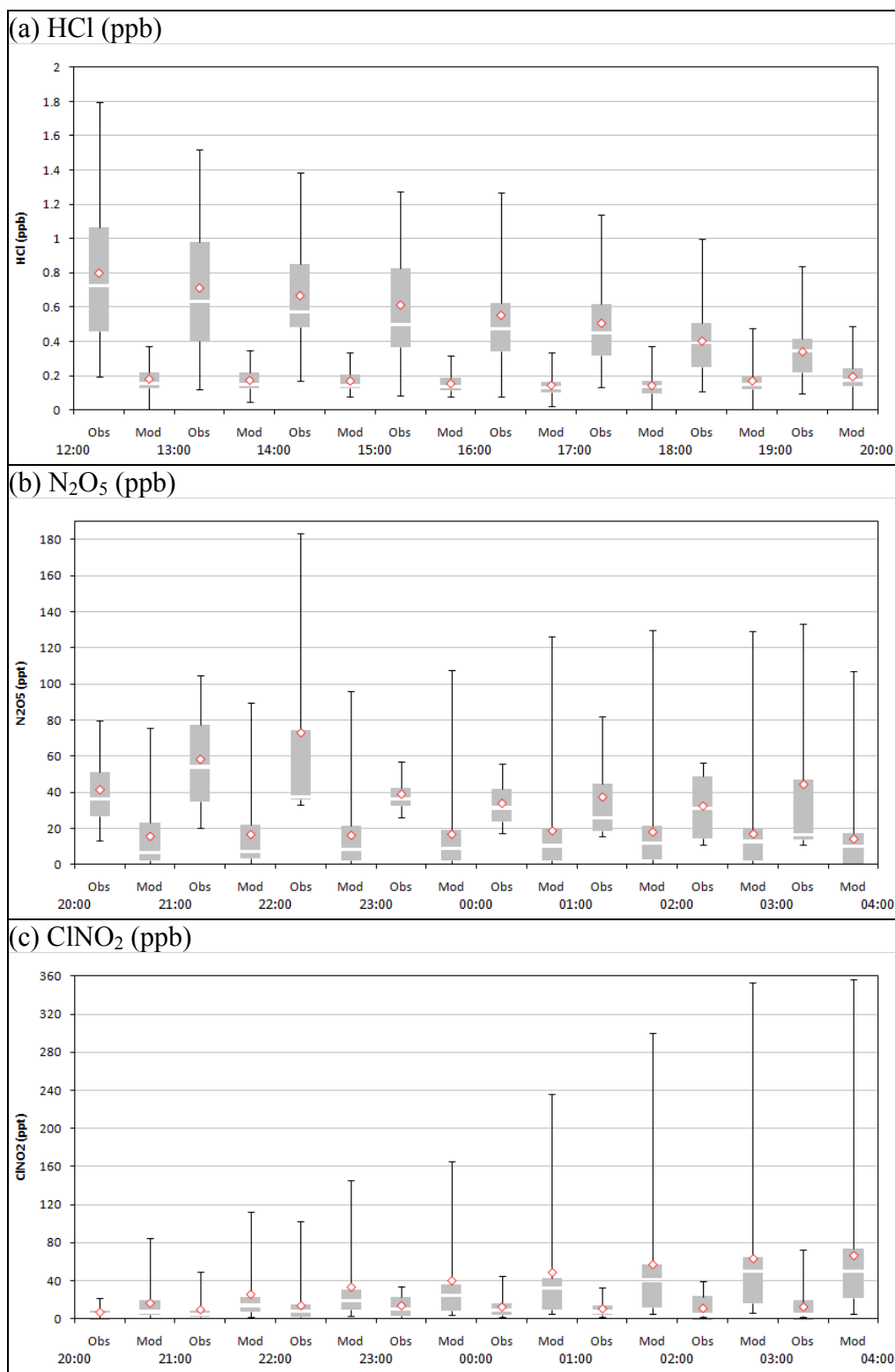
The CAMx photochemical grid model was applied to a month-long episode (July 2006) using the current EPA 2006 US modeling database. The modeling domain, which covers entire contiguous US, consists of 459 by 299 horizontal grid cells of 12-km resolution and 26 vertical layers. The CB05 chemistry mechanism of the latest CAMx code (version 5.4) was updated with a parameterization of nitryl chloride chemistry. Gas-particle equilibrium partitioning of chloride is modeled by a thermodynamic equilibrium model (ISORROPIA version 1.6) in CAMx. The reactive chlorine and particle chloride emission inventories in the EPA's modeling database were extended to include additional chlorine/chloride emission sources, e.g., sea salt, swimming pools and wildfires. ENVIRON has developed emissions of sea-salt particles (speciated into sulfate, sodium, and chloride) from open ocean and breaking waves in the surf zone, and average summer day chlorine ( $\text{Cl}_2$  and  $\text{HOCl}$ ) emissions from swimming pools for the 48 contiguous states. Particulate chloride (PCl) emissions from anthropogenic sources as well as wildfires were developed by EPA.

We first focused our analysis on the results at two ground sites: The Pasadena site (CalNex 2010) and the Moody Tower site (SHARP 2009). These sites provide continuous measurement data for a relatively longer period compared to other plume measurement data, allowing more meaningful evaluation of the grid model results. Since the model simulation period (July 2006) is not an exact match with the measurement campaign periods, the model results cannot be directly compared with the measurements. Instead, we compared diurnal patterns of the model predictions and observations using box and whisker plots. A simple box and whisker plot (as shown here) consists of a gray box showing the range from first to third quartiles (interquartile range), a white line indicating the median value, and two whiskers with lower whisker spanning from bottom of the gray box down to the minimum and upper whisker spanning from top of the box up to the maximum. The mean is shown by a diamond marker. At the Pasadena site (Figure 2), CAMx significantly underpredicts HCl and PCl while overpredicting  $\text{HNO}_3$ , which demonstrates a shortfall in the amount of chloride in the emission inventory. The missing chloride could be sea salt or additional chlorine and/or chloride emission categories that are missing in the current emission inventory. CAMx underpredicts HCl and  $\text{N}_2\text{O}_5$  at the Moody Tower site, but predicts similar to or higher  $\text{ClNO}_2$  concentrations than the measurements (Figure 3). The observed  $\text{ClNO}_2$  concentrations at Moody Tower are quite low with hourly average  $\text{ClNO}_2$  concentration rarely going above 0.1 ppb, which is inconsistent with measurements made on board the NOAA R/V Ron Brown during the TexAQS 2006 campaign that often show significantly higher  $\text{ClNO}_2$  concentrations.

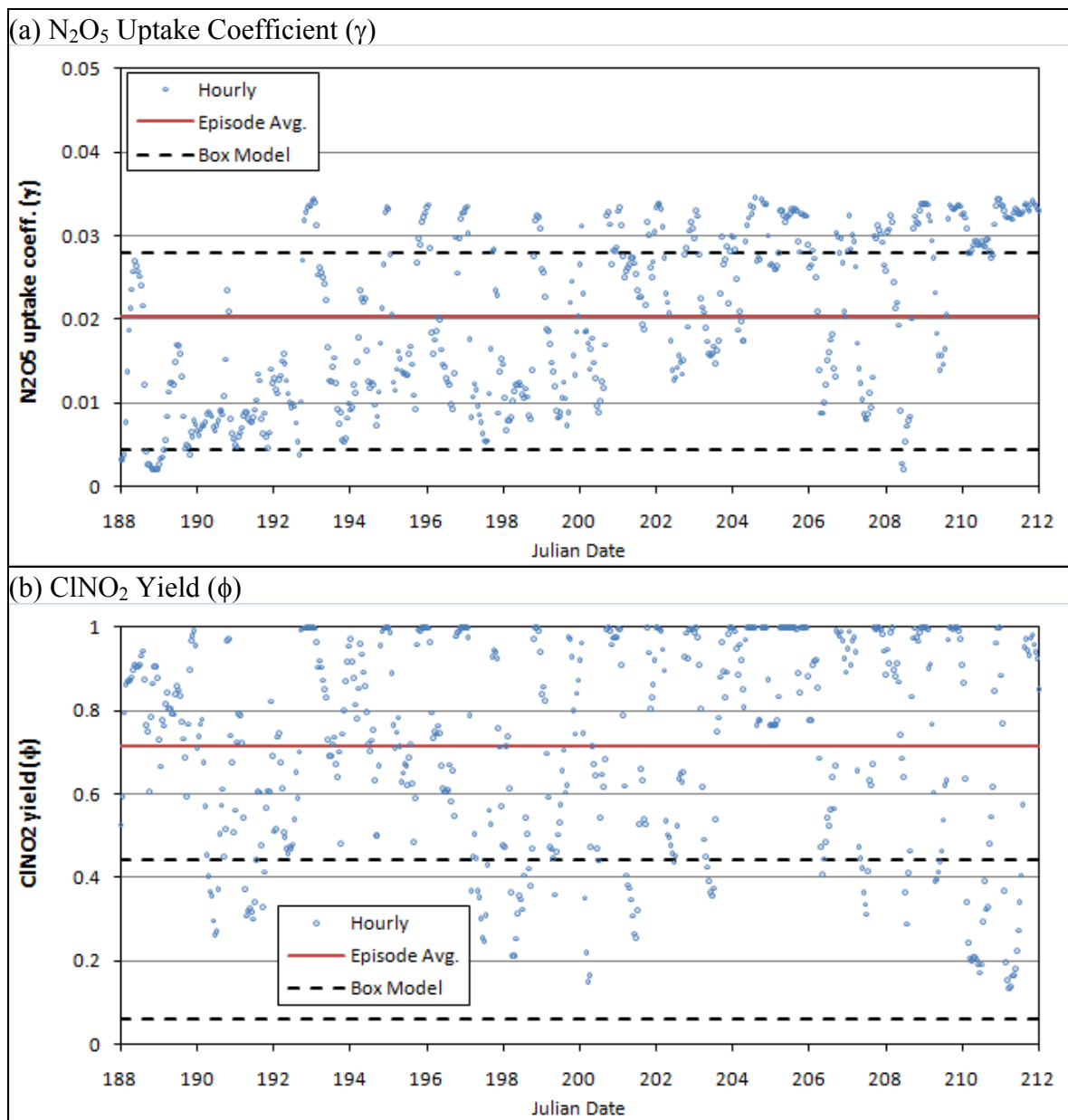
The  $\text{N}_2\text{O}_5$  uptake coefficients estimated by CAMx at the Pasadena site are within box model estimates based on the CalNex 2010 aircraft measurement data (Figure 4 (a)). However, CAMx estimates much higher  $\text{ClNO}_2$  yields than those based on the same box model analysis (Figure 4 (b)), which may indicate non-ideal aerosol liquid phase chemistry. At Moody Tower, CAMx estimates for the uptake coefficient and yield don't agree well with a few box model estimates based on the selected SHARP 2009 measurement data (Figure 5).



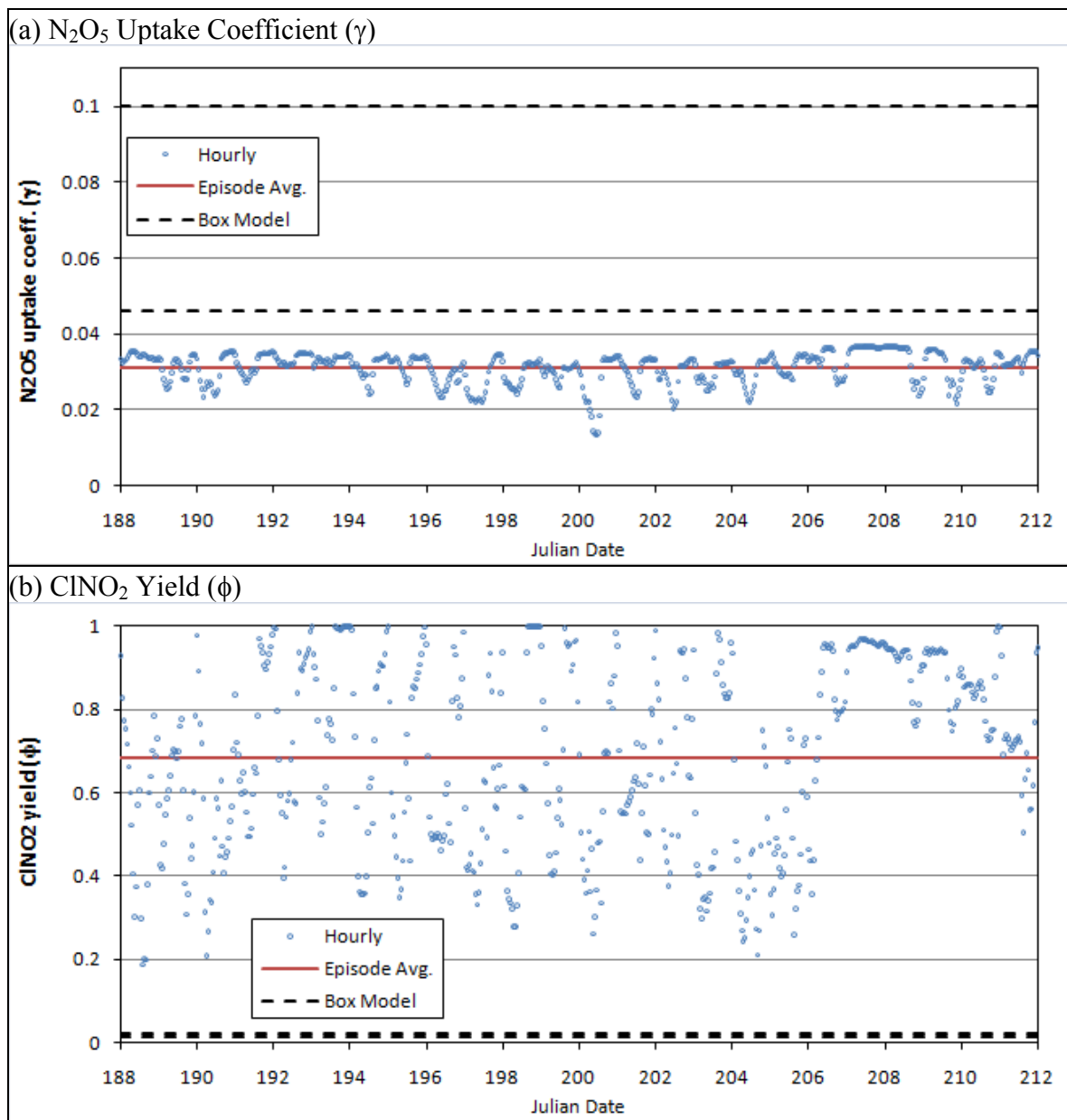
**Figure 2.** Box and whisker plots for modeled and observed concentrations of (a) HCl, (b) PCI and (c) HNO<sub>3</sub> at the Pasadena site.



**Figure 3.** Box and whisker plots for modeled and observed concentrations of (a) HCl, (b) N<sub>2</sub>O<sub>5</sub> (c) ClNO<sub>2</sub> at the Moody Tower site.



**Figure 4.**  $\text{N}_2\text{O}_5$  uptake coefficients and  $\text{ClNO}_2$  yields estimated by CAMx (blue circle and red solid line) and Box model (black dotted line) at the Pasadena site.



**Figure 5.**  $N_2O_5$  uptake coefficients and  $ClNO_2$  yields estimated by CAMx (blue circle and red solid line) and Box model (black dotted line) at the Moody Tower site.



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**Project 10-020**

**STATUS: Active – March 5, 2011**

**End Date Extended to November 30, 2011**

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***NO<sub>x</sub> 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<sub>3</sub>). Chemical transformations of nitrogen oxides (NO<sub>x</sub>) emissions that occur at night will influence their availability to participate in next day O<sub>3</sub> formation. The objective of this project is to utilize data for NO<sub>x</sub> plumes collected at night by the NOAA P-3 aircraft during the second Texas Air Quality Study in 2006 (TexAQS 2006). The data will be analyzed to assess the chemical transformations and plume dispersion that occurred for NO<sub>x</sub> plumes in Texas under nighttime conditions. Heterogeneous chemistry occurring in nighttime NO<sub>x</sub> 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<sub>3</sub> impacts. Study results will directly address current uncertainties in heterogeneous chemistry of NO<sub>x</sub> plumes. They will also address the potential for nighttime transport of NO<sub>x</sub> 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 NO<sub>x</sub> plumes from large point sources

Task 4 – Final Report

During this quarter, efforts were focused on Tasks 2 to 4.

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

The reactive plume model, SCICHEM (Second-order Closure Integrated puff model with CHEMistry), was used to simulate the Oklaunion power plant plume during the night of October 10, 2006. SCICHEM is an advanced reactive Lagrangian puff dispersion model with full chemistry treatment for ozone and particulate matter (PM). The model results were compared with measurements from the NOAA P-3 aircraft for a number of plume transects at different downwind distances from the power plant and different measurement periods. The data analysis in Task 3 below of the Oklaunion plume on October 10, 2006 showed that the plume remained narrow even at large downwind distances, and the mixing of the NO<sub>x</sub>-rich plume from the power plant with background air was inefficient at night, such that the chemistry within the plume was spatially confined. Based on this analysis, an appropriate model configuration was selected for the SCICHEM simulations, which limited plume growth and used high resolution puffs to capture the differences in chemistry between the plume core and plume edges. Model results were compared with aircraft measurements at downwind distances ranging from 14 km to 58 km. Except for the traverse at 58 km downwind, where the model predicted a much wider plume (3 km) than was observed (1 km), the model captured many of the features noted in the measurements for a majority of the plume traverses, such as: plume widths; peak SO<sub>2</sub> and NO<sub>y</sub> concentrations; titration of ozone and loss of N<sub>2</sub>O<sub>5</sub> in the plume core. The model also reproduced some of the features observed at the edges of the plume, such as production of N<sub>2</sub>O<sub>5</sub>, but the levels of N<sub>2</sub>O<sub>5</sub> production were generally lower than observed levels. This result suggests that even finer puff resolution than was used in this study may be required to reproduce the highest observed N<sub>2</sub>O<sub>5</sub> levels at the plume edges.

