AIR QUALITY RESEARCH PROGRAM

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

Quarterly Report

March 1, 2011 through May 31, 2011

Submitted to

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Texas Air Quality Research Program

Quarterly Progress Report

June 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. At the end of the current quarter, all of the sub-agreements were in place and Task Orders or Letter Agreements for all projects were activated. Work is currently underway on all projects and a description of project activities is described in this progress report.

Background

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

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

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

Research Project Cycle

The research Program is being implemented through an 8 step cycle. The steps in the cycle are described from project concept generation to final project evaluation for a single project cycle. During the first quarter of AQRP operation, steps 1-5 were completed for the first project cycle. During the second quarter, sub-agreements for most projects were established and Task Orders began to be initiated (step 6 and parts of step 7). In the third quarter, the final sub-agreements were executed and Task Orders were initiated for the majority of the projects. In the fourth quarter, Task Orders were finalized for the remaining Projects and work was in progress on every Project. The projected timeline for the remainder of the biennium is also outlined below.

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

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

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

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

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

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

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

8.) The AQRP Director and the Project Manager for each project describes progress on the project in the ITAC and Council meetings dedicated to on-going project review. The AQRP Director will ensure that at least 10% of project funds are available at the time of these presentations so that recommendations can be incorporated into final project deliverables.

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

August 2011: Project completion; Program final report completed.

RESEARCH PROJECTS

During the fourth quarter of operation, Program Administration focused on finalizing Task Orders for all approved projects and payment of monthly invoices for active projects. Project Managers worked with the Principal Investigators (PIs) to finalize project Work Plans, which include the Statement of Work, a detailed budget, and a Quality Assurance Project Plan (QAPP). As of the end of this quarter Agreements and Task Orders were fully executed with all participating institutions and all Projects are Active.

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

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

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

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

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

Executive Summary:

In a collaboration between the University of Houston and the Chalmers University of Technology in Gothenburg/Sweden, a measurement study will be conducted which will help to locate and quantify industrial emissions of VOCs (alkanes, alkenes and other species), NO_2 and SO_2 utilizing the Solar Occultation Flux (SOF) and the mobile Differential Optical Absorption Spectroscopy (DOAS) methods. During part of the campaign, a mobile extractive Fourier Transform Infrared Spectroscopy (meFTIR) 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_x) 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 eastern Texas during which industrial emissions of VOCs, formaldehyde, NO_2 and SO_2 has been measured using the Solar Occultation Flux (SOF) and mobile DOAS methods. 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 emissions of VOCs (alkanes and alkenes) and emission of SO_2, NO_2 and in some cases formaldehyde. In addition, by using a thermal FTIR we have carried out special alkene studies on approximately 10 flares to improve our understanding on flaring.

As part of the campaign, mobile extractive FTIR measurements, canister sampling and SOF measurements of alkanes were carried out in the Fort Worth area to investigate VOC emissions associated with natural gas production within the Barnett Shale. The measurements include source identification and in many cases quantification. A large number of emission sources, including wells, compressor stations and treatment plants, were identified, and several of these were analyzed in detail carrying out tracer gas releases to quantify the emissions and canister sampling to get improved speciation of the VOC composition. In Figure 1 an example of routes traveled during the Fort Worth campaign are shown.

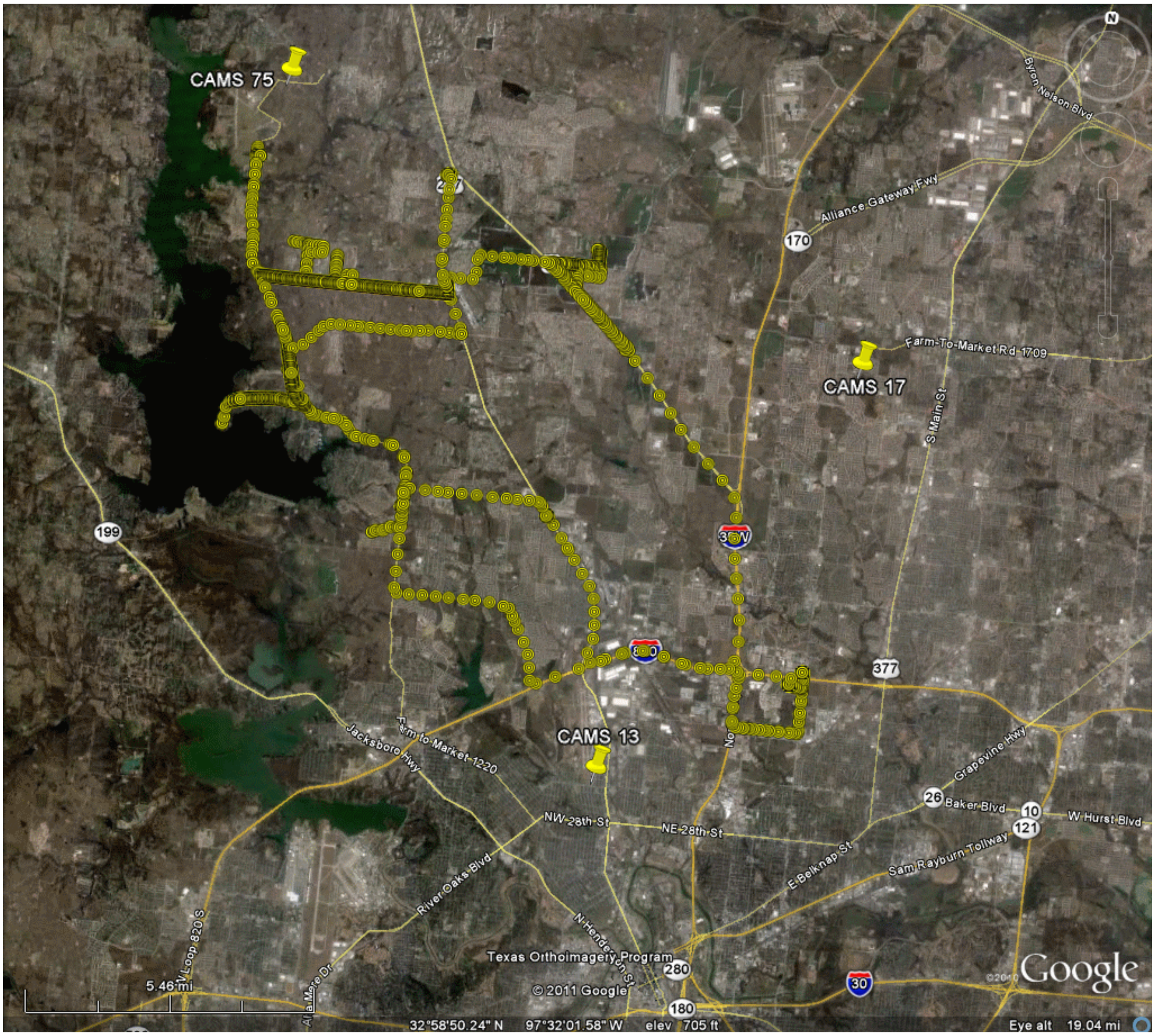


Figure 1. Example of routes traveled with a mobile extractive FTIR during campaign measurements northwest of Fort Worth area.

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. Furthermore we anticipate that the project will follow the scope of work and that all allocated funds will be used.

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

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 is on schedule. During the latest quarter, Environ developed an alternate CB-6 isoprene mechanism that produces more OH radicals at low NO_x conditions without breaking the mechanism evaluation against chamber experiments. Environ evaluated the alternate CB-6 mechanism by 6 chamber experiments using isoprene performed by UC Riverside. Performance differences evaluated by box model errors between the base and alternate CB-6 mechanisms are within experimental uncertainty range. The base and alternate CB-6 mechanisms have been used and compared in CAMx-DDM simulation of ozone concentrations and first-order sensitivities to anthropogenic NO_x and VOC emissions from five regions (DFW, HGB, Austin, San Antonio, and the rest of the 12-km domain).

Modelers at Rice are applying a Bayesian approach to weight the relative likelihood of different structural and parametric scenarios in the CAMx model by evaluating the model performance of each case against observations.

Initial screening of key structural factors identified chemical mechanism (CB-05 v. CB-6) and biogenic emissions (GloBEIS v. MEGAN) as the most influential structural factors. Within each structural scenario ozone concentrations and their first-order sensitivities to NO_x and VOC emissions from five regions (DFW, HGB, Austin, San Antonio, and the rest of the 12-km domain) have been simulated for both the June 2006 DFW episode and the Aug/Sept 2006 HGB episode. Rice also completed simulations needed for the selection of key uncertain parameters influencing ozone concentrations and its response to precursor emissions. The uncertain parameters that were studied include (1) domain-wide NO_x emission, (2) domain-wide biogenic VOC, (3) domain-wide anthropogenic VOC, (4) all photolysis rates, (5) reaction rate for

$R(NO_2+OH)$, (6) reaction rate for R(VOCs+OH), (7) reaction rate for $R(NO+O_3)$, (8) boundary condition of O_3, (9) boundary condition of NO_x, (10) boundary condition of HNO_3, (11) boundary condition of PAN, (12) boundary condition of HONO, and (13) boundary condition of N_2O_5.