The CAMx photochemical grid model was also used to simulate the dispersion and chemical evolution of the Oklaunion plume during October 10-11, 2006. This involved treating the plume in two distinct ways: (1) with the Plume-in-Grid (PiG) treatment, and (2) using a super high-resolution nested grid (flexi-nest) sufficiently large as to capture about 3 hours of the downwind plume. To investigate chemical evolution of the plume cross section in this study, each PiG puff was configured as a set of five reactors. In this approach, the total puff volume is divided into five equal sub-volumes that grow in proportion to the total puff, and emitted pollutant mass is initially distributed to each reactor according to a Gaussian distribution. As the puff moves and grows downstream, chemistry is calculated according to the conditions in each puff reactor, resulting in five plume regimes from the plume core to the plume edge. A super high-resolution flexi-nest was also used to simulate the evolution of the Oklaunion plume in lieu of the PiG model. Results were compared against PiG results and observed conditions on the evening of October 10, 2006. Predicted plume widths with the PiG treatment were generally higher than observed, while the high-resolution flexi-nest results were found to compare better with the observations both in terms of plume dispersion and plume chemistry.

Additional analyses of the SCICHEM and CAMx results are ongoing.

## **Task 3: Analysis of chemistry and mixing in NO<sub>x</sub> plumes from large point sources**

The aim of this analyses was to understand: 1) nighttime NO<sub>x</sub> plume widths and depths in order to characterize nighttime plume mixing; 2) the mass balance of ozone and total nighttime odd oxygen (=O<sub>3</sub> + NO<sub>2</sub> + 2NO<sub>3</sub> + 3N<sub>2</sub>O<sub>5</sub>) to measure the conversion of nitrogen oxides into both

reservoir and reactive compounds; and 3) direct measurement and/or estimates of nighttime nitrogen containing species that result from heterogeneous  $N_2O_5$  reactions, such as  $HNO_3$  and  $ClNO_2$ . An assessment was also conducted of the impact of  $NO_x$  emission control technology on nighttime  $NO_x$  transport and loss.

The analysis has been completed, and a draft manuscript detailing this analysis has been prepared and is currently under review. It is anticipated that the paper will be submitted to a peer-reviewed journal by August 31, 2011. A copy of the submitted paper (and the final version, once accepted for publication) will be provided. 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**

A preliminary draft report was submitted on August 1, 2011, and will be revised to include the results of additional ongoing analyses.

***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:**

Recent epidemiological analysis has underscored the importance of tropospheric ozone with respect to morbidity and mortality in the United States.<sup>1</sup> In January of 2010, the US EPA proposed to strengthen the 8-hour primary National Ambient Air Quality Standards (NAAQS) for ozone to between 0.060 and 0.070 ppm and to establish a new seasonal secondary standard. The increased stringency of the primary and secondary NAAQS is expected to result in nonattainment designations for many more counties throughout the United States, including in Texas. Models such as the Comprehensive Air Quality Model with extensions (CAMx), which is used by the State of Texas for attainment demonstrations and air quality planning, will play a central role in the design of strategies for complying with the revised NAAQS. Dry deposition (removal of ozone by physical and chemical processes on surfaces) is the most important removal process for ozone in Texas. It is critical that algorithms that represent this process in air quality models be improved in order to reduce uncertainties in predictions that will be used to implement ozone reduction strategies. Currently, CAMx does not account for ozone deposition to built environment surfaces such as roofing, building façades, parking lots, and roadways.

The overall objective of this project is to improve existing knowledge of the effects of the urban built environment on dry deposition of ozone, thus improving predictions of ozone concentrations. This project uses Austin, Texas, as the case study area but the experimental data and air quality modeling approach will be applicable to other ozone nonattainment and near nonattainment areas in eastern Texas. The project has the following objectives:

1. To conduct laboratory and field experiments to better characterize ozone reactivity with large-area outdoor built environment surfaces.
2. To characterize built environment surfaces in the Austin urban landscape using geospatial data.
3. To modify the dry deposition algorithms in CAMx, the air quality model used in regulatory applications for Texas, to include information from (1) and (2).
4. To conduct CAMx simulations to investigate the impacts of improvements in the characterization of dry deposition to built environment surfaces and of potential increases

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<sup>1</sup> Bell, M., Dominici, F., Samet, J.M. A meta-analysis of time-series studies of ozone and mortality with comparison to the National Morbidity, Mortality, and Air Pollution Study. *Epidemiology* **16** (2005) 436-445.

in built environment surfaces due to future urbanization on predicted ozone concentrations in Austin, Texas.

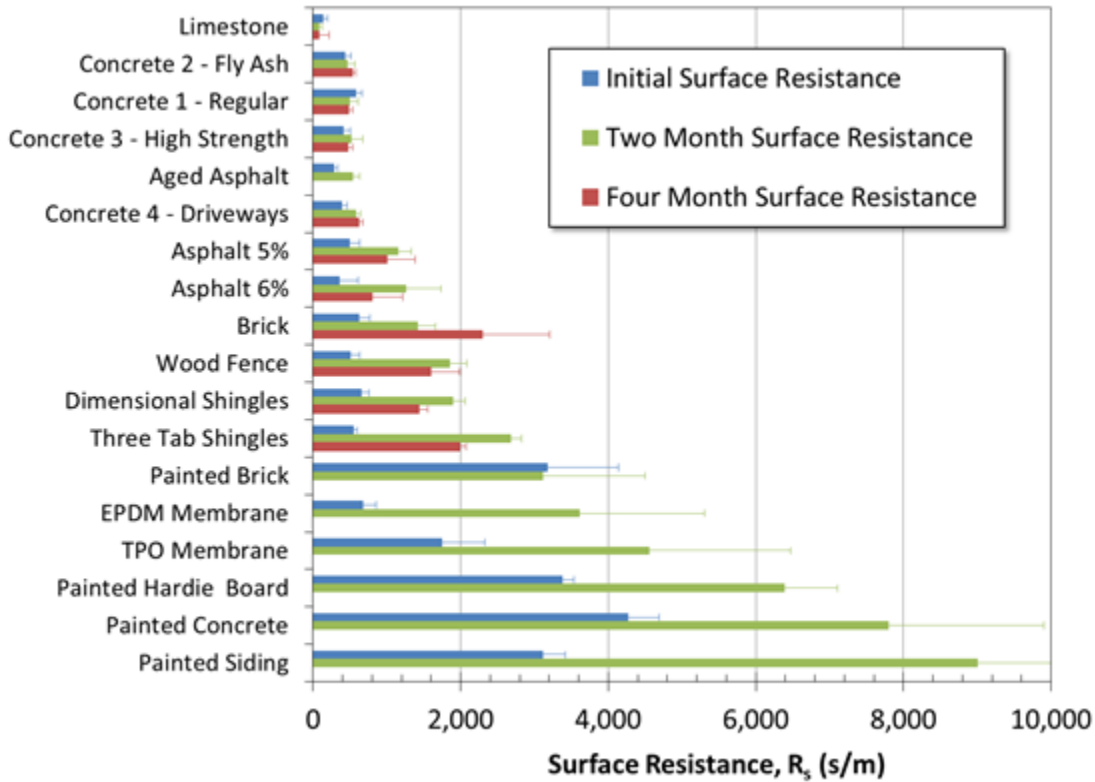
Additional experiments will also be completed to explore diffusion resistances near buildings and to compare these with output from the CAMx model.

**Project Update:**

The project consists of two primary components: (1) laboratory and field experiments, and (2) air quality modeling. Eighteen materials representing a range of urban built environment surfaces were selected for laboratory experiments to quantify ozone surface reactions. Experimental data are being used to modify the CAMx air quality model to provide a better representation of dry deposition to the urban built environment. An experimental system is being used to test the reaction of ozone with materials at 90°F and 30% relative humidity.

A total of 275 experiments were conducted on the eighteen materials. Each material was tested as a new material and after two months (and as time permitted after 4 months) of outdoor exposure to Austin spring weather. Surface resistances for each material are shown in Figure 1. Surface resistances are a measure of how non-reactive a material is with ozone; a high surface resistance (large bar in Figure 1) equates to low reactivity with ozone and a small surface resistance (small bar in Figure 1) equates to high reactivity. For example, limestone is far more reactive than other test materials and painted surfaces are less reactive.

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. New land use/land cover categories based on pavement, siding, or roofing material type were developed and replaced areas previously classified broadly as urban in Travis County. In addition, it was recognized that vegetative cover, in particular tree cover, is an important part of the Austin urban landscape. Although it was not the primary focus of this project, there was also an attempt to account for tree cover within areas currently classified as urban in Travis County.



**Figure 1.** Average surface resistances for materials during initial, two and four month experiments. Materials are listed in increasing order of the two month surface resistance value.

Among the findings from the characterization of the built environment was the dominant material in Travis County for almost all roadway classes was asphaltic concrete, i.e., more commonly known as asphalt. Residential properties represented a considerably larger percentage (72%) of total building floor area than commercial and tax-exempt properties (28%) in Travis County; single family residential homes and large apartment complexes dominated the residential building classes. Brick and painted wood siding were the predominant siding materials for single family residential homes in Travis County, followed to a lesser extent by glass, limestone, and vinyl/aluminum/fiberboard. Brick and vinyl/aluminum/fiberboard siding were more prevalent than other materials in homes built after 1990. In contrast, painted wood siding was more prevalent in homes built prior to 1990. Office buildings (35,000+ sq. ft), bulk warehouses (20,000+ sq. ft), warehouse (<20,000 sq. ft.), office buildings (6+ floors), and discount stores represented the most significant commercial classes. Siding materials for commercial and tax-exempt building materials exhibited considerable heterogeneity in Travis County, with glass, unpainted concrete, and painted concrete, and vinyl/aluminum/fiberboard siding among the most prevalent. Urban tree canopies were present over 12% of all building types in Travis County, and were more prevalent over single family homes and 2 - 5 family residential structures than over commercial and tax-exempt buildings. Tree canopies were also common over driveways and paved and unpaved alleys.

These land use/land cover data were matched with surface resistances for fresh and weathered materials, respectively, determined from the experiments described above to obtain new estimates of dry deposition velocities and ozone concentrations using CAMx. The framework for characterizing the urban built environment and experimental results for material surface resistances are applicable to other regions of Texas.

**Funding:**

All funds allocated to this project are expected to be used by the project end date of 8/31/2011.

***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/TNG/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 photochemically important pollution species for air-assist and steam-assist flares under open-air conditions. This project will (1) primarily use CFD modeling as a predicting tool for the Tulsa flare performance tests (2) further compare the CFD modeling with the flare performance data and speciated volatile organic compound (VOC) concentrations if the data are available by May 31, 2011. 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 NO<sub>x</sub> formation and handling light hydrocarbon combustion. This Lamar mechanism has been validated against methane, ethylene, and propylene experimental data. More photochemically important NO<sub>x</sub> species will also be added to the existing mechanism and an evaluation with lab data will be carried out for this new mechanism.

Lamar University (LU) will acquire the operating, design, and meteorological data of the flare test campaign from The University of Texas (UT) and conduct CFD modeling and prediction. The test data, if acquired by May 31, 2011, will be compared with the model results. The test data include Combustion Efficiency (CE), Destruction & Removal Efficiencies (DRE) and monitored CO/CO<sub>2</sub>, NO, NO<sub>2</sub>, methane, acetylene, ethylene, propylene, formaldehyde, acetaldehyde, and acetone concentrations. Cases will be 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, Request has been submitted to AQRP to obtain the needed input data (Flare Operation/Design Data) to start generate the needed flare geometries. Lamar University also presented 2 base cases (1 for air-assisted flare and 1 for steam-assisted flare) to serve as the starting point for CFD modeling.

Lamar University purchased a new high performance cluster (HPC) in order to enhance computational capability of the CFD lab in March, 2011. The use of newly acquired high performance cluster will greatly reduce the computational time. The cluster includes 1 Head Node (Dell PowerEdge R710) server and 2 Compute Nodes (Dell PowerEdge R410). To engage more cores or CPUs in solving a single or multiple CFD jobs, more licenses are required. With the support from Lamar University, 28 HPC FLUENT/CHEMKIN licenses were purchased, in addition to the based-line 5-seat research license.

New 50-species mechanism with NO<sub>2</sub> has been developed and is shown in good agreement with the full mechanism. FLUENT models (Species, Turbulence-Chemistry, Viscous, and Numerical Solution), model parameters, and boundary conditions have been selected.

Both Probability Density Function (PDF) and Eddy Dissipation Concept (EDC) turbulence-chemistry interaction approaches have been adopted to run Tulsa flare test cases. Two air-assisted flare test cases and one steam-assisted flare test case have been run and compared with the measured DRE/CE data. Even though the PDF approach was verified with University of Alberta wind tunnel data and was shown in good agreement; the more simplistic PDF model tends to predict somewhat higher flare efficiencies than the measured ones. The more rigorous EDC model, however, tends to give low DRE/CE due to the combined effect of the sophisticated flare tip geometry and the low fuel flow rates. The EDC approach also suffers from slow convergence and is sensitive to the missing of pilot flame. Efforts are being made to address these issues associated with the EDC approach.

More time is needed to resolve the aforementioned CFD simulation issues; consequently, no-cost contract extension to November 30, 2011 has been requested for the project.

***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:**

Ozone (O<sub>3</sub>) in the part of the atmosphere closest to the Earth's surface is an air pollutant that is a respiratory irritant and that causes damage to plant leaves and human-made structures. It is important to note that O<sub>3</sub> is not emitted directly from pollution sources but rather forms in the atmosphere when oxides of nitrogen (NO<sub>x</sub>) and volatile organic compounds (VOCs) mix in the presence of sunlight. While some amount of O<sub>3</sub> in the lower atmosphere is formed naturally, the amount of O<sub>3</sub> in the atmosphere of the Dallas-Fort Worth (DFW) region exceeds that which is allowable by the National Ambient Air Quality Standards (NAAQS) established by the Environmental Protection Agency.

In the DFW area, the most prevalent local emission sources of NO<sub>x</sub> and VOCs are automobiles and other motor vehicles and a number of large point sources, specifically electric power plants and cement kilns. However, O<sub>3</sub> levels have not decreased significantly in recent years despite gradual decreases in NO<sub>x</sub> and VOC emissions from automobiles. 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<sub>x</sub> sources, leading to the hypothesis that there is a relationship between O<sub>3</sub> levels and natural gas activities. A team from Rice University, the University of Houston (UH), and the University of New Hampshire (UNH) will investigate this hypothesis by performing an air quality sampling campaign that is described below.

The Rice, UH, and UNH team will install 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 15 to June 30, 2011. Eagle Mountain Lake is located approximately 30 kilometers to the northwest of downtown Fort Worth. This location was chosen for several reasons. First, there is a wealth of natural gas activity in this region. Second, wind in the DFW area often blows toward the northwest, indicating that the site will be subject to the emissions from Fort Worth. Lastly, other monitoring has noted the high levels of O<sub>3</sub> in the northwest corner of the DFW region. The timing of the campaign was selected to optimize

likely O<sub>3</sub> formation (due to favorable meteorological conditions), staff availability, and duration of the project.

Relevant measurements will include not only the concentrations of O<sub>3</sub>, NO<sub>x</sub>, and VOCs but also values for other relevant chemical and physical variables, including meteorological parameters. In addition, a group from the University of Michigan will conduct computational modeling that will be used in conjunction with the data generated from these measurements to determine the VOC emissions, atmospheric reactions, and meteorological conditions that lead to O<sub>3</sub> formation in the DFW region.

### **Project Update:**

The field project teams (Rice, UH, and UNH) focused on data collection from June 1 through June 30, with breakdown, packing, shipping, unpacking, restocking, and re-installment of equipment occurring over the first two weeks of July. With exceptions associated with instrument malfunction, repair, and calibration, as well as with power interruption at the site, nearly continuous data were collected for meteorological parameters, trace gas mixing ratios (including NO<sub>x</sub>, O<sub>3</sub>, VOCs, carbon monoxide, sulfur dioxide, total reactive nitrogen, nitric acid, nitrous acid, hydrochloric acid, sulfuric acid, and hydroxyl radicals), water-soluble sub-micron aerosol composition, non-refractory sub-micron aerosol composition, aerosol black carbon concentrations, and aerosol number-based particle size distributions. Over the period of mid-July through August, efforts focused on data quality assurance and analysis. Preliminary findings indicate that during the hot, dry period of the campaign, winds from the south/southeast dominated and carried aged and processed pollutants to the site. However, instances of local emissions also were observed.

Over the same time periods, the UM team made considerable progress on the modeling aspects of this project. Using a 2006 test case, the UM team established site-specific and wind-direction-specific emission factors for anthropogenic and biogenic VOCs and validated the model's ability to simulate vertical mixing. Once data from the field campaign became available, 2011 meteorological factors were assimilated, which in turn drove updated emissions. With appropriate emissions and meteorology, the model has been run for the campaign dates, and output has been compared to chemical parameters measured by the field project teams. With this information, factors controlling O<sub>3</sub> levels at the field site have been evaluated.

***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 is 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 project will obtain firmer conclusions regarding improved model performance by testing the procedure on other ozone episodes, increasing the number of considered model variables, and expanding the study to include a larger variety of meteorological conditions.

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 utilizes the WRF (Weather Research and Forecast) mesoscale meteorological model and the Asymmetrical Convection Model, version 2 (ACM2) vertical mixing scheme. The final results will include software modifications for use in WRF along with the appropriate documentation. TCEQ can use the results of this project to potentially improve the meteorological model performance in their own models, and to continue to refine or improve the EnKF technique. Any improvements in meteorological model performance may lead to improved photochemical model performance and improved development of ozone control strategies and forecasts.