The Reduced Form Model (RFM) based on Taylor expansion of sensitivity coefficients will be used to characterize O_3 concentration and responsiveness to DFW anthropogenic NO_x and anthropogenic VOC. Observed O_3 concentrations at monitors within DFW will then be used to perform Bayesian Monte Carlo analysis for selected O_3-metrics in order to determine the relative likelihood of each parametric case based on the model performance. Researchers at Rice are collaborating with a statistician and other scientists at US EPA to explore how the Bayesian Monte Carlo results compare with an alternate approach, Bayesian model averaging. The two approaches may provide complementary information for characterizing ozone concentrations and responsiveness to emission reductions in light of model uncertainties.

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

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 were 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 - The draft final report was prepared, reviewed by the TCEQ's Technical Review Panel and then submitted to the TCEQ on May 23. It was posted on May 24 for comment on the TCEQ's Flare Stakeholders' website.

Task 2 – Data from the flare tests was embargoed until early May. Limited progress was made in development of the model until then. The project is now underway and hopes to show the progress in development of the model in the next quarter.

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

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

ENVIRON International – Greg Yarwood

AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Jim Neece

Funding Requested: $201,280

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

This study 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_2 and PM chloride. Performance of the national CAMx model will be assessed to evaluate the chemistry included for $ClNO_2$ and the completeness of the chloride emission inventory. Then CAMx will be applied using a TexAQS 2006 database developed by the TCEQ.

Project Update:
Task 1. Assessment of Nitryl Chloride ($ClNO_2$) Formation in Urban Areas

Data from the TexAQS II 2006, SHARP 2009 and CalNex 2010 field studies were compiled and are under analysis with respect to the chemistry that converts dinitrogen pentoxide (N_2O_5) to $ClNO_2$. This chemistry is broken down into a series of steps with the uptake of N_2O_5 on aerosol (i.e., PM) surfaces, and the aqueous reaction of the NO_2^+ ion with NO_3^-, Cl^- or water, being the key processes. A simple box model of this chemistry is being used to refine important parameters such as uptake of the gaseous species by aerosol and the conversion efficiency of reactions within the aerosol.

Flight data from the CalNex 2010 campaign conducted in California are shown in Figure 1. The flight shown (May 31, 2010) was selected because the aircraft flew vertical profiles through the same air masses right after take-off and right before landing. Concentrations of $ClNO_2$ were higher on the descent after the passage of time had permitted formation of $ClNO_2$ to occur.

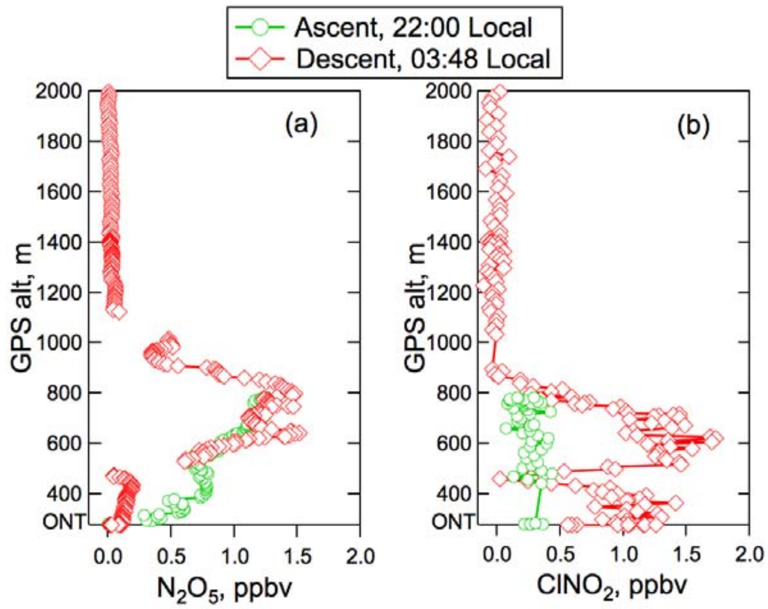


Figure 1. Measurements of N_2O_5 and $ClNO_2$ from the aircraft ascent and descent to Ontario, California, of the May 31, 2010 flight during the CalNex 2010 field study.

We have identified several other periods of contrasting $N_2O_5/ClNO_2$ chemistry, one in which showed high N_2O_5 content (> 3 ppb), with reasonable aerosol surface area (200 mm^2/cm^3) and virtually no $ClNO_2$ formed after ~9 hours, and another in which N_2O_5 had been converted to more than 3 ppb of $ClNO_2$ with only slightly higher aerosol surface area (300 mm^2/cm^3). The chief differences between these two periods were 1) the relative humidity in the first instance was only 30%, while it was above 60% during the second, and 2) the organic aerosol content was much higher in the first instance than in the second. Modeling must be able to account for differences in $ClNO_2$ formation such as these.

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

The ultimate amount of $ClNO_2$ that can be formed depends not only on the aerosol chloride availability, but also on the presence of sufficient gas-phase soluble chloride to supply the aerosol chemistry. This gas-phase chloride is thought to be almost entirely hydrogen chloride (HCl), which was measured by the NOAA group during CalNex 2010. Total soluble gas-phase chloride was measured by the University of New Hampshire (UNH) group during both the TexAQS 2006 and SHARP 2009 campaigns. A preliminary analysis on these data sets has been conducted to examine the displacement of chloride in sea salt particles by nitric acid (HNO_3).

Task 3. Modeling of Reactive Chlorine and Hydrogen Chloride

Chloride emissions in the EPA's 2006 national modeling database were analyzed as the first step in developing a national CAMx model for $ClNO_2$. EPA included anthropogenic emissions of reactive Cl (Cl_2 and HCl) hazardous air pollutant (HAP) emission inventories. We have added emissions of sea-salt PM (containing sodium, chloride and sulfate) estimated from the hourly, gridded meteorological data. Separately, EPA has estimated anthropogenic emissions of PM chloride and agreed to make them available for use in this project. Emissions of reactive Cl from swimming pools are missing from the current inventories and will be added. Emissions of reactive Cl from cooling towers have previously been estimated for the Houston region and will be added.

Figure 2 shows average daily total emissions of Cl_2 and HCl from anthropogenic sources and sea salt chloride for May and August 2006. Cl_2 and HCl emissions are similar in both months except for California where Cl_2 emissions are much higher in May than in August. PM chloride emissions are mostly concentrated in the surf zone where breaking waves generate sea salt particles.

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

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

ENVIRON International – Greg Yarwood

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

Funding Requested: $202,498

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

Project Update:
This project has four tasks:

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

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

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

Task 4 – Final Report

During this quarter efforts were focused on Tasks 2 and 3 in order to enable the start of modeling analyses as soon as possible.

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

Data collected by the P-3 aircraft during TexAQS 2006 were reviewed to identify flights which intercepted NOx source plumes at night. Two flights were identified that included intercepts of the Parish power plant near Houston on October 12, 2006 and the Oklaunion power plant near Wichita Falls, TX on October 10, 2006. The preliminary analysis identified 1) the number and location of plant intercepts; 2) their altitudes and widths; 3) their transport times from the source; and 4) their chemical composition, including the sulfur, nitrogen and ozone that are the focus of this study.

Data for the October 10 (Oklaunion plume intercepts) flight were formatted for modeling with SCICHEM. The model inputs prepared include meteorology, emissions and background concentrations. Hourly surface meteorological observations for the plume model simulations were obtained from the National Center for Atmospheric Research and upper air data were obtained from obtained from NOAA's National Climatic Data Center. Emissions data were obtained from the EPA Clean Air Markets database and are based on continuous emissions monitors (CEMS) installed at the Oklaunion power plant. Background concentrations for O_3 and other pollutants were determined from P-3 data when the aircraft was outside the power plant plume. The gas-phase chemistry mechanism in SCICHEM was updated to CB05 to make it consistent with the TCEQ's CAMx model. SCICHEM simulations for the October 10 (Oklaunion) flight have begun and attention is being turned to the October 12 (Parish) flight.

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

The Oklaunion power plant intercept data were analyzed as discussed under Task 2. This analysis included separation of plumes intercepts into those that included nighttime chemistry only, and those that included both nighttime and daytime chemistry. For the nighttime portions of the flight, the analysis has investigated reactions of NOx with O_3 to form reactive nitrogen compounds, including NO_3 and N_2O_5, and then un-reactive nitrogen compounds, such as nitric acid, which do not participate in O_3 formation chemistry on the following day. The rate at which nighttime chemistry proceeds depends upon how efficiently plume NOx mixes with ambient O_3 and proceeds via both gas-phase reactions and heterogeneous reactions on aerosol surfaces.

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

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:
In January of 2010 the USEPA proposed to strengthen the 8-hour primary National Ambient Air Quality Standards (NAAQS) for ozone to between 0.060 and 0.070 ppm and established 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 Texas. Photochemical grid models, such as the Comprehensive Air Quality Model with extensions (CAMx) that is used by the State of Texas, have a central role in the design of emission control strategies for attainment demonstrations and air quality planning. Dry deposition is the most important physical removal mechanism for ozone in Texas. Consequently, it is critical that related model algorithms be as accurate as possible in order to reduce uncertainties in predictions that will be used to implement ozone reduction strategies. Improvements in the dry deposition algorithms in CAMx are particularly important given the rapidly changing nature of urban landscapes, including increases in built environment surfaces such as roofing, building façades, 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 and predicted 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 removal by large-area outdoor built environment surfaces.
2. To characterize built environment surfaces in the Austin, Texas 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 in built environment surfaces due to future urbanization on predicted ozone concentrations in Austin, Texas.

The deliverables to TCEQ will include revised deposition information, obtained from laboratory experiments, for a minimum of sixteen materials representing a range of urban built environment surfaces. Modified CAMx code to recognize these new urban land use categories will be

provided, as well as an updated land use database for Austin, Texas, based upon the latest available geospatial information. Collectively, these deliverables should allow the TCEQ to readily adapt this work to photochemical modeling of other urban areas in Texas with similar built environment surfaces to that of Austin.

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 will be used to modify the CAMx air quality model to provide a better representation of dry deposition to the urban built environment. The experimental system used to test the reaction of ozone with materials at 90ºF and 30% relative humidity is shown in Figure 1.

A total of 223 experiments were conducted on the eighteen materials (134 of the experiments were conducted in the current quarter). Each material was tested as a new material and after two months of outdoor exposure to Austin spring weather. Surface resistances for each material are shown in Figure 2. Surface resistances are a measure of how non-reactive a material is with ozone; a high surface resistance equates to low reactivity and a small surface resistance (small bar in Figure 2) equates to high reactivity. Materials with higher surface resistance are less reactive with ozone. For example, limestone appears to be far more reactive than other materials that have been tested, and painted surfaces are far less reactive. Most of the surface resistances shown in Figure 2 are larger than typical existing CAMx urban land use surface resistances (370 s/m). This indicates that existing CAMx models may overestimate the reactivity of ozone with built urban environment materials, and possibly that ozone deposition is reduced as a result of urbanization.

Figure 1. Digital image of the experimental system used to characterize ozone reactions with built environment surfaces.

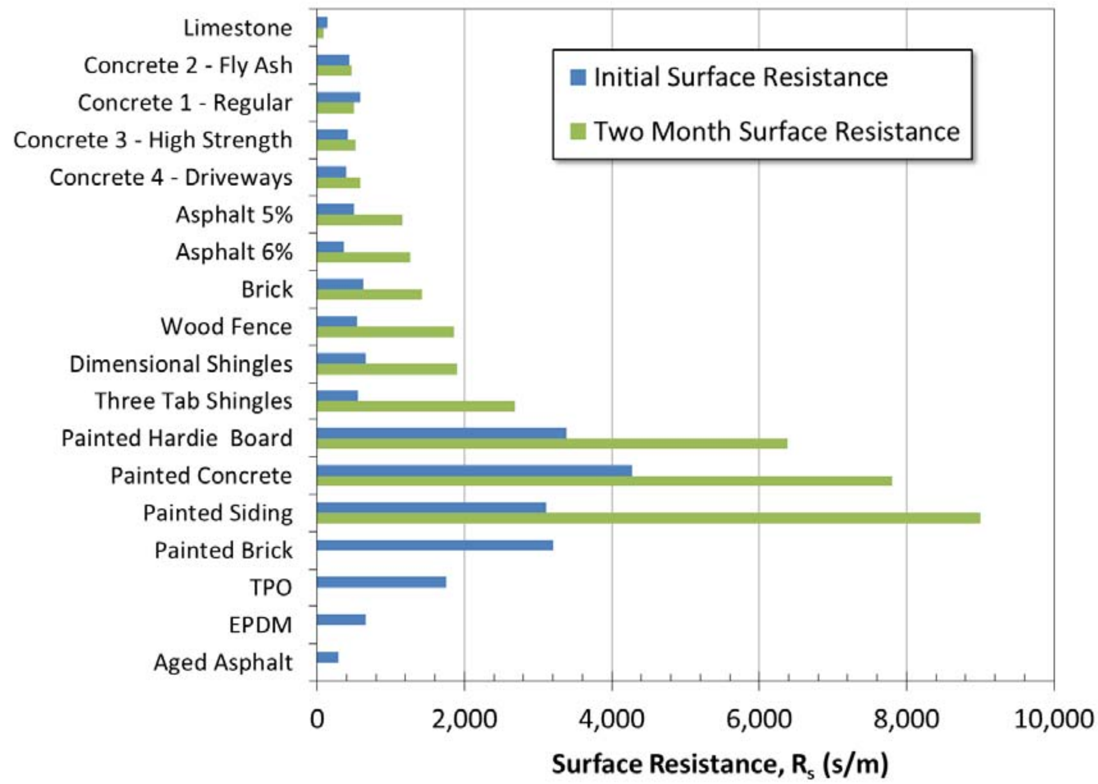


Figure 2. Average surface resistances for materials during initial and two month experiments. Materials are listed in increasing order of the two month surface resistance value. The last four materials have yet to be tested after two months of exposure.

The second component of the project incorporates the ozone surface resistances into the CAMx model. Since ozone reactions with the ground are dependent upon the area of surface, the CAMx model needed to be adapted to incorporate both the ozone surface resistances and the area of each building material in the Austin, Texas area. To do this the following steps were taken:

- Characterize built environment surfaces in the Austin urban landscape
- Pre-process the new land use/land cover data into the appropriate format for CAMx
- Modify the dry deposition algorithms in CAMx
- Model and analyze the impacts of accounting for ozone reactions with built environment surfaces on ozone concentrations.

Data collection efforts have focused on three types of built environment surfaces in Travis County: (1) paved surfaces in the transportation network and parking lots, (2) residential properties, and (3) commercial properties. Datasets were collected and surveys have been conducted by the team to provide information on the location, surface area, elevations, and types of built environment surface materials. These data were also used to guide the selection of materials for the experimental phase of the project.

Table 1 shows the siding area of single family residences by material type for Travis County. Table 2 shows similar information for single family residential roofing materials. Both were estimated using information provided by the Travis County Appraisal District (TCAD), which offered the most comprehensive and current data regarding real and business personal property in Travis County, and through surveys conducted by the project team. A survey of commercial buildings in the Austin area has been conducted and the analysis is on-going. For the Travis County transportation network, the team obtained data from the Texas Department of Transportation (TxDOT) Pavement Management Information System (PMIS) database for 2010 and the City of Austin's 2003 Transportation ArcGIS shape file. The area of surface materials in the Travis County transportation network is given in Table 3. The spatial distributions of the materials have been mapped throughout Travis County. The material types, area and locations will be joined with the experimental data to provide new input data to the CAMx air quality model.

Table 1. Siding area (km^2) of single family residences in Travis County by material type.

Material	Area (km^2) in Travis County
Asbestos	1.15
Stone	28.48
Stucco	0.81
Wood	15.42
Vinyl/Aluminum/Fiberboard	11.90
Total	57.77

Table 2. Roofing area (km^2) of single family residences in Travis County by material type.

Material	Area (km^2) in Travis County
Clay/Concrete Tile	0.34
Composite Dimensional	23.3
Composite Three Tab	26.1
Other	1.7
Total	51.44

Table 3. Surface area (km2) of transportation network in Travis County by UT transportation surface categories.

UT Transportation Surface Categories	Area (km^2) in Travis County
TxDOT_Concrete	3.07
TxDOT_Asphalt	13.99
COA_Paved_Street	77.13
COA_Parking	44.58
COA_Paved_Driveway	4.20

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

Project 10-022	STATUS: Active – February 16, 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 photo chemically 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 NOx formation and handling light hydrocarbon combustion. This Lamar mechanism has been validated against methane, ethylene, and propylene experimental data. More photochemically important NOx 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/CO2, NO, NO2, 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.