**Project Update:**

The project was initiated in late February. The four goals associated with the project are (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 is 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 is being upgraded to utilize the current version of WRF (version 3.3, released in April 2011). This porting process has 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.

The project during this quarter has focused on the porting process. Scripts for running the WRF model with the Ensemble Kalman Filter have been updated and made more robust. We have worked through user environment issues and are working through compiler issues.

A project extension has been granted through November 2011. This will allow the project team to achieve the remaining goals of the project with the newest modeling and software system while delivering a robust, up-to-date and working Ensemble Kalman Filter system. The project team will tackle the various goals in parallel and has consulted with TCEQ to identify specific episodes of current or future interest for parameter estimation testing during the remainder of the project.

***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<sub>2</sub>), together called HO<sub>x</sub>, 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<sub>x</sub> 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 will evaluate 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.

The purpose of this work is to inform policy decisions related to the development of ozone control strategies for State Implementation Plans in Texas; particularly those that rely on the use of appropriately represented chemical reactions in photochemical modeling. This project will directly support these goals by using statistical methods to analyze the observations related to ozone formation, and also using numeric zero-dimensional models with five different chemical mechanisms to simulate the oxidation processes during this study. Using the model results, the radical budget will be calculated and the sensitivity of ozone production to oxides of nitrogen (NO<sub>x</sub>) and volatile organic compounds (VOCs) will be analyzed. The model results also 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 include:

- Identify the variation of measured HO<sub>x</sub> and HO<sub>2</sub>/OH with NO<sub>x</sub> 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<sub>3</sub> + alkenes and NO<sub>3</sub> chemistry as nighttime OH sources.

- Compare and contrast the HO<sub>x</sub> levels in Houston to those in Mexico, Nashville and New York City.
- Investigate the instantaneous O<sub>3</sub> production and deviations of the NO<sub>x</sub> photostationary state due to clouds and aerosols. This analysis will also include comparison of observed and calculated HO<sub>2</sub> + RO<sub>2</sub> mixing ratios and net O<sub>3</sub> production.
- Study the sensitivity of O<sub>3</sub> production to NO<sub>x</sub> and VOCs.
- Investigate the potential of HONO as a daytime precursor of OH.
- Evaluate the role of nitryl chloride (ClNO<sub>2</sub>) as an early morning radical source and its contribution to ozone production.
- Investigate the processes creating strong correlations between HNO<sub>3</sub> and gas phase chloride, and their implications for coupled Cl and NO<sub>x</sub> chemistry in Houston.

### **Project Update:**

The UCLA team has continued to work on a manuscript on daytime HONO, which was discussed in the last quarterly report. The manuscript has been sent to the co-authors for comment and is expected to be submitted to AQRP soon. UCLA has also begun to use the 2009 data to study the altitude dependence of OH formation in Houston to determine what effect the HONO concentration gradients have on the OH budget.

In the past quarter, the PI team has been working on the preparation of the mechanism schemes (RACM2, CB05, MCM, SAPRC07, and LaRC) for the SHARP data analysis. Input files for these mechanisms have been created and the model mechanisms have been updated to the available constrained chemical and meteorological parameters. Model simulation runs are currently underway. The preliminary model results have been shared with all members of the PI team to help their data analyses. Initial model simulations with the RACM2 and LaRC chemical mechanisms has been completed and preliminary results for each of the project objectives are summarized below:

Objective 1. Identify the variation of measured HO<sub>x</sub> and HO<sub>2</sub>/OH with NO<sub>x</sub> and VOCs and compare to the model prediction. (UMiami and Penn State)

Objective 1A: Comparison of observed and modeled HO<sub>x</sub>

The measured and modeled OH and HO<sub>2</sub> exhibit similar diurnal and day-to-day variations, with maxima in the early afternoon and minima at night. The median daytime observed-to-modeled OH ratio is 1.08 with a correlation coefficient, *r*, of 0.68. The median daytime observed-to-modeled HO<sub>2</sub> ratio is 1.34 with a correlation coefficient, *r*, of 0.87.

Two oxidation pathways can contribute to nighttime HO<sub>x</sub> in the planetary boundary layer: (1) O<sub>3</sub> can react with alkenes to produce a significant amount of OH and HO<sub>2</sub>, and (2) NO<sub>3</sub> can produce HO<sub>x</sub> directly via reaction with HCHO or indirectly after conversion of the RO<sub>2</sub> that is initially produced by VOCs+NO<sub>3</sub>. These processes become more important for the nighttime HO<sub>x</sub> production because daytime HO<sub>x</sub> photolytic sources vanish at night. At night, the modeled HO<sub>2</sub>

agrees reasonably well with the measurements during nighttime, with a median measured-to-modeled ratio of 1.41, which is within the combined uncertainties of measured and modeled HO<sub>2</sub>. However, nighttime OH is significantly under-predicted, with a median measured-to-modeled ratio of 6.2. This difference indicates that the RACM mechanism fails to capture the processes that create nighttime OH in this urban environment.

Objective 1B: Observed-to-modeled ratios as a function of NO

The observed-to-modeled OH and HO<sub>2</sub> ratios can test our understanding of the HO<sub>x</sub> photochemistry because the cycling between OH and HO<sub>2</sub> is very fast and the photochemical equilibrium among OH and HO<sub>2</sub> is closely tied to the interconversion of NO to NO<sub>2</sub> in the troposphere. Both the measured and modeled HO<sub>2</sub>/OH ratios decrease with increasing NO. This decrease occurs because NO shifts HO<sub>x</sub> into OH by reacting with HO<sub>2</sub>. However, when NO is lower than a few hundred pptv, the modeled HO<sub>2</sub>/OH ratios are significantly higher than the measured. The agreement of measured and modeled HO<sub>2</sub> to OH ratios is good when NO is around a few hundred pptv. The slope of measured HO<sub>2</sub>/OH as a function of NO is significantly less than the modeled slope. This difference is consistent with measured OH being greater than modeled OH at low NO, while measured HO<sub>2</sub> is much greater than modeled HO<sub>2</sub> at high NO (Figure 1).



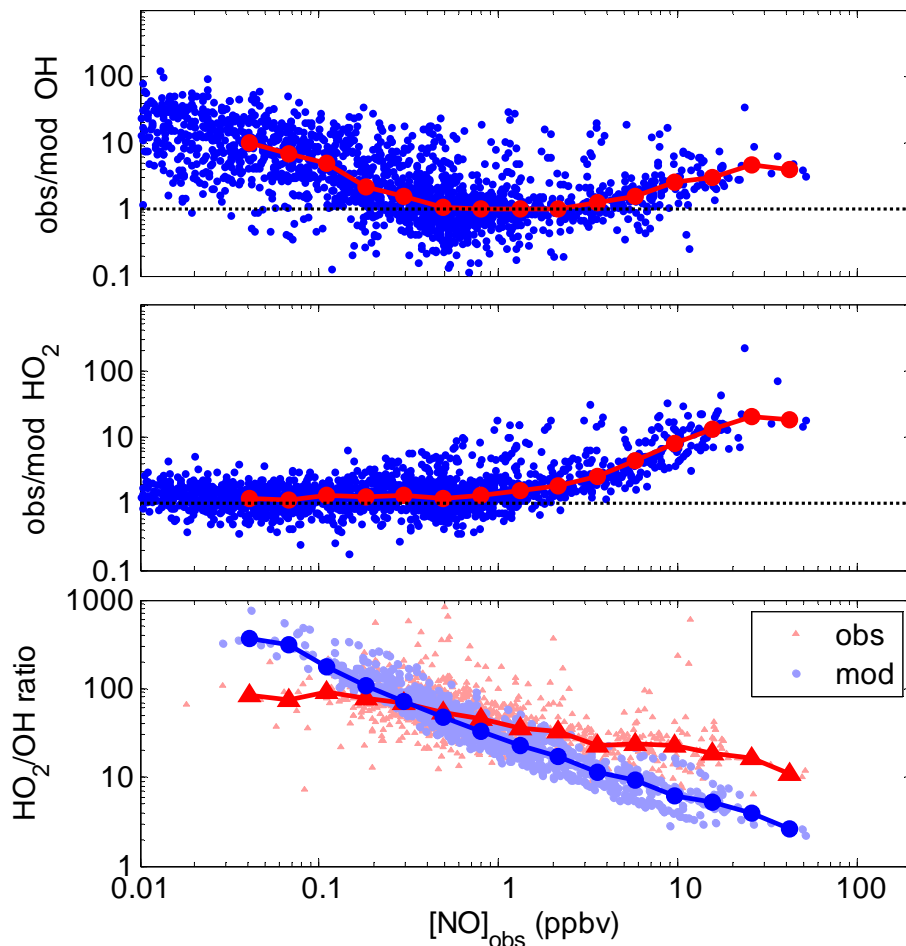


Figure 1. The ratios of observed to model OH (top), HO<sub>2</sub> (middle), and HO<sub>2</sub>/OH (bottom) as a function of NO.

**Objective 2.** Quantify OH reactivity and compare observed and calculated OH reactivity to examine any missing OH sink species. Examine HOx Budget. (Penn State and UMiami)

It is also useful to investigate the net HOx production and loss, since the balance between HOx production and loss indicates a good understanding of HOx sources and sinks. The total HOx production includes the processes: the ozone photolysis followed by the reaction of O(1D) with H<sub>2</sub>O, the HONO photolysis, the HCHO photolysis (the radical-produced pathway), and the O<sub>3</sub> reactions with alkenes. HOx loss includes the processes: the OH reaction with NO<sub>2</sub>, and the reactions between OH, HO<sub>2</sub> and RO<sub>2</sub>. Calculated HOx production is dominated by photolysis of HONO in the early morning and by O<sub>3</sub> photolysis in the midday (Figure 2), and is mainly from O<sub>3</sub> reactions with alkenes a night. On average, the daily HOx production rate was 23.8 ppbv day<sup>-1</sup>, of which 31% is from O<sub>3</sub> photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O<sub>3</sub> reactions with alkenes. For HOx loss, the clearly dominant process was the OH reaction with NO<sub>2</sub>, while the self-reactions between OH, HO<sub>2</sub>, RO<sub>2</sub> become important in the afternoon when their concentrations are the highest.

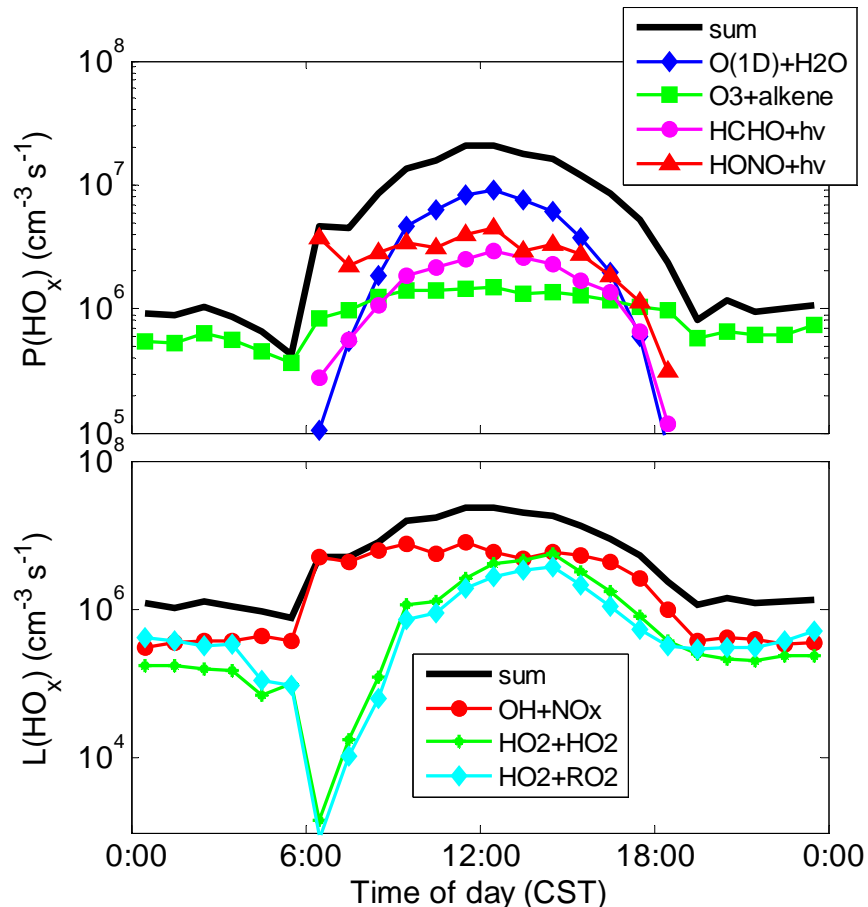


Figure 2. Diurnal variation of HOx production (top) and HOx loss (bottom). HOx production processes include ozone photolysis followed by the O(1D) + H<sub>2</sub>O reaction, the photolysis of HONO, the photolysis of HCHO, and ozone reactions the alkenes. HOx loss processes include OH reaction with NO<sub>x</sub>, HO<sub>2</sub>+HO<sub>2</sub> reaction and HO<sub>2</sub> + RO<sub>2</sub> reactions.

Objective 3. Examine the significance of nighttime OH and to determine the importance of both the reaction of O<sub>3</sub> + alkenes and NO<sub>3</sub> chemistry as nighttime OH sources. (UMiami)

Objective 3A. Nighttime OH

Studies have found that in the planetary boundary layer two oxidation pathways can contribute to HOx production at night: (1) O<sub>3</sub> reacts with alkenes to produce a significant amount of OH and HO<sub>2</sub> and (2) NO<sub>3</sub> reacts with a few VOCs such as HCHO, unsaturated aldehydes, methacrolein, and glyoxal to produce HOx directly or with RO<sub>2</sub> that is initially produced by VOCs+NO<sub>3</sub>. These processes become more important for the nighttime HOx production because daytime HOx photolytic sources vanish at night.

The median measured nighttime OH concentration is 0.038 pptv or  $9.4 \times 10^5$  molecules cm<sup>-3</sup>, while the modeled nighttime OH concentration is 0.009 pptv or  $2.1 \times 10^5$  molecules cm<sup>-3</sup>. The median measured nighttime HO<sub>2</sub> on is 5.9 pptv, while the modeled nighttime HO<sub>2</sub> concentration

is 3.9 pptv. This indicates that OH and HO<sub>2</sub> may also play important roles in the nighttime oxidation chemistry. The model underpredicts both nighttime OH and HO<sub>2</sub>. The median measured-to-modeled HO<sub>2</sub> ratio at night is 1.54, which is within the combined uncertainty of measured and modeled HO<sub>2</sub>. The median measured-to-modeled OH ratio at night is 4.46, which is significantly beyond the combined uncertainty of the measured and modeled OH. This difference indicates that the RACM2 mechanism fails to capture the processes that create nighttime OH in this urban environment.

Objective 3B. Importance of the O<sub>3</sub> + alkene reactions and NO<sub>3</sub> chemistry as nighttime HOx sources

Modeling results show that typical diurnal variations of HOx production from these two pathways were calculated. HOx production from O<sub>3</sub> + alkene reactions peaks in the midday when O<sub>3</sub> concentration reaches highest, while HOx production from NO<sub>3</sub> chemistry peaks at night because of low NO<sub>3</sub> concentration during the day due to its fast photolysis. In general, NO<sub>3</sub> chemistry contributes less HOx production than O<sub>3</sub> + alkene reaction, except for a few nights (e.g., the night of May 20 and 21) when NOx concentrations were high and NO titrated O<sub>3</sub> to very low levels while the reaction of NO<sub>2</sub> with O<sub>3</sub> produced high concentrations of NO<sub>3</sub> on these nights. Modeled NO<sub>3</sub> concentrations are used in the calculation due to the low data coverage in the DOAS NO<sub>3</sub> measurements. In general the modeled NO<sub>3</sub> is in good agreement with observed NO<sub>3</sub>, with the modeled NO<sub>3</sub> lower than the observed NO<sub>3</sub>, but within the uncertainty of the observed NO<sub>3</sub>.

On average HOx production rate from nighttime O<sub>3</sub>+alkene reactions is about  $5.7 \times 10^5$  molecules m<sup>-3</sup> s<sup>-1</sup>, or 84.0 pptv hr<sup>-1</sup>, while NO<sub>3</sub> chemistry contributes about  $2.6 \times 10^5$  molecules m<sup>-3</sup> s<sup>-1</sup>, or 38.8 pptv hr<sup>-1</sup> during nighttime. In another words, O<sub>3</sub> + alkene reactions contribute about two thirds (~68%) of nighttime HOx production while the other one third comes from NO<sub>3</sub> chemistry.

Objective 4. Compare and contrast the HOx levels in Houston to those in Mexico, Nashville and New York City. (UH, UMiami & Penn State)

Compared to the OH and HO<sub>2</sub> measurements in other two cities in Mexico City and New York City, the measured OH concentrations in Houston during SHARP are comparable to the OH measurements in the other two cities (Figure 3, top). However, the peak HO<sub>2</sub> concentration in Mexico City is the highest (Figure 3, bottom), while the HO<sub>2</sub> concentrations in New York City are the lowest, simply because of the high NOx concentrations in New York City throughout the day.

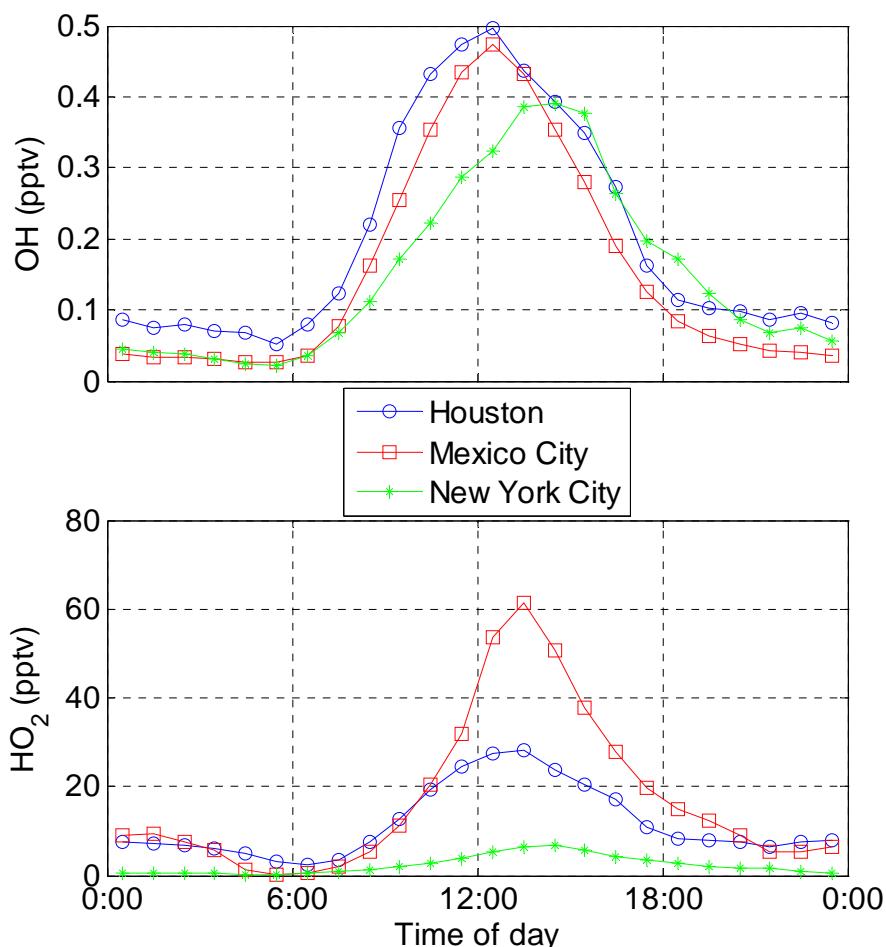


Figure 3. Diurnal variations of OH(top) and HO<sub>2</sub> (bottom) in Houston during SHARP2009, Mexico City during MCMA2003, and New York City during PMTACS2001.

**Objective 5.** Investigate the instantaneous O<sub>3</sub> production and deviations of the NO<sub>x</sub> photostationary state due to clouds and aerosols. This analysis will also include comparison of observed and calculated HO<sub>2</sub> + RO<sub>2</sub> mixing ratios and net O<sub>3</sub> production. (UH)

The UH team worked to investigate the impacts of clouds and aerosols on instantaneous O<sub>3</sub> production rates during the SHARP 2009 project. To accomplish this, modeled cloud and aerosol free actinic fluxes and photolysis rates were calculated using the 8-stream Tropospheric Ultraviolet and Visible (TUV) version 4.1 radiative transfer model. These cloud-free modeled (CFM) rates were used as alternates to the measured photolysis rates in the NASA Langley Research Center (LaRC) 0-D box model. Ozone production and loss rates were calculated using the LaRC photochemical box model. To assess the impacts of changes in actinic flux on ozone production and loss rates, the LaRC model was run with photolysis rates from both measured and modeled actinic fluxes. The majority of VOC mixtures used in the LaRC modeling used thus far were based off of measured species from the TRAMP project, conducted at the same site in Fall

2006, as mentioned previously. Additional VOCs used in the model were measured during SHARP by PTR-MS or CIMS.

The reduction in measured photolysis rates relative to modeled rates are quantified by taking the ratio of SAFS derived photolysis rates to the CFM rates generated by TUV. This ratio is referred to as the j-value impact factor (JIF). The median JIF for 6 cloud free days was 0.98, while the median JIF for the remaining 42 days was 0.83. Figure 4 shows two different modes for changes in net O<sub>3</sub> production with JIF. For JIFs of  $1 \pm 0.15$ , O<sub>3</sub> production can reach instantaneous rates greater than 50 ppbv/hour; however, below JIFs of 0.85 O<sub>3</sub> production decreases linearly with JIF under all conditions.

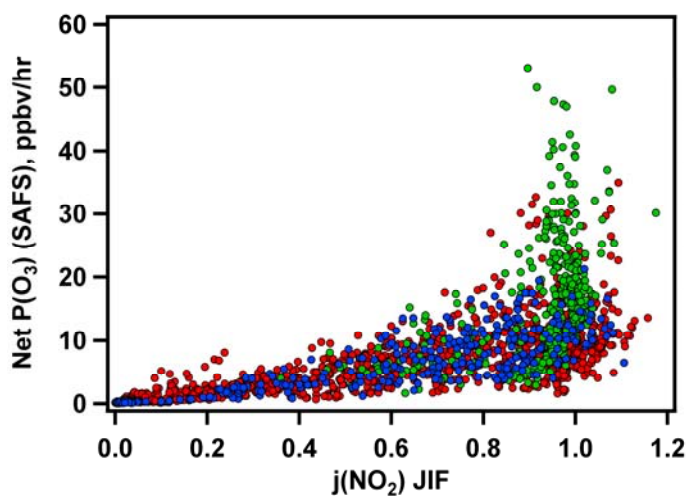


Figure 4. Net O<sub>3</sub> production as a function of cloud and/or aerosol reductions in actinic flux. Peak net P(O<sub>3</sub>) occurs at JIFs of  $\sim 0.85$  or greater. Below JIFs of 0.85 net P(O<sub>3</sub>) decreases with JIF.

With a 40% reduction in  $j(\text{NO}_2)$  (JIF of 0.6), O<sub>3</sub> production rates were capped at a maximum at 10 ppbv/hour (Fig. 7). While other factors besides j-values were also regulating ozone production during SHARP (wind speed & direction, boundary layer height, emissions, etc.), reductions in  $j(\text{NO}_2)$  correspond to reduced net O<sub>3</sub> production rates with a nearly one-to-one relationship, albeit of much smaller net O<sub>3</sub> production rates below JIFs of 0.85.

The ratio between calculated ozone production rates with measured (SAFS) and cloud free (CFM) photolysis frequencies highlights the importance of having good photolysis frequency measurements (not shown). This linear relationship with a slope near 1 shows that a 20% error in a photolysis rates will result in a 20% error in calculated ozone production. Cloud or aerosol reductions in UV radiation need to be properly accounted for in photochemical model simulations.

For all days of the SHARP, the median O<sub>3</sub> destruction terms are nearly an order of magnitude smaller than the formation rates. During the SHARP campaign, clouds and aerosols reduced the net O<sub>3</sub> production during the campaign by an average of  $\sim 3.1$  ppbv/hour out of 10.4 ppbv/hour. As mentioned previously, days with high ozone and high ozone production rates tend to be cloud

free. On high ozone days there was a 9% reduction in ozone production (average of 1.3 out of 14.3 ppbv) ozone per hour which was primarily due to aerosol reductions in solar UV radiation.

Objective 6. Study the sensitivity of O<sub>3</sub> production to NO<sub>x</sub> and VOCs. (UMiami)

VOC-NO<sub>x</sub>-O<sub>3</sub> chemistry has been studied for decades. However, the oxidation pathways are complex and most studies have been done in large environmental chambers with high NO<sub>x</sub> levels. As a result, even though the basic reaction pathways appear to be understood, much of the detailed chemistry remains to be unresolved. One of the most important consequences of this chemistry is the production of pollutants, particularly ozone. Thus, the ozone production rate is literally the production rate of NO<sub>2</sub> molecules from HO<sub>2</sub> + NO and RO<sub>2</sub> + NO reactions. The calculated instantaneous ozone production rate P(O<sub>3</sub>) can be written as the following equation (eq. 1):

$$P(O_3) = \left( k_{HO_2+NO}[HO_2] + \sum_i k_{RO_{2i}+NO}[RO_{2i}] \right) [NO] \quad (\text{eq. 1})$$

where  $k_{HO_2+NO}$  and  $k_{RO_{2i}+NO}$  are the reaction rate coefficients for reactions of HO<sub>2</sub> and RO<sub>2i</sub> with NO. At low NO conditions (NO<sub>x</sub>-sensitive), VOCs are more competitive than NO<sub>x</sub> for reacting with OH so that radical-radical reactions dominate HO<sub>x</sub> chemistry. The produced peroxy radicals can then convert NO to NO<sub>2</sub>. Every NO<sub>2</sub> molecule that is generated from this reaction sequence will make an O<sub>3</sub> molecule. So OH mainly reacts with VOCs, makes more radicals, and potentially increases O<sub>3</sub> in the presence of NO. In the high NO<sub>x</sub> condition (VOC-sensitive), the OH reaction with NO<sub>2</sub> should reduce the ozone production because HO<sub>2</sub> reacts with NO to form more OH, which then is terminated by the reaction with NO<sub>2</sub>.

Kleinman (2005) introduces a formula to evaluate the O<sub>3</sub> production sensitivity using the ratio of L<sub>N</sub>/Q, where L<sub>N</sub> is the radical loss via the reactions with NO<sub>x</sub> and Q is the total primary radical production. When L<sub>N</sub>/Q < 0.5, the atmosphere is in the NO<sub>x</sub>-sensitive region, and when L<sub>N</sub>/Q > 0.5, the atmosphere is in the VOC-sensitive region.

The ozone production sensitivity to NO<sub>x</sub> or VOCs has a similar behavior for TexAQS2000, TRAMP2006 and SHARP2009; it is VOC sensitive in the early morning and late afternoon but NO<sub>x</sub>-sensitive throughout the afternoon (Figure 5). This behavior is typical of US urban areas. These results are independent of the differences between the measured and modeled OH and HO<sub>2</sub>. Note that in the afternoon the ozone sensitivity in SHARP2009 has a longer NO<sub>x</sub>-sensitive period than TexAQS2000 and TRAMP2006, indicating that NO<sub>x</sub> control is an efficient approach for the O<sub>3</sub> control in springtime.

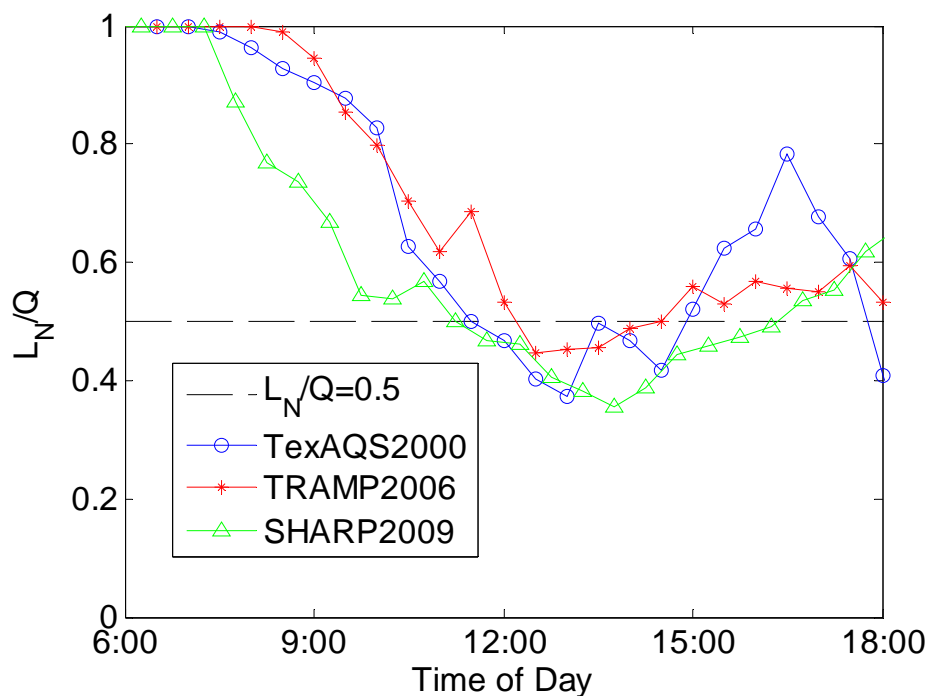


Figure 5. Median diurnal profiles of  $L_N/Q$  (lower panel) in TEXAQS2000, TRAMP2006, and SHARP2009.

Objective 7. Investigate the potential of HONO as a daytime precursor of OH. (UCLA)

The main results of UCLA activities in this reporting period was the study of the OH formation rate from the photolysis of ozone to  $O^1D$ , followed by its reaction with water, the photolysis of HCHO, assuming that the formed  $HO_2$  instantly reacts with NO, and the photolysis of HONO. In our previous report it was showed that the reaction of OH + NO is unimportant as a source of HONO, and thus UCLA did not correct the OH formation from HONO photolysis by the rate of this bac-reaction. The calculations were based on UCLA's LP-DOAS observations of  $O_3$ , HCHO, and HONO, as well as actinic flux and meteorological measurements by the Univ. of Houston.

In general, HONO photolysis dominates in the lowest and middle light path in the morning. Morning HONO photolysis in the upper height interval is about equally important as HCHO, and sometimes  $O_3$ , photolysis. At around 10:00 CST ozone photolysis becomes the most important OH source. However, both HCHO and HONO photolysis remain important. It is interesting to note that OH formation from ozone and HCHO photolysis show little altitude dependence, although it appears that  $O_3$  photolysis is slightly higher aloft. In contrast, OH formation through HONO photolysis shows very distinct gradients, with higher rates near the surface. In the lower two height intervals HONO photolysis is the second most important OH source after 10:00 CST. In the upper interval HCHO photolysis is equally or even more important than HONO photolysis. It should be noted that in the later afternoon HONO photolysis again becomes the dominant OH source in the lowest two height intervals. It will be interesting to compare these

results with those from our 1D model and urban air quality models to see if the observed behavior is reproduced by the models.

Objective 9. Investigate the processes creating strong correlations between  $\text{HNO}_3$  and gas phase chloride, and their implications for coupled Cl and  $\text{NO}_x$  chemistry in Houston. (UNH).

Gaseous nitric acid ( $\text{HNO}_3$ ) and gas phase soluble chloride ( $\text{Cl}^-$ ) were highly correlated on short (minutes to hours) time scales throughout the SHARP campaign. This correlation between soluble  $\text{Cl}^-$  and  $\text{HNO}_3$  was discovered during the early days of SHARP campaign and re-analysis of the 2006 TRAMP data revealed that is also phenomenon also occurred during that project. Peak mixing ratios of soluble  $\text{Cl}^-$  occurred during transport from south (i.e., clean conditions) with lower mixing ratios occurring in polluted from the north and east. Overall the opposite conditions resulted in peak  $\text{HNO}_3$  mixing ratios yet there is a remarkably strong correlation between  $\text{HNO}_3$  and soluble  $\text{Cl}^-$  from sample to sample and diurnally were observed regardless of wind direction.

It should be noted that the mixing ratios of soluble  $\text{Cl}^-$  are substantial in Houston. Even during intervals with sustained northerly flow (relatively low  $\text{Cl}^-$ ) daytime maxima routinely exceeded 1 ppbv. Similar observations made during TexAQS 2006 on the Moody Tower and the NOAA vessel Ronald H. Brown indicate that abundant soluble  $\text{Cl}^-$ , linked with  $\text{HNO}_3$  by processes not yet understood, is characteristic of the Houston-Galveston Bay region during both spring and summer.



***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 Dallas-Fort Worth-Arlington Metroplex (DFW) includes approximately 6.5 million people, making it the largest metropolitan area in Texas and the 4th largest in the United States. Given that the DFW area does not include large petrochemical facilities, the primary source of the anthropogenic ozone precursor NO<sub>x</sub> and VOCs emissions are the significant mobile source emissions and a number of large point sources, specifically electric power plants and cement kilns. While the ozone design value for DFW is very close to being in compliance with NAAQS 8-hr ozone standard of 84 ppbv it is interesting to note that ozone levels have not decreased significantly in recent years (Allen and Olaguer, 2004). In addition, improvements in the production of natural gas from a combination of horizontal drilling and hydraulic fracturing of the Fort Worth Basin of the Barnett Shale formation have resulted in a dramatic increase in both number natural gas wells and production of natural gas in the DFW region. The network of 18 TCEQ ozone monitoring sites in the DFW area is designed to capture both upwind and downwind ozone mixing ratios; the peak ozone values are frequently observed along the northwestern border of the network. This may be due to the prevailing southeast winds transporting polluted air from the urban areas, the recent increase in energy industry activities in the area, or some combination of the two.

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) are being deployed to continuously measure ozone production rates in the DFW region, beginning with the TCEQ Eagle Mountain Lake site (CAMS 75), and additional locations to be determined with the guidance of the AQRP and TCEQ.

The data will show the temporal and spatial variability of *in situ* net ozone production rates in the DFW area, as well as potential NO<sub>x</sub> sensitivity. This data will 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<sub>x</sub>, etc.) from the TCEQ CAMS sites where the instruments will be located will help determine how ozone production changes with varying air composition. This information will be useful in developing ozone control strategies and determining whether local or regional controls may be best suited for this area in the State Implementation Plan.

### **Project Update:**

Task 1 is to purchase and fabricate the various components of the MOPS instruments. In June the UH and PSU teams continued to purchase MOPS components and fabricate the MOPS components. Specifically the MOPS sample chambers and NO<sub>2</sub> photolysis cells were constructed. Figure 1 is a photograph of a stretched Teflon MOPS sample chamber that was tested for optimal ozone transmission at various flow rates to minimize wall losses. These chambers also include a variable heated stainless mesh screen to maintain a stratified layer which inhibits mixing in the chamber to minimize ozone wall losses. The stainless steel components in this chamber were treated with a vapor deposited silica glass coating (Silconert 2000 by Silcotek, Bellefonte, PA) to increase their inertness and improve the transmission of ozone and NO<sub>2</sub> through the chamber.