A turbulence model is needed to simulate the flare operations because turbulence enhances the mixing of momentum, energy, and reaction species. Among the many available FLUENT turbulence models, the realizable k-ε model will be chosen for our future flare CFD simulations. This model can offer benefits in dealing with crosswind and downwash conditions which may be significant in the Tulsa flare tests.

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

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

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

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

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

Executive Summary:
Ozone (O_3) 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_3 is not emitted directly from pollution sources but rather forms in the atmosphere when oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) mix in the presence of sunlight. While some amount of O_3 in the lower atmosphere is formed naturally, the amount of O_3 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_x and VOCs are automobiles and other motor vehicles and a number of large point sources, specifically electric power plants and cement kilns. However, O_3 levels have not decreased significantly in recent years despite gradual decreases in NO_x 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_x sources, leading to the hypothesis that there is a relationship between O_3 levels and natural gas activities. A team from Rice University, the University of Houston (UH), and the University of New Hampshire (UNH) 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 Forth 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 Forth Worth. Lastly, other monitoring has noted the high levels of O_3 in the northwest corner of the DFW region. The timing of the campaign was selected to optimize likely O_3 formation (due to favorable meteorological conditions), staff availability, and duration of the project.

Relevant measurements will include not only the concentrations of O_3, NO_x, and VOCs but also values for other relevant chemical and physical variables, including meteorological parameters. In addition, a group from the University of Michigan 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_3 formation in the DFW region.

Project Update:

Over the period of late February through early May, the field project teams (Rice, UH, and UNH) focused primarily on preparation for the field deployment. This included background research (including a site visit), purchasing of supplies, training of staff, and maintenance/calibration/quality control of instrumentation to be deployed. In late May, researchers began instrumentation of the site, with the deadline of being operational and collecting data of May 30. Data collection and analysis will continue through June 30, with breakdown occurring over the first two days of July. Data analysis and final reporting will occur in July and August.

Over the late February to late May time period, the UM team made considerable progress on the modeling aspects of this project. The UM team was involved in on-line discussions with the project team about the location and timing of the field campaign and the available on-site instrumentation to ensure that the necessary data to drive the computational model would be available. The UM team evaluated observed and satellite-derived land cover information for the Eagle Mountain Lake site in conjunction with literature values of VOC emissions from plants. The TCEQ has provided regional anthropogenic emission inventories. Based on these inputs, the UM team has started test simulations for a historical episode (June 2006) at the Eagle Mountain Lake site, with the goal of evaluating model sensitivities and the ability to reproduce regional chemistry. With the start of the field campaign, current meteorological and chemical data will be available, which will allow application of the model to this site during the period of the campaign. These efforts will occur over the June to July period, with final analysis and reporting occurring in August.

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

Wind Modeling Improvements with the Ensemble Kalman Filter

Texas A&M University – John Nielson-Gammon — AQRP Project Manager – Gary McGaughey; TCEQ Project Liaison – Bright Dormblaser

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.

Early in the project, the software and documentation for the Ensemble Kalman Filter system was delivered to TCEQ. Also delivered was an annotated list of references describing the evolution of this particular version of the Ensemble Kalman filter along with landmark scientific advances and findings achieved with the Ensemble Kalman Filter.

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. Work on goals 2-4 are on hold until we complete the port and verify the software system against previous results and observations.

The late start and porting issues have put the project behind schedule. At this point it is anticipated that all four goals will be achieved by the end of the project. If, on the other hand, all four goals are not met, the project may be able to return some funds to the AQRP or utilize a no-cost extension to complete the project. A firm projection of project completion will be possible in late July.

Project 10-032	STATUS: Active - February 9, 2011

SHARP Data Analysis: Radical Budget and Ozone Production

University of Houston – Barry Lefer	AQRP Project Manager – Cindy Murphy
UCLA – Jochen Stutz	TCEQ Project Liaison – John Jolly
University of New Hampshire -	

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

Executive Summary:
The chemistry of atmospheric radicals, especially the hydroxyl radical (OH) and hydroperoxyl radical (HO_2), together called HO_x, is deeply involved in the formation of secondary pollutants ozone and fine particles. Radical precursors, such as nitrous acid (HONO) and formaldehyde (HCHO), significantly affect the HO_x budget in urban environments such as Houston. These chemical processes connect surface emissions, both human and natural, to local and regional pollution, and climate change. This project 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_x) 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_x and HO_2/OH with NO_x and VOCs and compare to the model prediction.
- Quantify OH reactivity and compare observed and calculated OH reactivity to examine any missing OH sink species.
- Examine the significance of nighttime OH and determine the importance of both the reaction of O_3 + alkenes and NO_3 chemistry as nighttime OH sources.

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

Project Update:

The first task related to the "SHARP Data Analysis: Radical Budget and Ozone Production Project" was to prepare and submit the Work Plan and QAPP, which has been completed. Additional time was required to get signed Task Orders in place for all institutions receiving funds directly from AQRP (i.e., the University of Houston (UH), the University of New Hampshire (UNH), and the University of California-Los Angeles (UCLA)). The University of Houston received signed and executed Task Orders on April 27th, 2011. The UNH and UCLA task orders were finalized and executed approximately a week later. In addition, the UH Office of Contracts and Grants (OCG) is working on issuing purchase orders (POs) for the tasking being done in collaboration with scientists at The Pennsylvania State University (PSU) and the University of Miami (UMiami).

During this quarterly reporting period, the UH team has begun work on merging data from UNH and UCLA. It is also investigating the potential to use data from secondary sources, including PTR-MS (proton-transfer-reaction mass spectrometry) online sampling of VOCs.

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

Dallas Measurements of Ozone Production

University of Houston – Barry Lefer

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

Requested Funding: $195,054

Executive Summary:
The 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 NOx 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_x 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_x, 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 in the Scope of Work is to purchase and fabricate the various components of the MOPS instruments. The long lead items including the custom LED ozone instruments, the NO_2 LED photolysis cells, and the zero air generators have been ordered, as have many of the additional components needed to fabricate a MOPS instrument. The Penn State University (PSU) team has continued to optimize the design of the MOPS photochemical chambers to minimize wall interactions. Significant progress has been made in the new MOPS chamber design to minimize wall loss, but additional testing and possible design modification will probably be required, even during the initial deployment the MOPS system.

Task 2 was to identify CAMS sites with AQRP and TCEQ for potential MOPS deployment and conduct a site visit. Eagle Mountain Lake (C75) is an example of a downwind receptor site in area of active natural gas wells that has experienced high ozone levels in the past. The C75 site may experience a combination of locally produced ozone and transported ozone. This site also has an AutoGC which will aid in interpretation and modeling of ozone production.

The 2nd Generation MOPS flow diagram (Figure 1) gives a general overview of the new instrument design. One significant change is the incorporation of two ozone analyzers that will enable the new MOPS instrument to also measure Ox (the sum of O_3 and NO_2) directly.

All of the electrical components and their related connections have been mapped out in Figure 2. Many instrument “housekeeping” variables such as temperature, flowrate, and relative humidity will be monitored at multiple locations. The instrument will be controlled by a National Instruments LabVIEW code currently being constructed by Penn State. The data PC is a low powered fanless Stealth PC with a solid state memory disk. The overall physical design of the MOPS-2 instruments (Figure 3) shows the extruded aluminum rack with PC, ozone instruments, flow controllers, etc. This aluminum rack scaffold will be covered by 1/8” aluminum sheet and rubber gasket material to provide a waterproof enclosure. Note that the upper/top chamber is the “Solar Exposed” cell, and the lower/bottom chamber is the “shaded” MOPS cell.

It is important to note that the design shown in Figure 3 incorporates the new custom LED ozone instruments being built by the University of Colorado. Figure 3 does not include the zero air generator and air conditioning units that will be installed several meters away from the MOPS-2 sensor tower.

As a result of complex nature of the AQRP agreement the execution of the Task Orders took longer than anticipated. The original project schedule had a minimum of five months to complete Task 1: the purchase and fabricate various components of the two MOPS instruments to be deployed in the DFW region. Much of this five-month lead-time is constrained by the acquisition of the custom LED ozone instruments. Since the custom LED ozone instruments will not be available until the end of July, two standard commercial TECO 49C instruments will be utilized for the initial MOPS-2 instrument testing and deployment. The short term goal is to have this preliminary version of the MOPS-2 instrument deployed to the Eagle Mountain Lake site in mid- to late-June 2011.

At this time we do not anticipate that any funds might be returned as a release of claims from the research team.