Additional progress was made in the construction of the NO<sub>2</sub> photolysis cell (Figure 2), where the NO<sub>2</sub> in the chambers is converted to O<sub>3</sub> to be measured by the ozone instrument. Initial testing shows greater 90% conversion efficiency of NO<sub>2</sub> to O<sub>3</sub> at NO<sub>2</sub> levels approaching 30 ppbv. This high conversion efficiency is much greater than commercially available blue light converters used in NO<sub>2</sub> instruments. This initial testing was done at high LED power settings which could reduce LED lifetime and generated considerable excess heating. The initial laboratory tests of the first completed MOPS system showed that zero air flushing of the chambers may not be a suitable method to get a good “zero” for ozone production from this system. The PI team developed a new zeroing method which employs a plexiglass cover that encloses both of the MOPS photochemical chambers to shut off photochemical production in both chambers simultaneously. While this adds a bit more complexity to the design, this new method is significantly faster and more importantly provides a better measure of the “background” ozone production for the MOPS system.

Task 2 was to identify CAMS sites with help of AQRP and TCEQ for MOPS instrument deployments. During the month of June the UH team received permission from the City of Fort Worth and TCEQ to setup MOPS instruments at the Eagle Mountain Lake (C75) site for Summer and Fall of 2011. Given that C75 (Eagle Mountain Lake) is often a receptor site experiencing high transported ozone is the afternoon/evening, the PI team decided to set up the second MOPS instrument at a site closer to the DFW urban core where ozone production may be higher and/or ozone production may be suppressed by high NO<sub>x</sub> levels. In addition, the team feels that is essential to restrict the search to CAMS sites in the DFW region that have both NO<sub>x</sub> and auto-GC instruments. The VOC and NO<sub>x</sub> measurements will provide the team with good

understanding of the VOC reactivity and NO<sub>x</sub> levels which will be required to interpret changes in ozone production. Given these multiple search constraints the MOPS team decided to locate the second MOPS instrument at the Fort Worth Northwest (C13). In early August the PI team received permission from the City of Fort Worth, TCEQ, and Meacham International Airport to install 2<sup>nd</sup> MOPS instrument at the Fort Worth Northwest CAMS 13 measurement site.

Task 3 was to deploy two MOPS instruments for an extended period of time in the DFW area. The MOPS team installed the 1<sup>st</sup> MOPS instrument at the Eagle Mountain Lake (C75) site during the first week of August 2011 (Figure 3). The instrument performed quite well during the first week of onsite testing but after a couple of days of unattended operation the 1<sup>st</sup> MOPS instrument started to have some communication problems. In addition, the MOPS mechanical zeroing cover (Figure 4) became physically stuck and required a site visit to manually unjam the cover. When the second MOPS system was installed at the Fort Worth Northwest (C13) site during the 3<sup>rd</sup> week of August (Figure 5) the MOPS team also installed a remote network power switch in both MOPS instruments which seems to have improved the communications problems. The team also made some modifications to the auto-zeroing cover to improve pivot arm alignment including a softer spring mechanism and slight hardware adjustments to the cover pivot points. Unfortunately, these modifications did not significantly improve the MOPS zeroing cover performance. The PI team has completely redesigned the zeroing cover mechanism including upgrading from a single to a dual drive motor with a pivot arm counter balance in place of the return spring. This new mechanism is currently undergoing construction and testing in the lab and will be installed in both MOPS instruments in early September.

During the last two weeks of August the MOPS instruments have been working consistently however the zeroing cover has been jamming frequently. The MOPS PI team is currently evaluating the August MOPS data, a month with a number of DFW ozone exceedances.



Figure 1. Photograph of the 2<sup>nd</sup> Generation MOPS chamber. Note the coated stainless steel screen at the chamber inlet to which a temperature gradient is applied to maintain a stable boundary layer and minimize wall reactions. Photo shows leak testing of evacuated chamber with compressed walls.



Figure 2. Photograph of the NO<sub>2</sub> conversion cell. In this cell a high powered LED Ultraviolet radiation source (blue) is interfaced to a polished aluminum box which contains two quartz tubes, one for each MOPS chamber (shaded and unshaded).



Figure 3. The MOPS instrument installed at Eagle Mountain Lake (C75). This photo shows MOPS zeroing cover in the normally open (non-zeroing) position.



Figure 4. Close up photo of the MOPS instrument installed at Eagle Mountain Lake (C75) showing the cover zeroing mechanism.



Figure 5. Overall site view of the MOPS instrument installed at Fort Worth Northwest (C13) site.





Figure 6. Close up of the MOPS instrument installed at Fort Worth Northwest (C13) site with auto-zeroing cover in the closed (zeroing) position.

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**Project 10-042**

**STATUS: Active – October 8, 2010**

**End Date Extended to November 30, 2011**

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***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 NO<sub>x</sub> and VOCs and air quality management planning seeks the combination of NO<sub>x</sub> and VOC emission reductions that will most effectively reduce ozone. When VOCs undergo chemical reactions in the atmosphere they can reduce the availability of NO<sub>x</sub> by converting it to un-reactive compounds which we call NO<sub>x</sub>-sinks. However, some of these “NO<sub>x</sub>-sink” compounds can react further in the atmosphere and may return the NO<sub>x</sub> to an active form, which we refer to as NO<sub>x</sub>-sources. The chemical reactions of VOCs with NO<sub>x</sub> can be characterized by environmental chamber experiments which expose controlled amounts of VOC and NO<sub>x</sub> to light and measure the products (e.g., ozone) that are formed. This project will carry out new environmental chamber experiments to characterize NO<sub>x</sub> 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. The project benefit will be more accurate modeling of the ozone benefits of emission control strategies in Texas and elsewhere.

**Project Update:**

**Experiments Performed**

A total of 33 dual reactor environmental chamber experiments were performed for this AQRP project at the University of California at Riverside (UCR), of which 29 obtained data of potential utility for modeling, either for either mechanism evaluation or chamber characterization. Because of the dual reactor design, each successful experiment provides data for two separate reactor irradiations, each of which can be treated as a separate experiment for modeling purposes. Modeling input and experimental output data were obtained for a total of 55 such reactor irradiations (runs), as summarized below.

**Table 1.** Numbers of experiments of different type performed at UCR for this AQRP project.

Number of Runs	Type
20	NOx Sink with base case (10 test runs, each with a base case)
4	NOx Sink without base case (test reactant accidentally injected into both reactors)
8	NOx Source (two methods)
3	Isoprene - NOx, with varied initial concentrations (one duplicate experiment excluded)
6	Ethene or Propene - NOx Control (two duplicate experiments excluded)
3	NOx Source control (NOx added)
9	Background NOx characterization (two methods)
2	Radical source characterization

NOx Sink Experiments: NOx sink experiments were carried out for toluene, o-cresol, furan (a precursor to the aromatic fragmentation product 2-butene-1,4-dial), and isoprene, using ethene - NOx as the base case experiment in all cases, and also using propene - NOx as the base case for toluene. These experiments demonstrated that all of the compounds tested inhibited ozone formation by mixtures of ethene and NOx because the test compounds have strong NOx sinks that convert NOx to inactive forms. Results from these experiments have been used by SmogReyes and ENVIRON to evaluate chemical mechanisms and guide mechanism improvements for aromatic hydrocarbons (toluene, xylene, etc.) and isoprene.

NOx Source Experiments: NOx source experiments were carried out using two different methods with the test compounds isopropyl nitrate, isobutyl nitrate and 2-nitrophenol. Experiments mixed the test compound with hydrogen peroxide and acetaldehyde or CO. The purpose of adding hydrogen peroxide is to produce OH radicals that can react with the test compound. The additions of acetaldehyde or CO are two different approaches to preserving NOx released by the test compound for quantification. In all cases, release of NOx from the test compound was observed with ozone formation resulted providing firm evidence for NOx recycling from NOx source compounds. These experiments have been used by SmogReyes and ENVIRON to improve the CB6 mechanisms for aromatic hydrocarbons (i.e., for nitrophenol type compounds formed from benzene, toluene, xylene, etc.) and alkanes (i.e., for alkyl nitrates from propane, butane, etc).

Isoprene Experiments: Three isoprene - NOx experiments were completed at lower NOx concentrations than previous experiments performed at UCR. These data are needed to understand the extent to which the products of isoprene reactions depend upon NOx concentrations and, in particular, whether isoprene is a strong source of hydroxyl radicals under low NOx conditions. Results from these experiments are being used by SmogReyes and ENVIRON to evaluate the CB6 isoprene mechanism and develop improvements if needed.

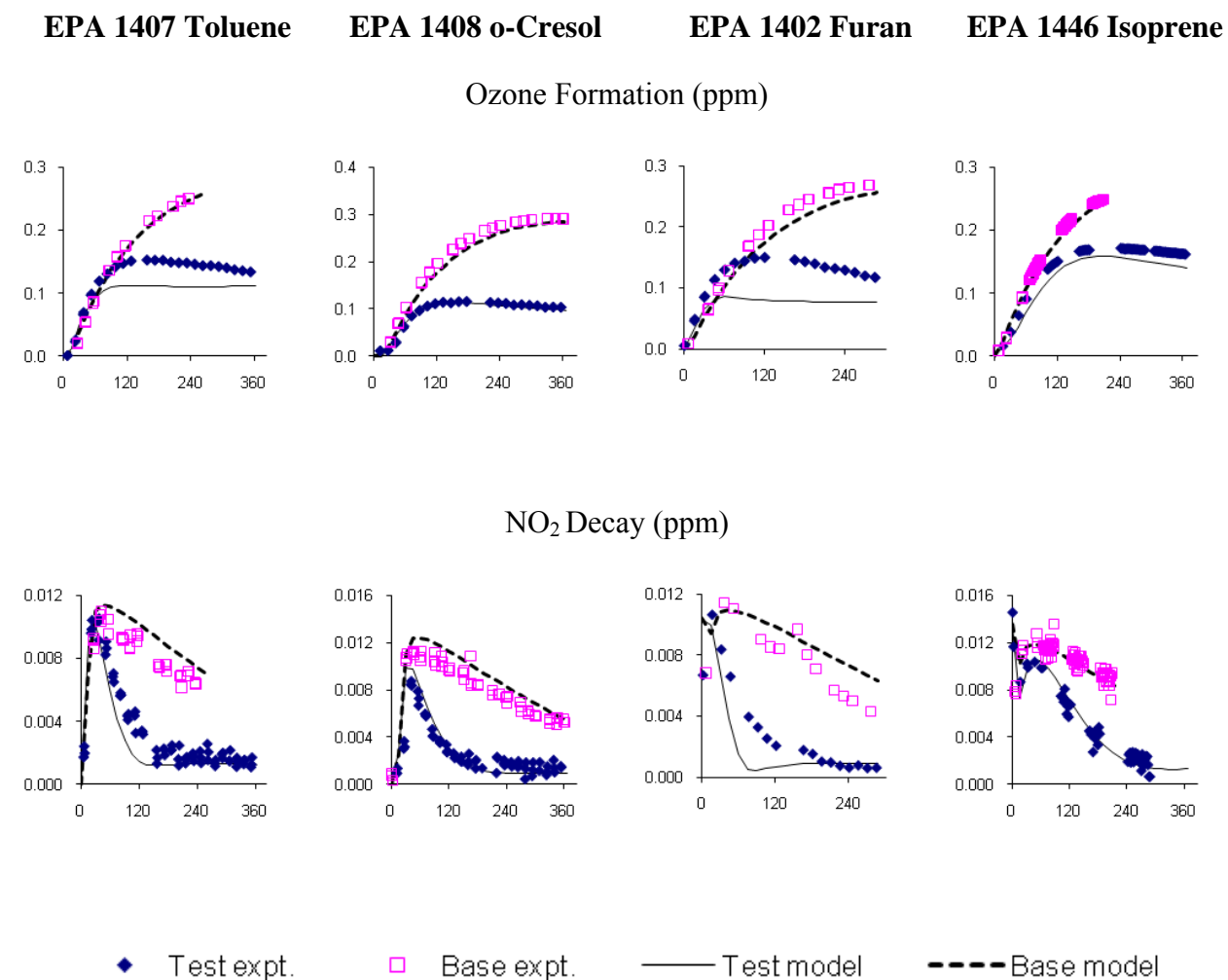
### **Chemical Mechanism Development**

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 UCR, combined with experiments retrieved from the European EUPHORE chamber for this project, are being used to improve the Carbon Bond 6 (CB6) mechanism. The revised mechanism is to be called CB6r1.



### NO<sub>x</sub> Sink Experiments

The results of NO<sub>x</sub> sink experiments conducted with toluene, o-cresol, furan (a precursor to 2-butenedial) and isoprene are shown in Figure 2. The effect on ozone and NO<sub>2</sub> of adding the test compound was simulated very well for o-cresol and isoprene and fairly well for toluene and furan. These results suggest that CB6r1 is performing well in representing the strengths of the NO<sub>x</sub>-sinks present for toluene, o-cresol, and isoprene. The results for furan are complicated by the fact that furan is not the compound of interest but rather was used as a precursor to make 2-butenedial (the compound of interest) during the chamber experiment. Results from a EUPHORE experiment (not shown) that was performed using 2-butenedial directly are being used to complement results from the experiment with furan shown in Figure 2.

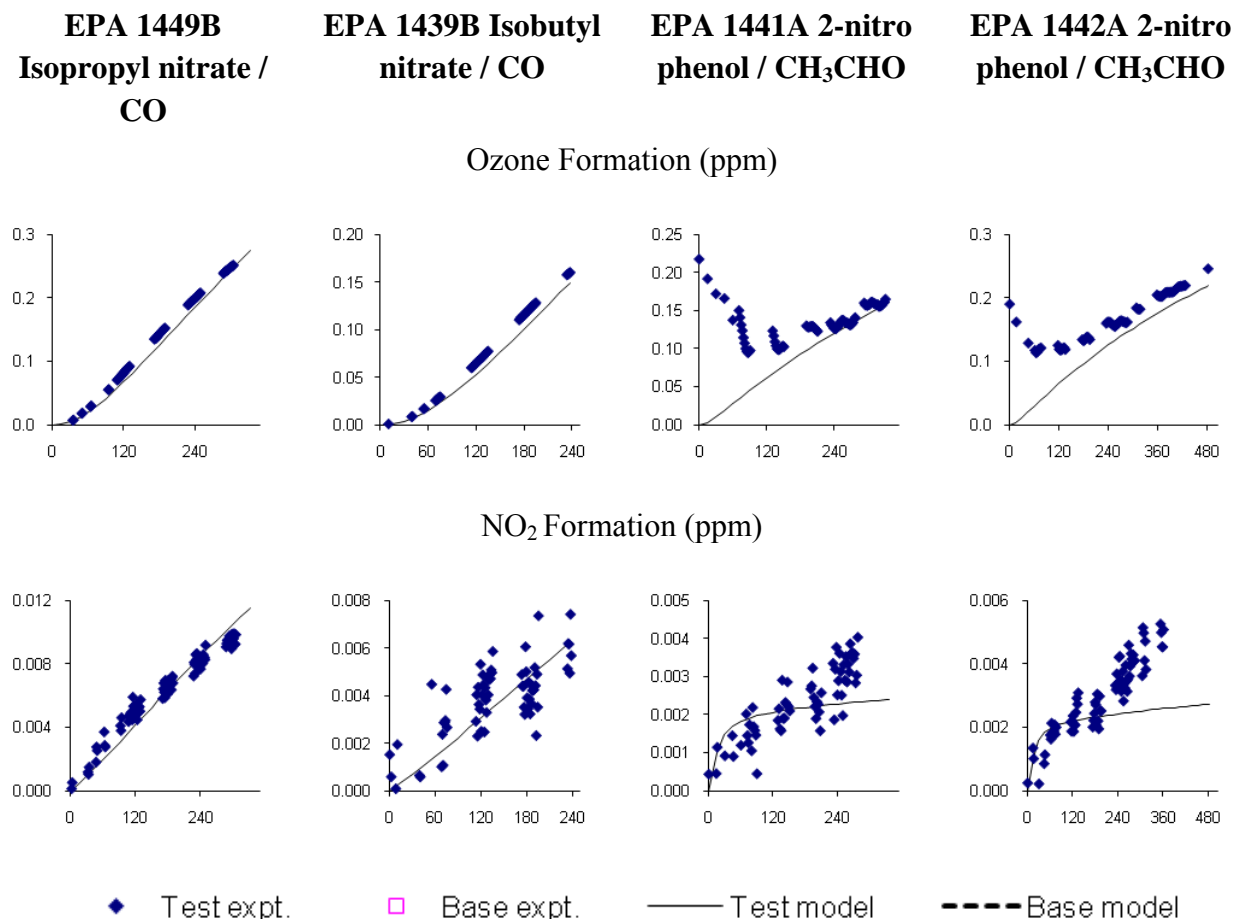


**Figure 2.** Model simulations with CB6r1 of NO<sub>x</sub> sink experiments with toluene, o-cresol, furan and isoprene added to a base mixture of ethene and NO<sub>x</sub>.

## NOx Source Experiments

The NOx source experiments with alkyl nitrates (isopropyl nitrate and isobutyl nitrate) support formation of NOx when organic nitrates undergo photolysis and reaction with OH. The evidence is stronger for photolysis than OH reaction because photolysis dominated the decay of the organic nitrates in the experiments performed. Figure 3 shows results of NOx source experiments and simulations with CB6r1. The yields of NO<sub>2</sub> (and O<sub>3</sub>) are simulated very well by CB6r1 for experiments with isopropyl nitrate and isobutyl nitrate.

Simulations of experiments with 2-nitrophenol are shown in Figure 3. Simulations using several test mechanisms confirm that 2-nitrophenol decayed rapidly by photolysis and this reaction was added in CB6r. Formation of NO<sub>2</sub> was observed and CB6r1 simulates the NO<sub>2</sub> fairly well. Formation of O<sub>3</sub> was observed although the measurement suffers from strong interference (i.e., UV absorption) by 2-nitrophenol and the apparent good agreement for the final O<sub>3</sub> may be misleading. The NOx source experiments for 2-nitrophenol provided important evidence for photolysis of nitrophenols accompanied by formation of NOx and this process has been included in CB6r1 for the decomposition products of aromatic hydrocarbons.