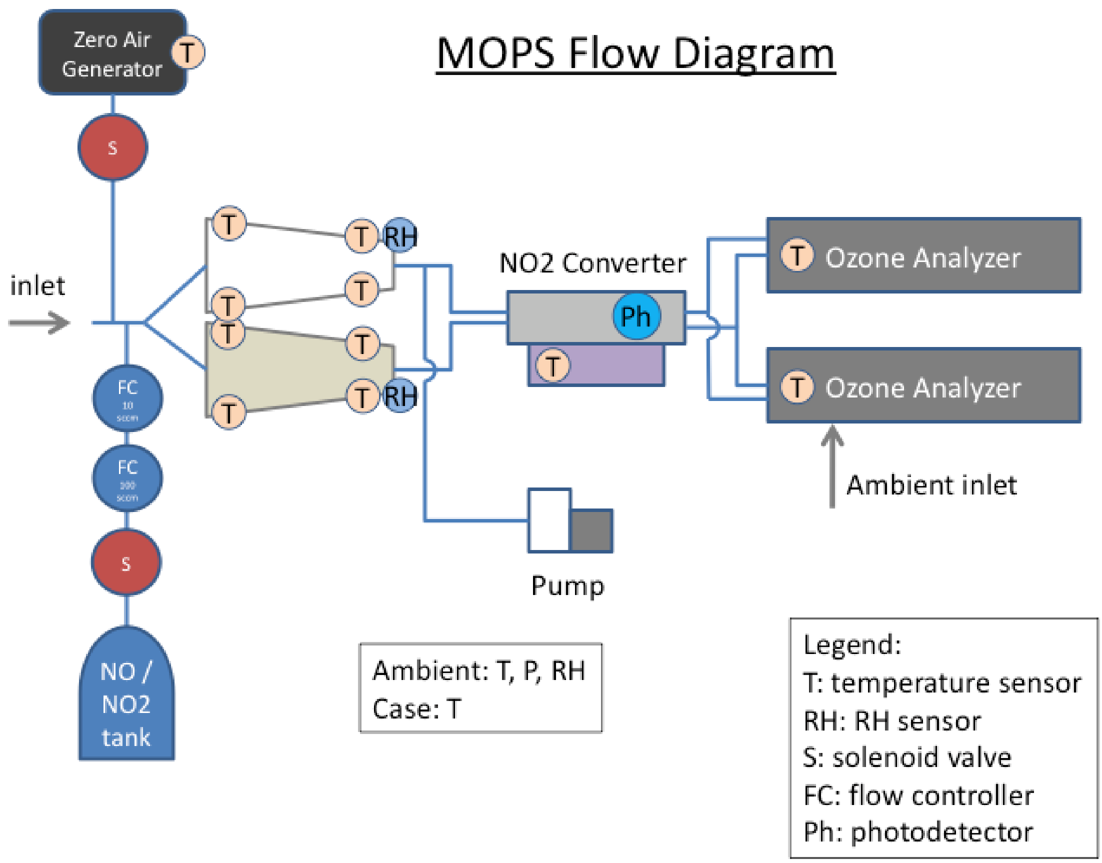


Figure 1. New MOPS Flow Diagram (by David O. Miller, PSU).

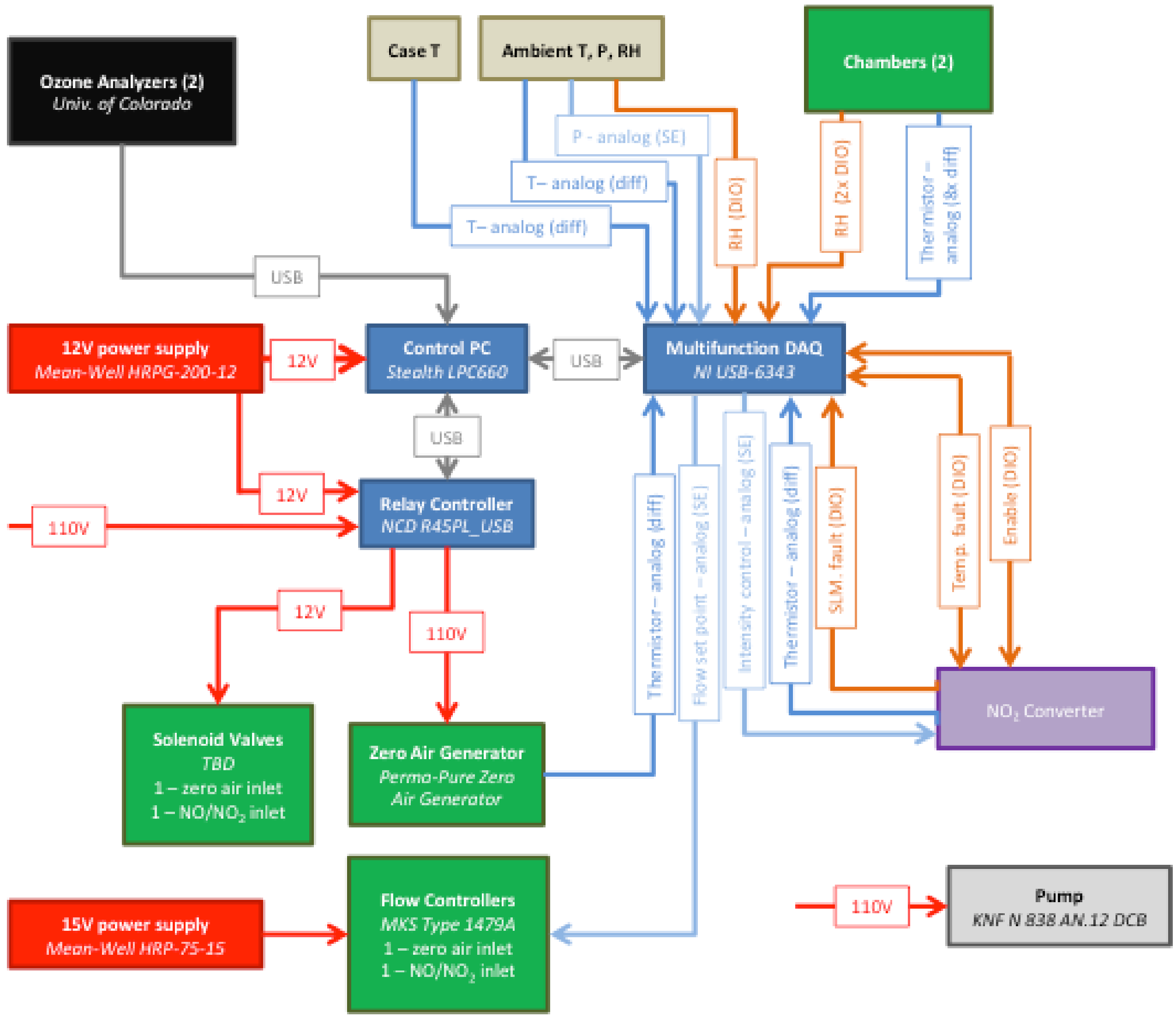
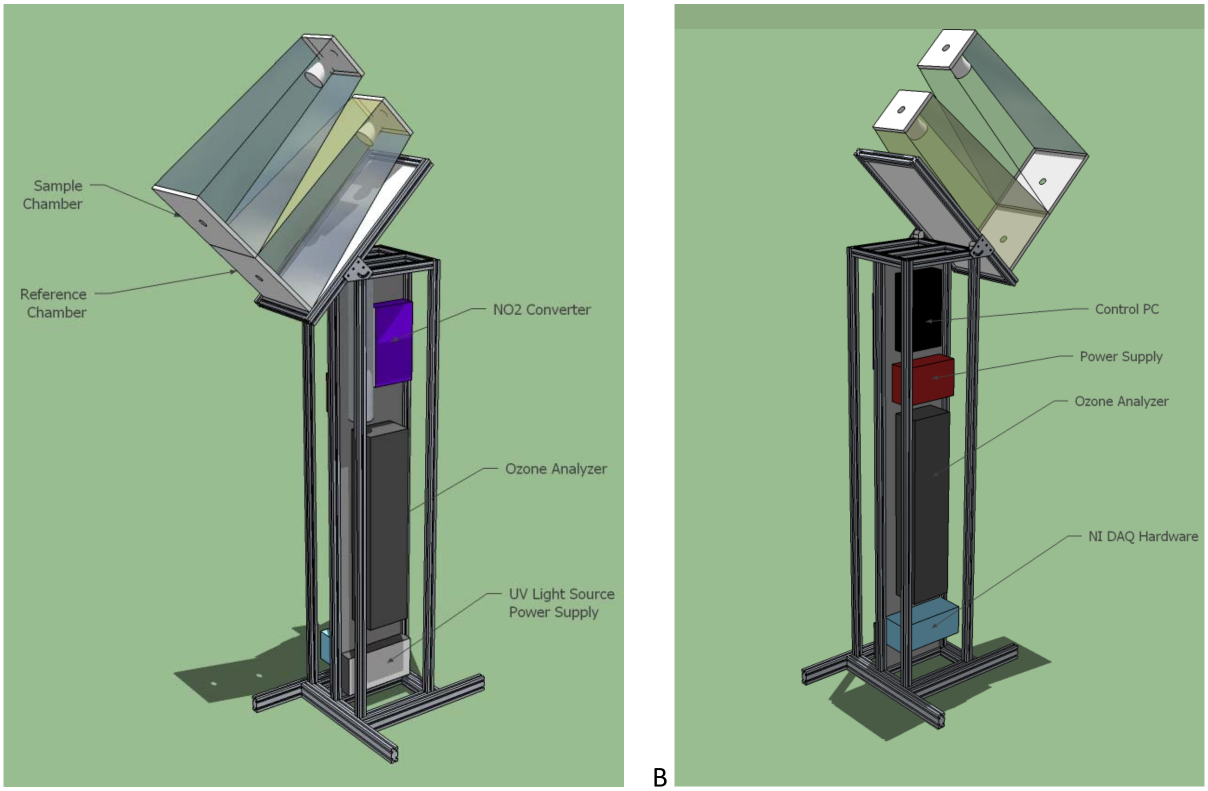