**Figure 3.** Model simulations with CB6r1 of NOx source experiments with organic nitrates added to mixtures of CO and H<sub>2</sub>O<sub>2</sub> or CH<sub>3</sub>CHO and H<sub>2</sub>O<sub>2</sub>.

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**Project 10-044**

**STATUS: Active – March 25, 2011**

**End Date Extended to November 30, 2011**

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***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 will conduct an airborne measurements investigation in the Dallas Fort Worth (DFW) area during the 2011 ozone season. The proposed measurement campaign includes 45 flight hours to be conducted during mid-May to mid-July 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 will 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.

UH will collect airborne monitoring samples on a minimum of five flights in and around DFW. The UH team will develop detailed flight plans in coordination with AQRP. Flights will have specific sampling goals; potential flights might be designed to:

- (1) map pollutant concentrations throughout DFW on high ozone days in DFW.
- (2) measure pollutant concentrations downwind of power plants.
- (3) measure pollutant concentrations in the vicinity of active gas wells and/or compressor stations located on the Barnett Shale.
- (4) investigate the impact in DFW of biomass burning episodes that might occur during the period of the study.

The University of Houston Aztec aircraft will provide observations of ozone, nitrogen oxides, sulfur dioxide, formaldehyde, reactive alkenes, volatile organic compounds, and meteorological parameters.

### **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 21<sup>st</sup> and June 30<sup>th</sup>, four science flights were completed. A total of 42.1 hours were flown in the AZTEC aircraft during the month of June.

On July 2<sup>nd</sup> the last Barnett Shale science flight was flown. On July 3<sup>rd</sup> a pressure altitude calibration flight was flown and on July 5<sup>th</sup> 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. These efforts are ongoing.

A preliminary in-progress report was submitted on July 20<sup>th</sup> and a cleaner copy of the report was submitted on July 22<sup>nd</sup>. All data sets collected are in the process of being organized, validated and reviewed by the team.

The preliminary data plots were submitted following each flight and results of the VOC canisters analyses have been received. As an example of the ongoing data revision work, a description of the June 30<sup>th</sup> flight and related graphs are herein included:

**Barnett Shale Flight on June 30, 2011:** The aircraft took off from McGregor Municipal Airport at 11:00 CST, and flew 3 downwind traverses and 7 upwind traverses covering the area shown in the figures below. VOC samples were collected at Italy, Eagle Mountain Lake, Pilot Point and Decatur as shown in the plots below. Approximately 682 statute miles were flown over 5.0 hours of flight time. The aircraft stopped at Decatur, refueled and returned to McGregor Municipal Airport to prepare for the following day's flight.

**Discussion:** On the DFW flight conducted on the afternoon of June 30, 2011 the aircraft made east-west transects over the upwind and downwind areas of the Barnett Shale including downwind areas north of DFW. The flight transects north of DFW almost completely covered the DFW downwind area under these synoptic conditions (south winds at about 10 to 15 mi/hr).

Ozone Levels for Thursday June 30, 2011 15-16:00 CDT

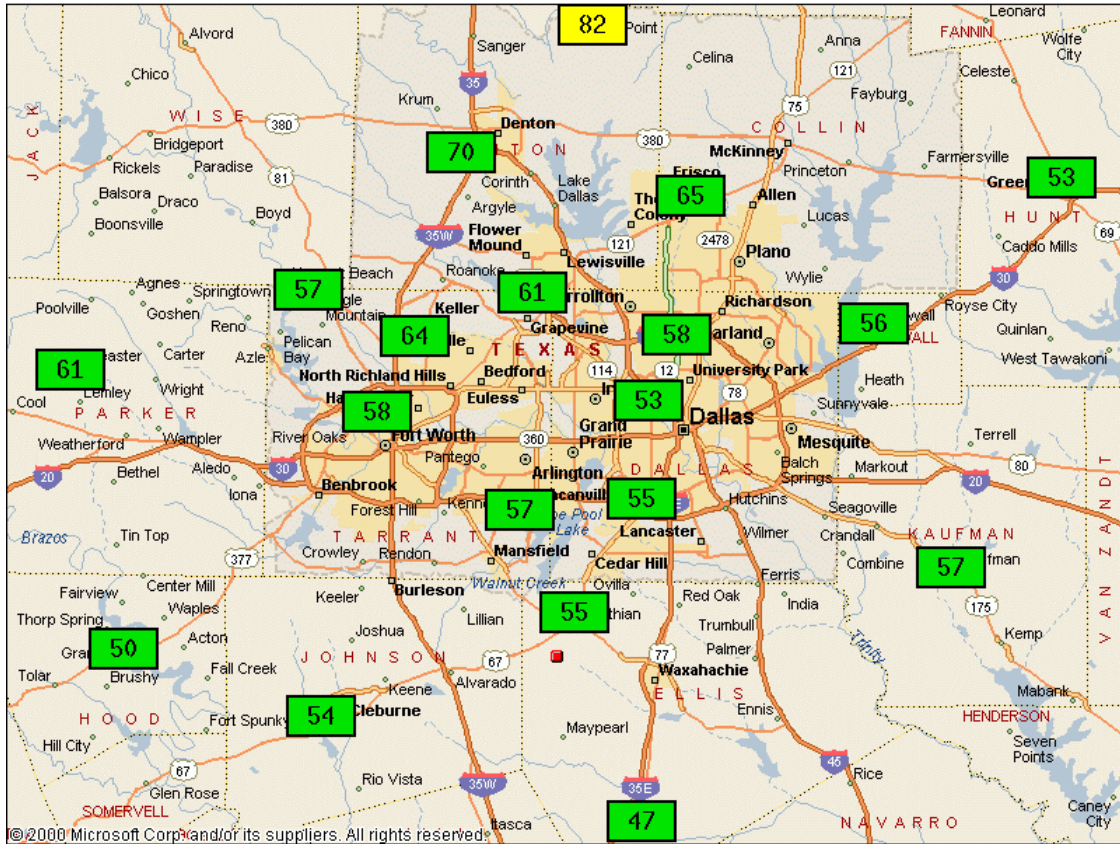


Figure 1. Spatial distribution of ozone in the DFW area on June 30, 2011, 15-16:00 CDT (source: TCEQ website).

As seen in the spatial distribution of ozone (Figure 1) the overall surface ozone levels in the DFW area were modest. Highest values around 80 ppbv were observed north of Dallas. This is also reflected in the airborne measurements (Figure 2), in particular over the Barnett Shale area characterized by ozone levels barely surpassing 60 ppbv. However, again, there is a clear increase of ozone in the DFW downwind area visible, reaching ozone levels of 80 ppbv on the ground (see Figure 2) and more than 90 ppbv at an altitude of about 600 meters above mean sea level.

Coinciding with ozone in the downwind DFW also  $\text{NO}_y$  (see Figure 3) and CO (not shown) display higher levels. This likely indicated photochemically processed air masses due to the DFW urban area under these synoptic flow conditions.

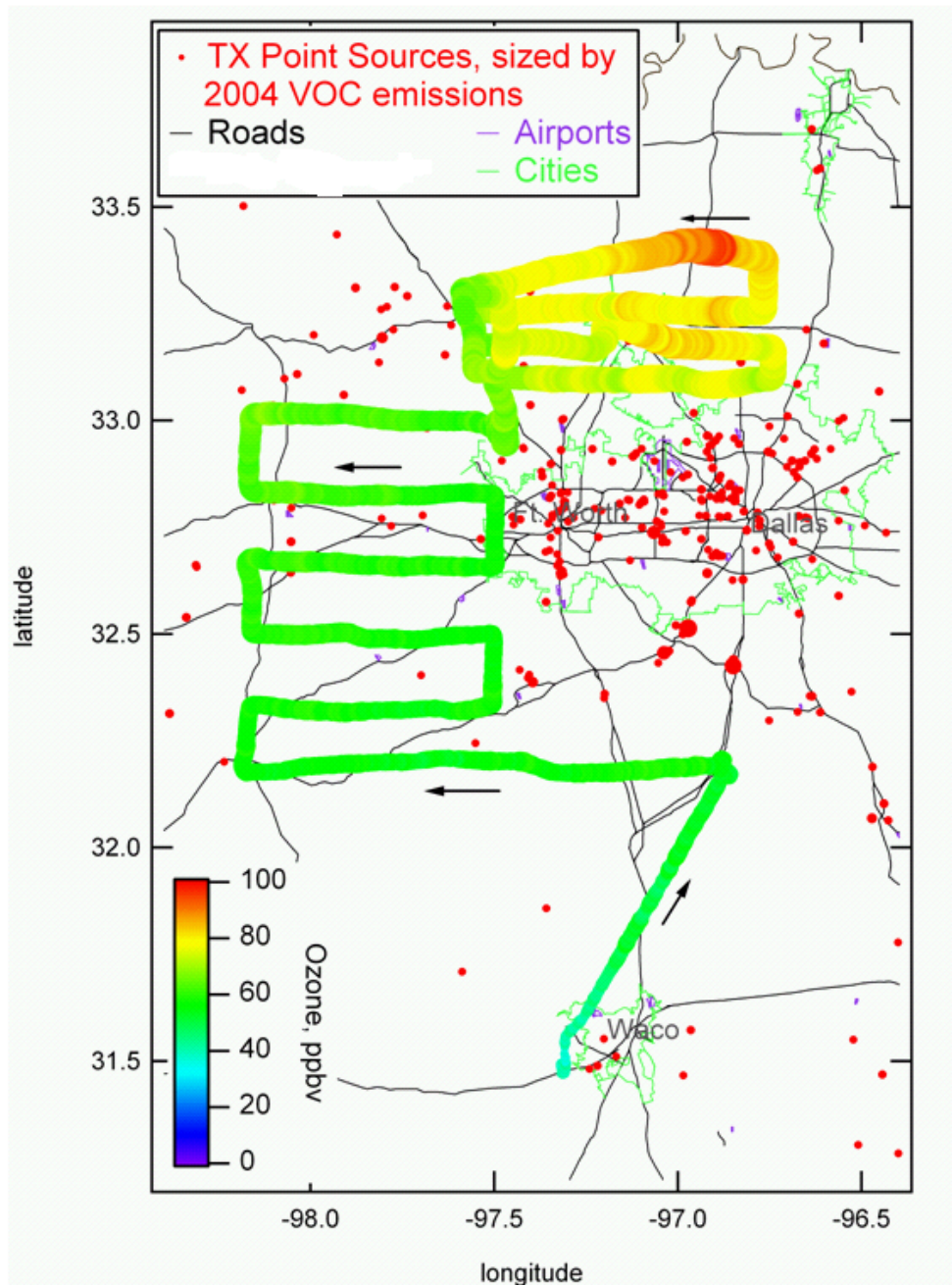


Figure 2. June 30, 2011 ozone concentrations over the Barnett Shale and downwind of Dallas and Fort Worth metroplex. The color-coded flight path represents ozone mixing ratios scaled from 0 to 100 ppbv as shown on color scale on the lower left corner of map. The red dots plotted are VOC emission sources and are sized based on emissions.



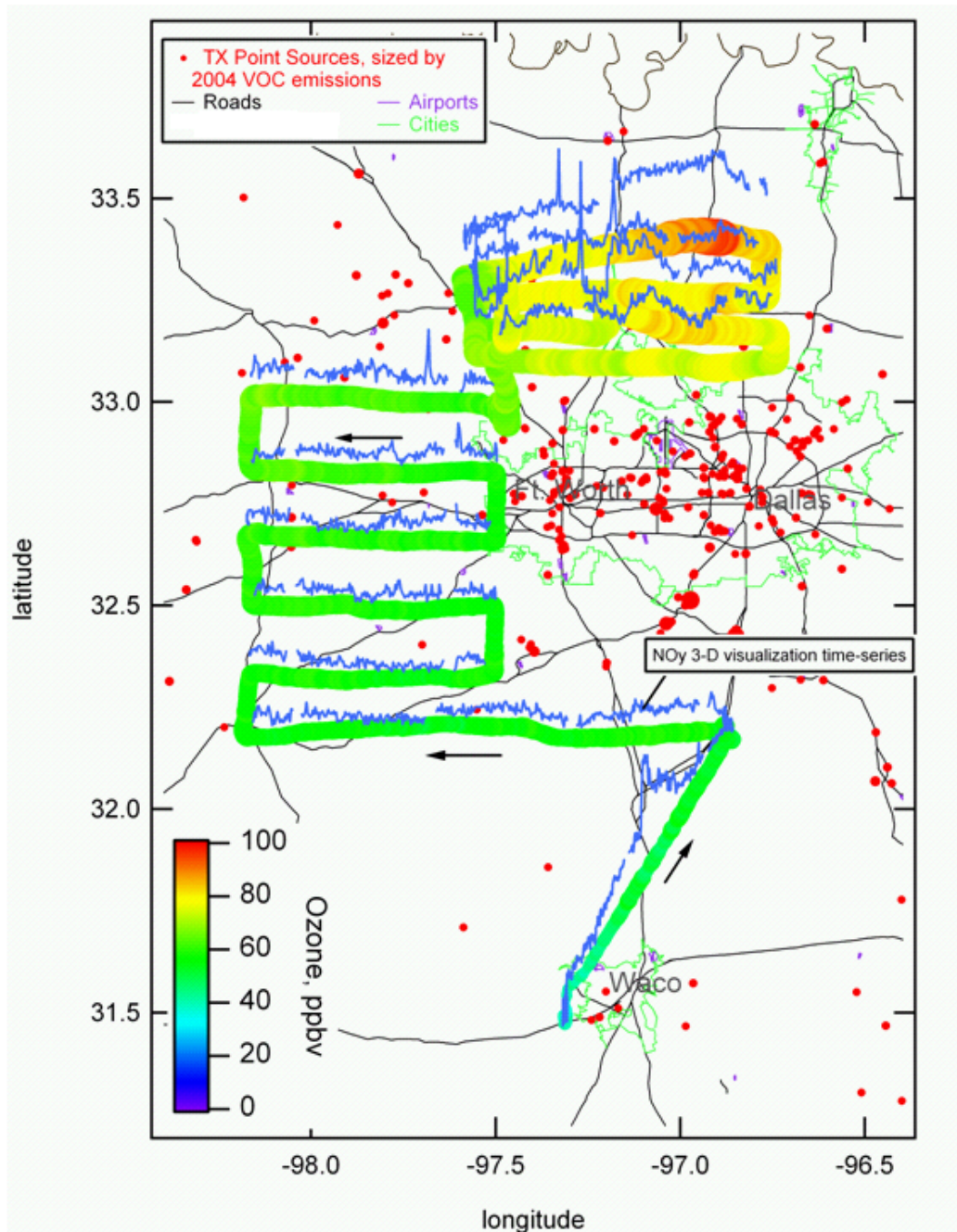


Figure 3. June 30, 2011 over Barnett Shale and downwind of Dallas and Fort Worth metroplex. The color-coded flight path represents ozone mixing ratios scaled from 0 to 100 ppbv as shown on color scale on the lower left corner of map. Overlaid are  $\text{NO}_y$  time series. The red dots plotted are VOC emission sources and are sized based on emissions.

**Any delays or issues as related to the projects during the reporting period:**

Despite the delay in starting the program and the consequent challenges experienced during the field study, the tasks outlined in the Task Order were completed within the scheduled time frame. However, due to the delays experienced during the field campaign, the data validation effort was initiated only upon returning to the University. For this reason an extension was requested and obtained.

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

No funds are estimated to be returned.



***Quantification of Hydrocarbon, NO<sub>x</sub>, and SO<sub>2</sub> emissions from Petrochemical Facilities in Houston: Interpretation of the 2009 FLAIR dataset***

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

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

**Funding Awarded: \$398,401**

(\$150,132 UCLA, \$33,281 UNC, \$164,988 Aerodyne, \$50,000 Washington State)

**Executive Summary:**

In Spring 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 volatile organic compounds (VOCs), oxides of nitrogen (NO<sub>x</sub>) and formaldehyde (HCHO), which all contribute to ozone formation. At the same time an Imaging Differential Optical Absorption Spectrometer (I-DOAS) operated by the University of California Los Angeles (UCLA) sampled flares and other individual sources for emissions of HCHO and NO<sub>2</sub>. 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 in order to determine facility-wide emissions of HCHO and NO<sub>2</sub>. As a result of all above mentioned efforts, a unique observational dataset of VOCs, HCHO, and NO<sub>x</sub> observations was created.

The current project is a collaborative effort between the University of California Los Angeles (UCLA), Aerodyne Research Inc. (ARI), Washington State University (WSU) and University of North Carolina Chapel Hill (UNC), to interpret the observational dataset collected during 2009 FLAIR campaign. The observational data acquired by the different groups will be used to estimate emission rates of ozone precursors, such as VOCs, HCHO and NO<sub>x</sub>, for the specific times and locations of the observation. These emission rates then will be compared to the hourly special inventories (SI) to provide an illustrative comparison for emission sources that are potentially critical for ozone formation.

Specific goals of this project are:

1. Characterize source-and date-specific emissions and atmospheric chemistry using the ARI mobile laboratory FLAIR dataset. Identify where the pollutant sources are, how much is emitted, and what happens to these pollutants in the atmosphere.
2. Determine of facility averaged fluxes of NO<sub>2</sub>, HCHO, and SO<sub>2</sub> using dual MAX-DOAS data acquired during FLAIR 2009.

3. Characterize source-and date-specific fluxes of HCHO, NO<sub>2</sub> and SO<sub>2</sub> from point sources in Houston based on I-DOAS observations during FLAIR.
4. Estimate source-specific emission rates through interpretation and consolidation of the combined observations of all platforms during FLAIR. Qualitatively compare observations with hourly special inventories for 2006 and determine the uncertainty of the observations.

### **Project Update:**

#### **Data Workshop:**

June 21-22, 2011 the FLAIR data workshop was held at the University of Texas, Austin Pickle Research Center. Each research group was represented by the following members:

UCLA – Jochen Stutz and Olga Pikelnaya

WSU – George Mount and Elena Spinei

ARI – Scott Herndon, Ezra Wood, Oluwayemisi Oluwole

UNC – Evan Couzo

Johan Mellqvist and John Johansson from the Chambers University also joined the workshop.

All workshop participants would like to thank AQRP staff for help in organizing this workshop.

During the first day of the workshop, each group gave an overview of the work completed so far within the project and their main findings. The second day of the workshop was dedicated to general a discussion of the integration of the findings from the different groups and the overall conclusions of the project. During the discussion, in particular with the TCEQ participants, the main research direction for the remainder of the project, as well as the main topics of the final reports, were identified. In general the workshop was a success and the open discussion benefitted the FLAIR participants as well as the TCEQ and AQRP attendants.

#### **Overall Update:**

Updates for each task of the project are presented below. Collectively, all groups worked on refining their results and on assembling their findings for the draft final report. The draft final report for the project was written and submitted to AQRP on July 20, 2011. The report contained detailed description of the work performed by the participants during the entire project. It included a summary of the overall results of the project, which provided a qualitative assessment of trace gas emissions in Texas City and Mont Belvieu.

#### **Task 1: Determination of facility averaged fluxes of NO<sub>2</sub>, HCHO, and SO<sub>2</sub> in Texas City using dual MAX-DOAS data acquired during FLAIR 2009. – UCLA and WSU**

During this quarter, the UCLA and WSU groups completed the spectral evaluation for all species, resulting in slant column density, SCD, values for HCHO, NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>4</sub>. The

oxygen dimer, O<sub>4</sub>, provides information on radiative transfer conditions at the time of the measurement. Radiative transfer (RT) conditions affect the values of measured trace gas SCDs. Correlations between O<sub>4</sub> SCD values measured at the two sites were performed in order to learn if RT conditions were different. This comparison showed that, for most of the time, they were very similar; therefore no additional correction was needed for trace gas flux calculations. The WSU group developed a radiative transfer code for computing vertical column densities of trace gases, which was then be used for flux calculations using measured trace gas slant column densities and retrieved aerosol extinction. The average fluxes of HCHO, NO<sub>2</sub> and SO<sub>2</sub> from the Texas City industrial complex based on dual MAX-DOAS measurements and the RT calculations were found to be:

average HCHO flux: 25 kg/h

average SO<sub>2</sub> flux: 360 kg/h

average NO<sub>2</sub> flux: 100 kg/h

The WSU group also examined the relationship between HCHO and SO<sub>2</sub> from the MAX-DOAS measurements taken at the Texas City courthouse site. East viewing and west viewing data from the MAX-DOAS location at the courthouse are quite different. HCHO and SO<sub>2</sub> sources are expected to be SE of the courthouse, and consequently were larger in eastern direction. Under normal meteorological conditions the slope between HCHO and SO<sub>2</sub> SCDs was found to be 0.06 +/- 0.01. A similar relationship was found by ARI and the SOF group, and shows the relation of HCHO to SO<sub>2</sub> over Texas City during the FLAIR campaign.

**Task 2: Determination of source specific fluxes of HCHO, NO<sub>2</sub>, HONO, and SO<sub>2</sub> from point sources in Houston based on I-DOAS observations during FLAIR. - UCLA**

During this quarter the methodology for flux calculations from the I-DOAS measurements was developed and applied to observations of HCHO, NO<sub>2</sub> and SO<sub>2</sub> emissions during FLAIR 2009.

A combination of the I-DOAS trace gas slant column density images and meteorological information was used to determine pollutant fluxes from the individual sources observed in the

Houston area. From the I-DOAS SCD images, vertically integrated SCDs ( $\sum_{j=1}^{51} SCD_j$ ) were

calculated at azimuth viewing angles just downwind of the source of emissions. These vertically integrated SCDs were converted into fluxes using the distance between the I-DOAS and the emission source (D), wind speed (V<sub>w</sub>) and the angle between the I-DOAS line of sight and the wind speed (α) by equation 2.1:

$$F = \gamma * D * \sum_{j=1}^{51} SCD_j * V_w * \sin \alpha \quad \text{Equation 2.1}$$

In order to account for the variability of the emissions, flux calculations were performed for several neighboring azimuth viewing angles to obtain an averaged flux value. Therefore  $\sum SCD_j$  in equation 1 is an average value of 8 to 10 azimuthal steps downwind from the flare.

To account for the possible “background” amount of the respective trace gas the vertically integrated trace gas SCDs from the part of the image that is upwind of the source was determined. This background value was then subtracted from the downwind  $\sum SCD_j$ . The “background” vertically integrated SCD is also averaged over the 10 azimuthal steps. The final fluxes reported here are thus calculated using equation 2.2:

$$F = \gamma * D * \left( \sum SCD_j(\text{downwind}) - \sum SCD_j(\text{upwind}) \right) * V_w * \sin \alpha \quad \text{Equation 2.2}$$

The error of the trace gases fluxes were calculated using statistical error propagation. The uncertainties for the distance between the instrument and the flare/stack, wind speed and wind direction as well as the I-DOAS azimuth viewing direction were assumed to be 10 m, 1 m/s and 5° respectively. These errors were combined with the errors of trace gas SCDs from the DOAS analysis.

Figure 2.1 shows an example of a HCHO flux calculation for a burning flare of a chemical manufacturing facility in the Houston Ship Channel. The top panel of figure 2.1 shows the HCHO SCD image. The flare stack was located at vertical pixel 20 and horizontal pixel 22. HCHO clearly originated from the observed flare. Between columns 23 and 40, the entire HCHO plume can be observed in the SCD image, beyond the pixel 40, plume is partially outside of the image. Therefore, columns 24-34 (directly downwind from the flare) were used for HCHO flux determination (figure 2.1, bottom panel). Columns 8-18 were used for the HCHO background value (directly upwind from the flare) (figure 2.1, bottom panel). For this flare, the HCHO flux was determined to be 2.24 +/- 0.64 kg/hr.

A large HCHO plume observed by the I-DOAS instrument on May 13, 2009 was investigated for possible sources. Source triangulation using Google maps and I-DOAS observation geometry as well as comparison with ARI mobile lab measurements, lead to the conclusion that a FCCU regeneration unit was the source of observed HCHO. An idealized plume model was developed to explain the recorded HCHO SCD images and to estimate the HCHO flux. As a result, the HCHO flux was demined to be 18.2 +/- 4.8 kg/hr.

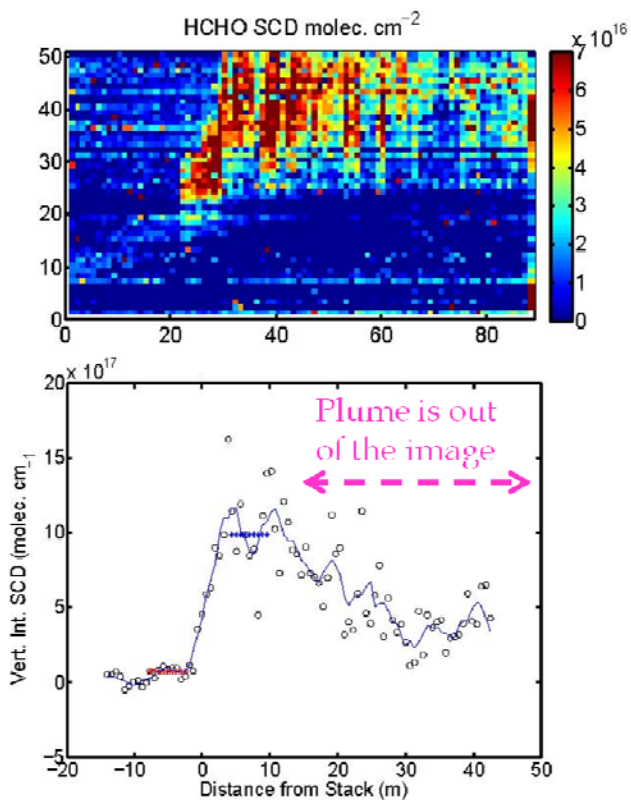


Figure 2.1. HCHO flux calculation example for an ethylene-burning flare of a chemical facility observed by the I-DOAS on May 29, 2009 at 21:12 UTC. The top panel shows the HCHO SCD image, the bottom panel shows vertically integrated HCHO SCDs. Blue crosses in the bottom graph show average vertically integrated HCHO SCDs used for the flux calculation. Red crosses in the bottom graph show the average background vertically integrated HCHO SCD upwind of the flare. The flux of HCHO is equal to  $2.24 \pm 0.64$  kg/hr.

Table 2.1 provides examples of trace gas fluxes that were determined based on the I-DOAS observations during FLAIR 2009 experiment.

**Table 2.1.** Examples of trace gas fluxes demined from the I-DOAS observations.

Date	Location	Trace gas fluxes
05/08/09	Acid Gas flare in Texas City industrial complex	F(SO <sub>2</sub> ) = 0.5 – 5 kg/hr and F(NO <sub>2</sub> ) ~ 0.23 +/- 0.11 kg/hr F(HCHO) = 0 – 0.8 kg/hr (might not be associated with this flare)
05/08/09	flare of the chemical plant in Texas City industrial complex	F(HCHO) = 0.58 – 0.74 kg/hr
05/19/08	Flare of a chemical plant in Mont Belvieu	F(HCHO) = 0 kg/hr (unlit flare), F(HCHO) ~ 0.26 +/- 0.07 kg/hr
05/29/09	Burning flare of the chemical facility in the Houston Ship Channel area	F(HCHO) = 1.79 – 2.23 kg/hr
FCCU regeneration unit		
05/13/09	Texas City, near the WSU MAX-DOAS site	F(HCHO) = 18.2 +/- 4.8 kg/hr

**Task 3: Characterization of source specific emissions and atmospheric chemistry using the mobile laboratory FLAIR dataset. Identification of where the pollutant sources are, how much is emitted, and what happens to these pollutants in the atmosphere. – ARI**

In-situ data collected by the ARI mobile laboratory during the transects through the Texas City industrial complex as well as stationary measurements at the Texas City courthouse revealed a continuous source of HCHO within the Texas City complex. This source was identified most likely to be a FCCU regeneration unit. Based on ARI measurements, this source of formaldehyde has been quantified to emit 17.7 kg of HCHO per hour. This value agrees very well with HCHO emissions estimated by the I-DOAS and SOF measurements for this unit. The ratio between HCHO and SO<sub>2</sub> from the stationary data at the Texas City court house varied between 0.07 and 0.16, with the median value of 0.12.

A suite of species measured by the ARI mobile lab allowed deriving ratios of different trace gases that can be used to determine DRE and CE values for individual flares in Texas City, Mt. Belvieu and the Houston Ship Channel. 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). Table 3.1 lists the detailed results of these observations.

Table 3.1. All pollutant ratios are in molar units (ppb/ppb). Cells highlighted in green indicate where the [CO<sub>2</sub>] changes were estimated (or for DRE and CE cells, calculated using an estimated value).

Date	time (CST)	Where	Latitude	Longitude	note	HCHO/CO	C2H4/CO	prop/CO	butene/CO	CO2/CO	DRE(C2H4)	DRE(C3H6)	DRE(C4H8)	CE
4/29/2009	15:23:00	Texas City	29.227	-94.547	Burning flare	0.046	0.64			35	0.9662			0.938
5/26/2009	7:54:03	Tidal Road	29.716	-95.113	spatially small	0.050	0.048			32	0.9975			0.965
5/26/2009	8:21:28	Tidal Road	29.716	-95.113	spatially small	0.120	0.034			32	0.9985			0.964
5/26/2009	8:21:37	Tidal Road	29.716	-95.113	spatially small	0.053				1060				0.999
5/26/2009	8:23:30	Tidal Road	29.716	-95.113	spatially small	0.045	0.041							
5/21/2009	6:42:30	Mt. Belv	29.813	-94.939	200 ppb C2H4		1.0 to 1.7							
5/21/2009	6:49:30	Mt. Belv	29.813	-94.939	170 ppb C2H4									
5/21/2009	4:12:30	Mt. Belv	29.810	-94.938	80 ppb C2H4		4				0.9843			
5/21/2009	3:46:21	Mt. Belv	29.820	-94.922	South of facility	0.045	4	0.120	0.130	91	0.9200	0.9964	0.9950	0.902
5/21/2009	4:11:00	Mt. Belv	29.810	-94.936	butene leaks									
5/21/2009	4:13:22	Mt. Belv	29.810	-94.936	benzene leaks									
5/21/2009	4:12:22	Mt. Belv	29.810	-94.936	ethene leak									
5/19/2009	09:25 to 09:30	K-ranch	29.831	-94.938	minute plumes		3.5			438	0.9843			0.982
5/19/2009	12:00 to 04:00	K-ranch	29.831	-94.938	hour plumes		2	0.400	0.250	0.1	0.2157			0.014
5/19/2009	10:44:01	K-ranch	29.831	-94.938	short plume		14.1			2000	0.9843			0.986
5/19/2009	13:10:11	Mt. Belv	29.858	-94.916	Unlit flare									0.000
5/15/2009	19:42:00	Mt. Belv	29.521	-94.551	mobile	0.110	2.800			232	0.9963			0.972
5/15/2009	19:47	Mt. Belv	29.518	-94.551	mobile	0.086	0.23			146	0.9968			0.990
5/16/2009	11:27	Mt. Belv	29.507	-94.537	mobile	0.009		0.16		15		0.9701		
5/16/2009	12:17:22	Mt. Belv	29.531	-94.550	steaming flare		3.2	0.534125	0.28189911	30	0.7989	0.9597	0.9726	0.746
5/16/2009	23:45:33	K-ranch	29.831	-94.938	overnight slow plumes		8.4							
5/16/2009	22:25:44	K-ranch	29.831	-94.938	overnight slow plumes		6.3			210	0.9436			0.939
5/20/2009	8:12:33	K-ranch	29.831	-94.938	stationary	0.62		4.4		629		0.9795		0.977
5/20/2009	8:26:44	K-ranch	29.831	-94.938	stationary		13.2							
5/20/2009	09:12 to 09:30	K-ranch	29.831	-94.938	stationary		5			200	0.9526			0.948
5/20/2009	13:16:45	Mt. Belv	29.780	-95.119	mobile	0.001	21							
5/22/2009	12:45:22	K-Ranch	29.831	-94.938	stationary									
5/23/2009	4:25:33	K-Ranch	29.831	-94.938	stationary		2.8 to 6.1							
5/24/2009	01:20 onwards	K-ranch	29.831	-94.938	anti-correlated HCHO, Cox		0.72							
5/24/2009	4:49:30	Mt. Belv	29.811	-94.901	propene 50 ppb									
5/24/2009	4:49:30	Mt. Belv	29.811	-94.901	benzene 13 ppb									
5/24/2009	4:49:30	Mt. Belv	29.811	-94.901	butenes 25 ppb									
5/24/2009	7:48:30	Mt. Belv	29.840	-94.892	ethene 600 ppb									
5/24/2009	7:49:15	Mt. Belv	29.843	-94.890	propene 150 ppb									
5/24/2009	7:49:05	Mt. Belv	29.843	-94.890	benzene 7 ppb									
5/24/2009	7:54:00	Mt. Belv	29.851	-94.896	propene 160 ppb									
5/24/2009	7:54:30	Mt. Belv	29.850	-94.897	ethene 1 ppm		1000			3030	0.6025			0.602
5/24/2009	7:59:20	Mt. Belv	29.850	-94.897	ethene 0.6 ppm									

**Task 4: Determination of source specific emission rates through interpretation and consolidation of the combined observations of all platforms during FLAIR. Comparison to existing TCEQ emission inventories. – UCLA, WSU, ARI, UNC**

**Emission Inventories:**

UNC continued extracting information from 2005 and 2006 inventories provided by TCEQ. Specifically, 2005 acid rain (ARD) and non acid rain databases as well as 2006 special inventories were studied. Guided by the observational data the inventories were examined for sources and source strengths for the measurements during FLAIR 2009 campaign. Specific attention was given to the FCCU unit in the Texas City complex as all groups identified it as a strong source of HCHO and SO<sub>2</sub>. There are no FCCU records in the ARD SO<sub>2</sub> files, but emissions data exists in the non-ARD SO<sub>2</sub> files. In 2005, the FCCU unit emitted 7.4 tons per day of SO<sub>2</sub>. In 2006, the unit emitted 12.0 tons per day of SO<sub>2</sub>. Hourly emissions data is not available. For other species, only 2006 data is available, the unit emitted 0.07 tons per day of HCHO, 1.06 tons per day of CO, and almost no benzene (0.0004 tons per day).

Since the model emissions inventories do not contain facility- or unit-specific identifying information, a search area was defined, and all modeled point sources located within that area were analyzed. One modeled point source was found that is essentially collocated with FCCU3. The point source that is collocated with FCCU3 is the dominant FORM (HCHO-like) source based on modeled inventories. During the 2005 episodes, hourly FORM emissions at the modeled FCCU3 source were 95.3 mol/hr. During the non-SI 2006 episodes, FORM emissions at the modeled FCCU3 source were 41.8 mol/hr. And during the SI 2006 episode, FORM emissions at the modeled FCCU3 source were 53.1 mol/hr.