Figure 2. MOPS-2 Power and Electrical Connections Overview (by David Miller, PSU).



A B

Figure 3. East (A) and West (B) views of the MOPS-2 instrument (David Miller, PSU).

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

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 – Jim Neece

Funded Amount: $237,481

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

Project Update:

Experiments Carried Out

During this quarter a total of 32 environmental chamber experiments (each yielding results from sides A and B of the chamber) were carried out to investigate NOx-sinks and sources. Of these experiments, 15 were for control experiments for chamber testing and characterization, 12 were for NOx-sinks and 5 were for NOx-sources. The NOx-sink experiments investigated the test compounds toluene, toluene degradation products (cresol, butenedial) and isoprene. The NOx-source experiments investigated the test compounds isopropyl nitrate, isobutyl nitrate and 2-nitrophenol. All experiments for this project were completed during this reporting period.

Control experiments. Several control experiments were carried out to test for side equivalency, obtain data to test NOx measurement methods, obtain data concerning the base case for the NOx sink experiments, and to test methods to measure the impact of chamber walls on NOx. Also, several experiments were carried out with isoprene to provide needed mechanism evaluation data for isoprene at low concentration levels.

NOx sink experiments. Most of these used a base mixture of 1 ppm ethene and 15 ppb NOx with toluene, furan, o-cresol, or isoprene added to Side A of the dual chamber to determine the effects of the added reactant on final O_3 and NOx levels. One experiment with toluene as the test compound used 0.3 ppm propene in place of 1 ppm ethene in order to evaluate the effect of changing the base mixture. The NOx was injected either as NO or NO_2. Addition of the test compounds to Side A decreased the maximum O_3 concentration on Side A compared to Side B of the chamber, indicating that all these compounds have NOx sinks which consume NOx and therefore reduce O_3 formation.

NOx-source experiments. These experiments introduced the test compound (e.g., 2-nitrophenol) with hydrogen peroxide as a source of OH radicals to react with the test compound. NOx formed by decomposition of the test compound was detected either as NO_2 or by introducing another VOC that promotes PAN formation (e.g., acetaldehyde) from NO_2 and then measuring the amount of PAN formed. NOx was formed in experiments with each of the test compounds and the results are being analyzed to quantify the amount of NOx formed from each compound.

Preliminary Analysis

Ozone formed in some of the NOx-sink experiments is shown on Figure. The symbols labeled base experiment are for Side B of the chamber with just the base mixture of ethene and NOx. The symbols labeled test experiment are for Side A of the chamber with the test compound added to ethene and NOx. The fact that O_3 is lowered by addition of the test compound demonstrates that NOx sinks can decrease O_3 formation, and the magnitude of the O_3 decreases indicates the strength of the NOx-sink for each compound tested. Model results also shown in Figure 1 are for a developmental version of the SAPRC mechanism. Model performance for O_3 is reasonably good for toluene and isoprene, fair for o-cresol but not satisfactory for furan. Furan is used because it is expected to promptly form butenedial (which is a degradation product from aromatics) in near-100% yield, so it provides a means to test mechanisms for butenedial and related compounds. During the next quarter work will focus on improving the performance of current chemical mechanisms in simulating NOx-sinks and NOx-sources for the compounds tested.

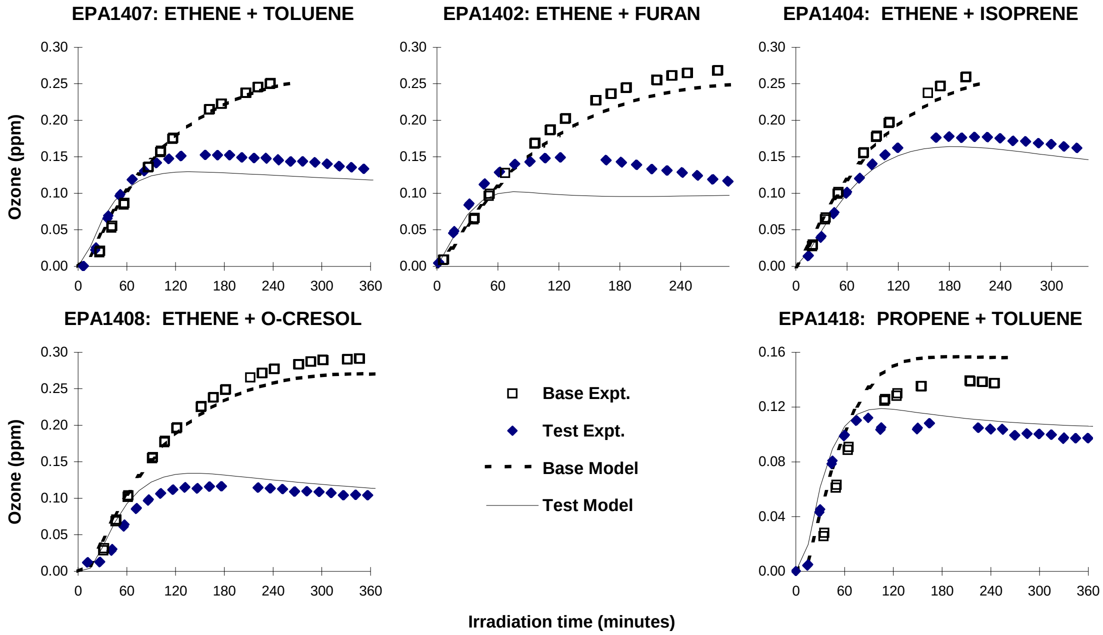


Figure 1. Ozone formation in NOx sink experiments carried out during the period of this report. "Base experiment" refers to the ethene - NOx irradiation, and "test experiment" refers to the irradiation with the test compound added. Model simulations were using a developmental version of the SAPRC mechanism.

Issues as related to the project during the reporting period:

The UCR environmental chamber has two alternate sources of UV radiation for conducting experiments, an arc light and black lights. The arc light approximates the spectrum of solar radiation whereas the black lights are designed to produce UV light and so have a different spectrum than natural sunlight. The arc light source has experienced problems as reported in the previous quarterly report. Despite repair attempts and assistance from the manufacturer, UCR was unable to get the arc light to operate consistently. Consequently, experiments for this project have been completed using black lights. Although experiments using black lights are considered less desirable than arc light experiments, the experiments completed for this project are providing useful information for mechanism evaluation and development. Problems with the arc light delayed the project schedule by about 2 months, but the project can still be completed on schedule.

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

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

University of Houston – Maxwell Shauck

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

Funding Requested: $279,642

Executive Summary:
The University of Houston (UH) aircraft-based Air Quality Monitoring Team 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:
Work began on April 14, 2011. The team is currently deploying to McGregor Airport in McGregor, Texas. McGregor Airport provides the necessary support equipment and hanger and is an ideal base in the event of any problems that develop during the initial portions of the field program. All team members were in the field as of May 28 and ready to begin field operations on May 30, 2011.

During April and May, the aircraft annual inspection and the instrumentation suite assembly and design for aircraft certification were completed. Aircraft parts and supplies and spare parts for instrumentation were ordered as necessary. All instrumentation was installed aboard the aircraft and certified according to FAA regulations. General functional tests on all air chemistry instruments have been performed, and pre-season calibration and system checks are on-going. Five hours of aircraft flight tests have been performed and testing of the air chemistry platform and instrumentation pressure calibration is ongoing.

During April and May, seven pre-planned flights were provided by the AQRP Project Manager (Gary McGaughey) and have been reviewed by the UH aircraft team. In addition, UH developed a plan to sample the Big Brown and Limestone power plant plumes during southeasterly wind conditions. An example pre-planned flight is attached as Figure 1.

The flight team has discussed flight planning operations with the AQRP Project Manager and will participate in daily 1300 CDT mini-DFW field campaign calls that begin May 30, 2011. Based on the meteorological and air quality forecasts reviewed on the call, the aircraft team and AQRP will determine possible flight days. The flight planning will be based on the pre-planned flights but will be customized for the specific forecast weather conditions. The customized flight plan will be provided to the AQRP Project Manager for review and approval prior to the actual flight. On flight days, an additional pre-flight conference call will be held to confirm both aircraft readiness and the weather forecast.

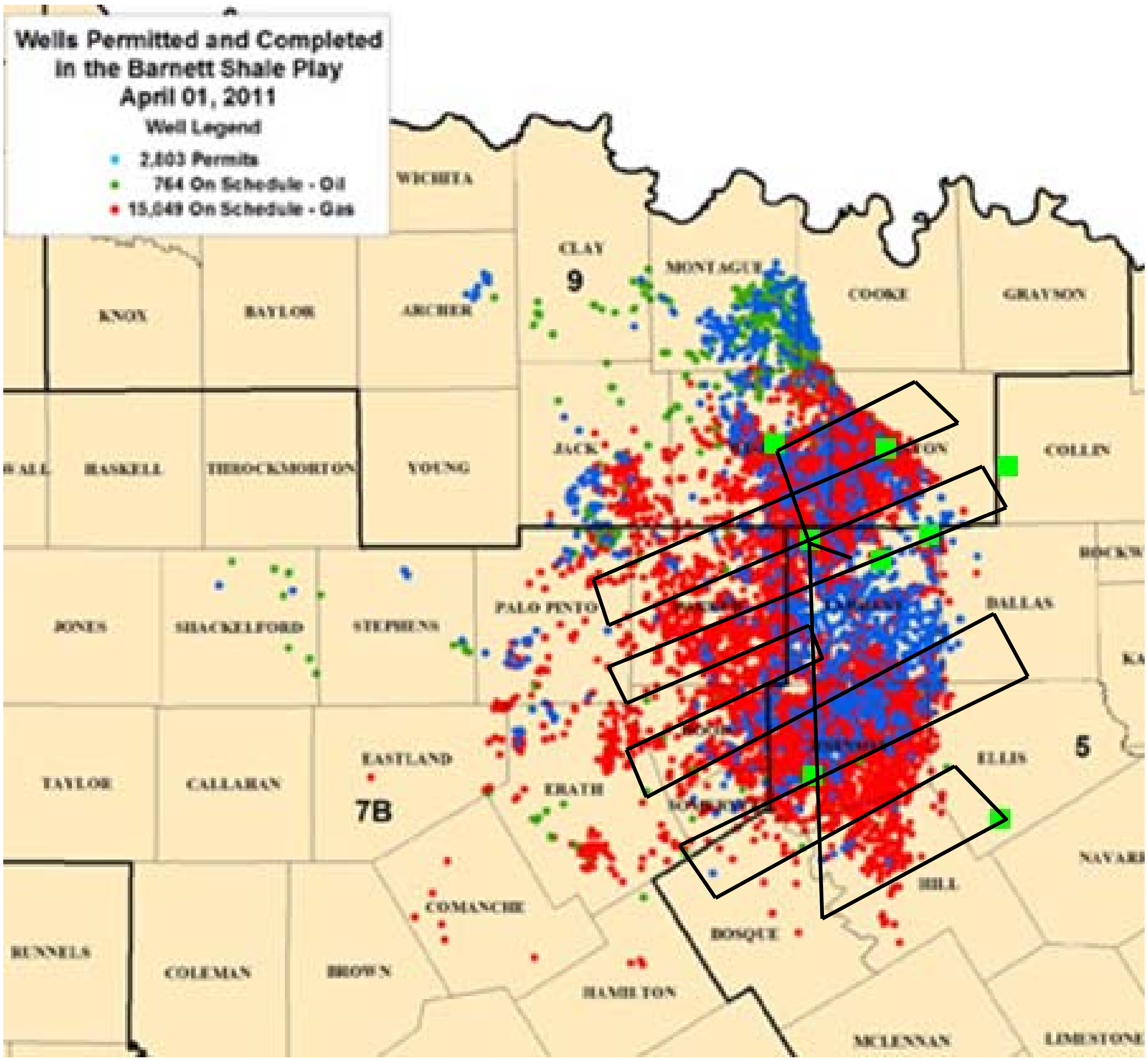
Any delays or issues as related to the projects during the reporting period:

The calibration gases were ordered on April 14, 2011 from Scott Marrin, Inc. The order was expedited and the calibration gas cylinders were received on May 11, 2011. Additional technical issues have surfaced with the CO instrument. Work to resolve this issue is ongoing in collaboration with Aero Laser, the manufacturer of the CO instrument. The flight program was originally scheduled to be conducted during mid-May through mid-July but will now begin May 30, 2011.

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

No funds are estimated to be returned.

Figure 1. Pre-Planned Flight #6: Large-scale Barnett Shale survey on days with near-surface winds from the south-southeast. Wind speeds should be low. Overcast conditions: mapping of NOx and VOC plumes. Sunny conditions: mapping of ozone.



- Black line shows estimated flight track.
- Green squares show locations of selected ground monitoring stations.

[Basemap downloaded from the Railroad Commission of Texas (http://www.rrc.state.tx.us/barnettshale/countyproducing.php) on April 21, 2011.]

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

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

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

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

Funding Awarded: $398,401
($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_x) 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_2. Two Multi-Axis Differential Optical Absorption Spectrometers (MAX-DOAS) operated by UCLA and Washington State University (WSU) sampled air masses upwind and downwind of a large petrochemical complex in order to determine facility-wide emissions of HCHO and NO_2. As a result of all above mentioned efforts, a unique observational dataset of VOCs, HCHO, and NO_x 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_x, 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_2, HCHO, and SO_2 using dual MAX-DOAS data acquired during FLAIR 2009.

3. Characterize source-and date-specific fluxes of HCHO, NO_2 and SO_2 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:

Task 1: Determination of facility averaged fluxes of NO_2, HCHO, and SO_2 in Texas City using dual MAX-DOAS data acquired during FLAIR 2009. – UCLA and WSU

During this reporting period the UCLA and WSU groups completed the development of the spectral retrieval procedures for the MAX-DOAS NO_2, HCHO, SO_2 and O_4 path integrated concentrations collected during the 2009 FLAIR campaign. The groups coordinated spectral evaluation parameters as well as literature reference absorption cross sections. Spectral analysis for O_4, critical to determination of optical path lengths, has been completed by both groups. In addition the WSU group has completed the analysis of their SO_2 and NO_2 data and an improved re-analysis of the HCHO data. Thus, all of the species data collected in Texas City has been analyzed by both groups.

The observed path-averaged trace gas concentrations, i.e. trace gas slant column densities, depend on the atmospheric absorption pathlength, i.e. the radiative transfer (RT) of sun light through the atmosphere. The original experimental approach for the dual MAX-DOAS method was based that the assumption that the RT conditions south and north of the Texas City complex would be similar and that path lengths could be approximated by geometrical application. However, the proximity to the coast may have caused a change in the RT conditions within the 2.8 km that the two instruments were separated. There were clear micrometeorological conditions that occurred in the Texas City area during the 2009 campaign that would have affected photon paths differently at the two sites which make the RT commonality assumption incorrect, and the meteorological conditions experienced clearly voided the geometrical assumptions made at that time. The ongoing comparison of the measurements of the slant column densities of the O_2-O_2 collision complex, O_4, provides an estimate of how similar or different RT conditions are at two locations, since the O_4 vertical profile is well known and constant in time. A qualitative comparison shows that both MAX-DOAS sites experienced a variety of RT conditions during FLAIR, ranging from relatively “simple” clear sky conditions (for example April 24, 2009) to more complex days with broken cloud cover (for example May 06, 2009) that made the optical paths radically different at the two sites. In the next months RT calculations will be performed so that the slant column density observations of HCHO, NO_2, and SO_2 can be corrected for RT effects, and thus enable determination of the facility-averaged fluxes of these compounds.

Task 2: Determination of source specific fluxes of HCHO, NO_2, HONO, and SO_2 from point sources in Houston based on I-DOAS observations during FLAIR. - UCLA

During this quarter, a number of I-DOAS observations were re-analyzed in order to improve detection of individual emission plumes. The analysis software was further improved to plot the results of the I-DOAS spectral retrievals more efficiently and to estimate emission fluxes based on the I-DOAS images and meteorological data.