### **Inverse Modeling:**

The Aerodyne Inverse Modeling System (AIMS) was applied to parts of the FLAIR 2009 data set, in order to identify and quantify emission sources most likely responsible for the measured concentrations. The following cases were modeled during this project:

1. Mont Belvieu measurements on May 24, 2009 (~4:30 am – 5:50 am CST)
  - a. Ethene emissions
  - b. Propene emissions
2. Texas city Benzene measurements on May 7, 2009 (~11:15am – 2:45pm CST)
3. Ship channel Butadiene measurements on April 26, 2009 (~11:30am – 1:30pm CST)
4. Courthouse SO<sub>2</sub> measurements on April 25-26, 2009

The ethene and propene emission rates computed by AIMS for Mont Belvieu are summarized in Table 4.1. The AIMS emissions rates were computed based on an emission height of 60m (the actual stack heights for Mt Belvieu were unknown, so we used the reported stack height for the courthouse); and the values largely agree with those estimated previously using the SOF technique.



Table 4.1. Emission rates computed using AIMS.

	<b>Ethylene (Mt Belv)</b>	<b>Propylene (Mt Belv)</b>
<b>Source area (min. Lat)</b>	29.82	29.82
<b>Source area (max. Lat)</b>	29.883	29.883
<b>Source area (min. Lon)</b>	-94.941	-94.941
<b>Source area (max. Lon)</b>	-94.878	-94.878
<b>Emission Rates (Inventories)</b>	53±17 lb/hr	7.5±13.4 lb/hr
<b>Emission Rates (SOF Aug-Sep 06)</b>	606-1333 lb/hr	489-1424 lb/hr
<b>Emission Rates (AIMS 2009 ARI truck)</b>	127-664 lb/hr	218-4095 lb/hr

Calculations of SO<sub>2</sub> emissions in Texas City complex focused on modeling emissions from the FCCU regeneration unit. For this modeling effort, wind data were obtained from CAMS 147 station located at Texas City Ball Park. Table 4.2 summarizes AIMS calculations for SO<sub>2</sub> emissions from the FCCU unit within the Texas City industrial complex.

Table 4.2. SO<sub>2</sub> emission rates (lb/hr) computed by AIMS.

Wind Station Location:	Source1 Location:
-94.9312, 29.3847	-94.9184, 29.3726
Times: (24hr CST, April 26, 2009)	Release Rates: (lb/hr)
0:00	190
0:12	258
0:24	190
0:27	428
0:30	238
0:39	607
1:06	1014
1:12	646
1:18	882
1:27	644
1:30	682
1:36	431
1:48	344
1:54	70

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**Project 10-DFW & 11-DFW**

**STATUS: Active - February 1, 2011**

**Project Complete: August 31, 2011**

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***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 are 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 consists 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)**

<b>Budget Category</b>	<b>FY10</b>	<b>FY11</b>	<b>Total</b>	<b>Expenses</b>	<b>Pending Expenses</b>	<b>Remaining Balance</b>
Personnel/Salary	\$195,100	\$148,755	\$343,855	\$281,894.52		\$61,960.48
Fringe Benefits	\$38,082	\$32,726	\$70,808	\$51,271.43		\$19,536.57
Travel	\$500	\$7,500	\$8,000	\$346.85		\$7,653.15
Supplies	\$24,015	\$2,744	\$26,759	\$12,802.66		\$13,956.34
Equipment	\$0	\$0	\$0			\$0
Other		\$4,007	\$4,007			\$4,007.00
<b>Total Direct Costs</b>	<b>\$257,697</b>	<b>\$195,732</b>	<b>\$453,429</b>	<b>\$346,315.46</b>	<b>\$0</b>	<b>\$107,113.54</b>
Authorized Indirect Costs	\$19,510	\$14,876	\$34,386	\$28,189.46		\$6,196.54
10% of Salaries and Wages						
<b>Total Costs</b>	<b>\$277,207</b>	<b>\$210,608</b>	<b>\$487,815</b>	<b>\$374,504.92</b>	<b>\$0</b>	<b>\$113,310.08</b>
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 June and July are included in the spreadsheet above. August fringe benefit expenses have not posted as of the writing of this report.

Supplies and materials expenditures included monthly telecom charges, postage, and office supplies.

Indirect costs for the months of June and July are included in Table 1. August 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 Administration funds, to better reflect the expenditures of this portion of the program.

## ITAC

There were no ITAC expenses during this reporting period.

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	\$8,990.45		\$24,109.55
Supplies	\$2,364	\$2,800	\$5,164	\$249.38		\$4,914.62
Equipment						
Other						
Contractual						
Total Direct Costs	\$18,864	\$19,400	\$38,264	\$9,239.83	\$0.00	\$29,024.17
Authorized Indirect Costs						
10% of Salaries and Wages						
<b>Total Costs</b>	<b>\$18,864</b>	<b>\$19,400</b>	<b>\$38,264</b>	<b>\$9,239.83</b>	<b>\$0.00</b>	<b>\$29,024.17</b>

## **Project Management**

Project Managers (PMs) have been assigned to each of the research projects. During the period from June 1, 2011 through August 31, 2011, PMs have worked with PIs to accomplish project goals and ensure that all reporting requirements are met.

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 funds are expected to be fully expended well before these dates.

During the previous period, all of the expenses relating to the DFW Field Study Site preparation were allocated to the Project Management account. Per direction from the TCEQ, in June the AQRP established two separate Research Projects for the DFW Field Study Site. The first account was established utilizing the remainder of the FY 10 Research Project funds (10-DFW). The second account utilized the remainder of the FY 11 Research Project funds, and a portion of the FY 11 Project Management funds (11-DFW). Thus a request was submitted to rebudget funds from the Project Management pool to the Research Project pool. This was done because there were not enough funds remaining in the Research Project pool to cover the expenses anticipated for the DFW Site.

The expenses initially charged to Project Management have been moved to these new accounts. It is anticipated that the expenses related to the DFW Field Study Site will fully utilize the previously unallocated Research Project funds in FY 10 and FY 11. Any funds remaining unspent in the 11-DFW account will be returned to the Project Management pool.



Table 3: Project Management Budget

**Project Management Budget**

<b>Budget Category</b>	<b>FY10 Budget</b>	<b>FY11 Budget</b>	<b>Total Budget</b>	<b>Expenses</b>	<b>Pending Expenses</b>	<b>Remaining Balance</b>
Personnel/Salary	\$144,380	\$83,434	\$227,814	\$161,593.46	\$0	\$66,220.54
Fringe Benefits	\$30,724	\$17,764	\$48,488	\$32,178.45	\$0	\$16,309.55
Travel	\$0	\$5,200	\$5,200	\$0		\$5,200.00
Supplies	\$458	\$1,465	\$1,923	\$267.44		\$1,655.56
Equipment						
Other						
Contractual						
<b>Total Direct Costs</b>	<b>\$175,562</b>	<b>\$107,863</b>	<b>\$283,425</b>	<b>\$194,039.35</b>	<b>\$0</b>	<b>\$89,385.65</b>
Authorized Indirect Costs	\$14,438	\$10,101	\$24,539	\$16,159.34		\$8,379.66
10% of Salaries and Wages						
<b>Total Costs</b>	<b>\$190,000</b>	<b>\$117,964</b>	<b>\$307,964</b>	<b>\$210,198.69</b>	<b>\$0</b>	<b>\$97,765.31</b>

## **Research Projects**

As of August 31, 2011, six projects were complete and the others remained active. Table 4 on the following 2 pages illustrates the funding awarded to each project and the total expenses reported on each project as of August 31, 2011. Please note that this reflects expenses that have posted to the UT-Austin accounting system as of August 31, 2011. There may be additional expenses pending that will not post until the following month.

At this time, all funding for research projects has been allocated to the projects or to the DFW Field Study. As discussed on page 7 of this report, projects 10-021, 10-DFW, and 11-DFW are complete, though a final invoice has not yet been received for any of the projects; 30-day contract extensions have been granted to projects 10-008, 10-024, and 10-045; and 90-day contract extensions have been granted to all remaining projects.

Table 4: Contractual Expenses

<b>Contractual Expenses</b>				
<b>FY 10 Contractual Funding</b>		<b>\$2,286,000</b>		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
10-008	Rice University	\$128,851	\$96,765	\$32,086
10-008	Environ International	\$49,945	\$46,670	\$3,275
10-009	UT-Austin	\$591,332	\$590,747	\$585
10-021	UT-Austin	\$248,786	\$244,068	\$4,718
10-022	Lamar University	\$150,000	\$9,631	\$140,369
10-032	University of Houston	\$176,314	\$2,589	\$173,725
10-032	University of New Hampshire	\$23,054	\$0	\$23,054
10-032	UCLA	\$49,284	\$14,195	\$35,089
10-034	University of Houston	\$195,054	\$34,913	\$160,141
10-042	Environ International	\$237,481	\$156,574	\$80,907
10-045	UCLA	\$149,773	\$65,026	\$84,747
10-045	UNC - Chapel Hill	\$33,281	\$28,711	\$4,570
10-045	Aerodyne Research Inc.	\$164,988	\$88,707	\$76,281
10-045	Washington State University	\$50,000	\$31,591	\$18,409
10-DFW	UT-Austin	\$37,857	\$37,857	\$0
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*			\$1,448,044	
FY 10 Contractual Funds Remaining to be Spent				\$837,956

<b>FY 11 Contractual Funding</b>		<b>\$1,736,063</b>		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
10-006	Chalmers University of Tech	\$262,179	\$118,651	\$143,528
10-006	University of Houston	\$222,483	\$146,892	\$75,591
10-015	Environ International	\$201,280	\$107,044	\$94,236
10-020	Environ International	\$202,498	\$130,290	\$72,208
10-024	Rice University	\$225,662	\$50,855	\$174,807
10-024	University of New Hampshire	\$70,747	\$37,779	\$32,968
10-024	University of Houston	\$64,414	\$19,212	\$45,202
10-024	University of Michigan	\$98,134	\$16,477	\$81,657
10-029	Texas A&M University	\$80,108	\$54,136	\$25,972
10-044	University of Houston	\$279,642	\$12,973	\$266,669
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*			\$723,571	
FY 11 Contractual Funds Remaining to be Spent				\$1,034,528
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*			\$2,171,615	
Total Contractual Funds Remaining to be Spent				\$1,872,484

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

## **Appendix**

### **Financial Reports by Fiscal Year**

(Expenditures reported as of August 31, 2011. Does not include all expenditures for the month of August 2011.)

**Administration Budget (includes Council Expenses)**

**FY 2010**

<b>Budget Category</b>	<b>FY10 Budget</b>	<b>Cumulative Expenditures</b>	<b>Pending Expenditures</b>	<b>Remaining Balance</b>
Personnel/Salary	\$195,100	\$195,028.64		\$71.36
Fringe Benefits	\$38,082	\$36,849.42		\$1,232.58
Travel	\$500	\$346.85		\$153.15
Supplies	\$24,015	\$12,802.66		\$11,212.34
Equipment	\$0			\$0
Other				
Contractual				
<b>Total Direct Costs</b>	<b>\$257,697</b>	<b>\$245,027.57</b>	<b>\$0</b>	<b>\$12,669.43</b>
Authorized Indirect Costs	\$19,510	\$19,502.88		\$7.12
10% of Salaries and Wages				
<b>Total Costs</b>	<b>\$277,207</b>	<b>\$264,530.45</b>	<b>\$0</b>	<b>\$12,676.55</b>

**Administration Budget (includes Council Expenses)**

**FY 2011**

<b>Budget Category</b>	<b>FY11 Budget</b>	<b>Cumulative Expenditures</b>	<b>Pending Expenditures</b>	<b>Remaining Balance</b>
Personnel/Salary	\$148,755	\$86,865.88		\$61,889.12
Fringe Benefits	\$32,726	\$14,422.01		\$18,303.99
Travel	\$7,500			\$7,500.00
Supplies	\$2,744			\$2,744.00
Equipment				
Other	\$4,007			\$4,007.00
Contractual				
<b>Total Direct Costs</b>	<b>\$195,732</b>	<b>\$101,287.89</b>	<b>\$0</b>	<b>\$94,444.11</b>
Authorized Indirect Costs	\$14,876	\$8,686.58		\$6,189.42
10% of Salaries and Wages				
<b>Total Costs</b>	<b>\$210,608</b>	<b>\$109,974.47</b>	<b>\$0</b>	<b>\$100,633.53</b>

**ITAC Budget  
FY 2010**

<b>Budget Category</b>	<b>FY10 Budget</b>	<b>Cumulative Expenditures</b>	<b>Pending Expenditures</b>	<b>Remaining Balance</b>
Personnel/Salary				
Fringe Benefits				
Travel	\$16,500	\$8,990.45		\$7,509.55
Supplies	\$2,364	\$249.38		\$2,114.62
Equipment				
Other				
<b>Total Direct Costs</b>	<b>\$18,864</b>	<b>\$9,239.83</b>	<b>\$0.00</b>	<b>\$9,624.17</b>
Authorized Indirect Costs				
10% of Salaries and Wages				
<b>Total Costs</b>	<b>\$18,864</b>	<b>\$9,239.83</b>	<b>\$0.00</b>	<b>\$9,624.17</b>

**ITAC Budget  
FY 2011**

<b>Budget Category</b>	<b>FY11 Budget</b>	<b>Cumulative Expenditures</b>	<b>Pending Expenditures</b>	<b>Remaining Balance</b>
Personnel/Salary				
Fringe Benefits				
Travel	\$16,600			\$16,600.00
Supplies	\$2,800			\$2,800.00
Equipment				
Other				
<b>Total Direct Costs</b>	<b>\$19,400</b>			<b>\$19,400.00</b>
Authorized Indirect Costs				
10% of Salaries and Wages				
<b>Total Costs</b>	<b>\$19,400</b>	<b>\$0.00</b>	<b>\$0.00</b>	<b>\$19,400.00</b>

**Project Management Budget  
FY 2010**

<b>Budget Category</b>	<b>FY10 Budget</b>	<b>Cumulative Expenditures</b>	<b>Pending Expenditures</b>	<b>Remaining Balance</b>
Personnel/Salary	\$14,380	\$138,706.71		\$5,673.29
Fringe Benefits	\$30,724	\$27,899.29		\$2,824.71
Travel	\$0	\$0		\$0
Supplies	\$458	\$7.44		\$450.56
Equipment				
Other				
<b>Total Direct Costs</b>	<b>\$175,562</b>	<b>\$166,613.44</b>	<b>\$0</b>	<b>\$8,948.56</b>
Authorized Indirect Costs 10% of Salaries and Wages	\$14,438	\$13,870.67		\$567.33
<b>Total Costs</b>	<b>\$190,000</b>	<b>\$180,484.11</b>	<b>\$0</b>	<b>\$9,515.89</b>

**Project Management Budget  
FY 2011**

<b>Budget Category</b>	<b>FY11 Budget</b>	<b>Cumulative Expenditures</b>	<b>Pending Expenditures</b>	<b>Remaining Balance</b>
Personnel/Salary	\$83,434	\$22,886.75		\$60,547.25
Fringe Benefits	\$17,764	\$4,279.16		\$13,484.84
Travel	\$5,200			\$5,200.00
Supplies	\$1,465	\$260.00		\$1,205.00
Equipment				
Other				
<b>Total Direct Costs</b>	<b>\$107,863</b>	<b>\$27,425.91</b>	<b>\$0</b>	<b>\$80,437.09</b>
Authorized Indirect Costs 10% of Salaries and Wages	\$10,101	\$2,288.67		\$7,812.33
<b>Total Costs</b>	<b>\$117,964</b>	<b>\$29,714.58</b>	<b>\$0</b>	<b>\$88,249.42</b>



**AQRP Budget  
FY 2010**

Budget Category	FY10 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary	\$195,100	\$195,028.64	\$0.00	\$71.36
Fringe Benefits	\$38,082	\$36,849.42	\$0.00	\$1,232.58
Travel	\$500	\$346.85	\$0.00	\$153.15
Supplies	\$24,015	\$12,802.66	\$0.00	\$11,212.34
Equipment	\$0	\$0.00	\$0.00	\$0.00
Other	\$0	\$0.00	\$0.00	\$0.00
Contractual	\$2,286,000	\$1,448,044.00	\$0.00	\$837,956.00
ITAC	\$18,864	\$9,239.83	\$0.00	\$9,624.17
Project Management	\$190,000	\$180,484.11	\$0.00	\$9,515.89
<b>Total Direct Costs</b>	<b>\$2,754,761</b>	<b>\$1,882,795.51</b>	<b>\$0.00</b>	<b>\$869,765.49</b>
Authorized Indirect Costs	\$19,510	\$19,502.88	\$0.00	\$7.12
10% of Salaries and Wages				
<b>Total Costs</b>	<b>\$2,772,071</b>	<b>\$1,902,298.39</b>	<b>\$0.00</b>	<b>\$869,772.61</b>

**AQRP Budget**

**FY 2011**

<b>Budget Category</b>	<b>FY11 Budget</b>	<b>Cumulative Expenditures</b>	<b>Pending Expenditures</b>	<b>Remaining Balance</b>
Personnel/Salary	\$148,755	\$86,865.88	\$0.00	\$61,889.12
Fringe Benefits	\$32,726	\$14,422.01	\$0.00	\$18,303.99
Travel	\$7,500	\$0.00	\$0.00	\$7,500.00
Supplies	\$2,744	\$0.00	\$0.00	\$2,744.00
Equipment	\$0	\$0.00	\$0.00	\$0.00
Other	\$4,007	\$0.00	\$0.00	\$4,007.00
Contractual	\$1,758,099	\$723,571.00	\$0.00	\$1,034,528.00
ITAC	\$19,400	\$0.00	\$0.00	\$19,400.00
Project Management	\$117,964	\$29,714.58	\$0.00	\$88,249.42
<b>Total Direct Costs</b>	<b>\$2,091,195</b>	<b>\$854,573.47</b>	<b>\$0.00</b>	<b>\$1,236,621.53</b>
Authorized Indirect Costs 10% of Salaries and Wages	\$14,876	\$8,686.58	\$0.00	\$6,189.42
<b>Total Costs</b>	<b>\$2,106,071</b>	<b>\$863,260.05</b>	<b>\$0.00</b>	<b>\$1,242,810.95</b>