I-DOAS observations were crossed-references with those from the ARI mobile lab during the times when both groups performed simultaneous observations, in order to refine the comparison between the two platforms. First, this comparison was applied to the observations of ship plumes in the Houston Ship Channel on May 28, 2009. The methodology and algorithm of the comparison will be applied to other source areas, for example in Texas City. The quantification of ship emissions is also of scientific interest as HCHO and HONO emissions are currently not well quantified, but are suspected to contribute to anthropogenic pollution in the Houston area. As one of the main results of this effort the previously unknown HONO/NO_X emission ratios were determined to be in the range of 0.5 – 0.7%, similar to literature values for non-ship diesel engines.

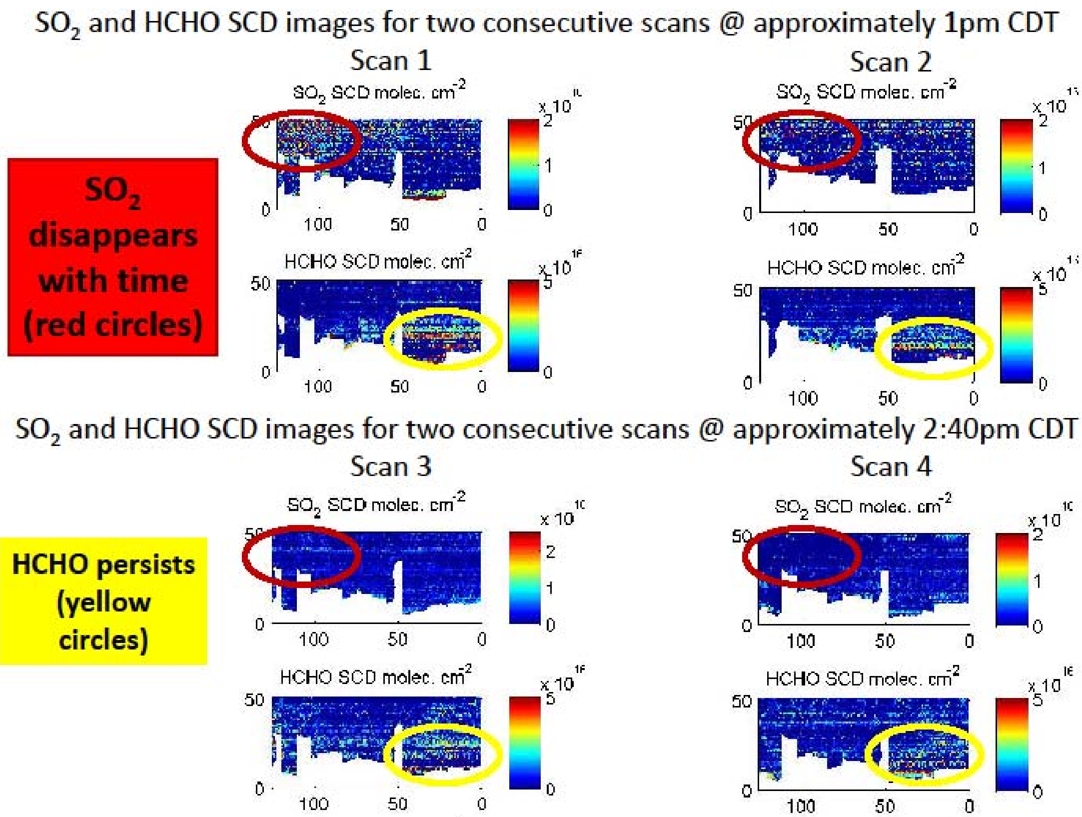


Figure 1. Example of SO_2 and HCHO SCDs images taken by I-DOAS instrument in Texas City on May 06, 2009. White shadows on SCD images are obstructions - buildings of the observed facilities.

I-DOAS data collected in Texas City was examined in order to identify/locate pollution sources. Several days of I-DOAS observations from different locations were combined in order to "triangulate" specific source areas of the Texas City industrial complex from where HCHO enhancements originated. The identification of the HCHO source area is important for the flux determination from the I-DOAS measurements in Texas City, as the distance between pollution source and I-DOAS instrument have to be taken into account for the flux calculation. This analysis also revealed that emissions observed by the I-DOAS in the Texas City complex, were variable in time. Figure 1 which shows an example of I-DOAS slant column density, SCD, images for SO_2 and HCHO over the Texas City industrial complex taken over a period of ~3.5 hours on May 6, 2009. SO_2 plumes observed during the first scan (red circle on SO_2 SCD image from scan 1) was smaller during the scan 2, and was no longer detected during scans 3 and 4, 1.5 hours later. At the same time, formaldehyde plume persisted throughout all scans (yellow circles on HCHO SCD images).

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

Alkene plumes observed in the Mount Belvieu area on May 21, 2009 were investigated in order to determine HO_X production rates ($P(HO_X)$) and OH concentration in the plume. The OH concentration in the alkene plumes is an important to determine the rate at which alkenes are oxidized and produce ozone and formaldehyde as by-products. Steady-state calculations resulted in the lower limit for OH concentration in the plume of 1.7×10^5 molecules/cm^3.

In addition, the data collected by the ARI mobile laboratory in the Texas City industrial complex was finalized. This work involved applying calibration factors and refitting spectra recorded by the quantum cascade tunable infrared laser differential absorption spectrometers (QC-TILDAS)for measurement of HCHO, CO, NO_2, and C_2H_4. Work was also performed to identify and flag periods where the mobile lab sampled its own exhaust.

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

The UNC team has identified the relevant grid cells encompassing Texas City in the TCEQ regulatory modeling domain. Maps have been created overlaying model grid cells on a GIS shapefile for future reference. Using these grid cells UNC extracted emission inventory data created by the TCEQ, and named "Reg 10." This is a "basecase" emission inventory used to determine model performance in the recently submitted state implementation plan for southeast Texas. This inventory has data for dates that include May through July 2005, and June through September 2006, with a special inventory for 8/15 - 9/15/06. The extracted data includes HRVOC, NMVOCs, NO_X, and formaldehyde emission rates from grid cells and point sources.

Inverse model calculations were performed by the ARI group in order to determine emission rates for ethylene and propylene using measurements from the Aerodyne Mobile Lab from May 24, 2009 at Mont Belvieu. Modeling was performed using multiple consecutive mass releases emitted from each location over the course of the studied measurement period. The reason to use multiple releases, as opposed to one long release, is the ability to represent episodic releases. Average emission rates were calculated as the total mass from each potential release location divided by the total duration of the release. In previous calculations, these averages were skewed by non-impacting releases; i.e. emission episodes predicted to occur at locations and times such that they were never detected by the ARI mobile laboratory. The correction in the new calculation consists of discarding such modeled release episodes that, based on wind direction and truck location, have no possibility of impacting the truck. Consequently, the revised estimated emission rates for ethylene and propylene are higher than those previously reported.

DFW Field Study Committee

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).

Regular conference calls have continued throughout the reporting quarter to facilitate the planning and coordination of the DFW Field Study. On April 28, 2011, a Surface Use Agreement was fully executed between UT and the Adjutant General's Office allowing the field study to commence at Eagle Mountain Lake. Site Access Agreements were put in place with each of the participating institutions and work began to prepare the site, install power, and install fencing. Teams began setting up equipment at the Site in mid-May and on May 30. 2011, operations officially began.

Vincent Torres is acting as the lead AQRP Project Manager for the Committee, handling the site logistics and site access agreement negotiation.

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, issuing Task Orders, and invoicing functions. Mr. Denzil Smith is responsible for the AQRP Web Page development and for data management.

Table 1: AQRP Administration Budget

Administration Budget (includes Council Expenses)

Budget Category		FY10	FY11	Total	Expenses	Pending Expenses	Remaining Balance
Personnel/Salary		$173,100	$148,755	$321,855	$221,984.85	$20,461.00	$79,409.15
Fringe Benefits		$38,082	$32,726	$70,808	$40,042.63	$4,710.10	$26,055.27
Travel		$8,500	$7,500	$16,000	$346.85		$15,653.15
Supplies		$34,215	$2,744	$36,959	$12,418.77		$24,540.23
Equipment		$6,000	$0	$6,000			$6,000.00
Other			$4,007	$4,007			$4,007.00
Total Direct Costs		$259,897	$195,732	$455,629	$274,793.10	$25,171.10	$155,664.80
Authorized Indirect Costs		$17,310	$14,876	$32,186	$21,470.58		$10,715.42
10% of Salaries and Wages							
Total Costs		**$277,207**	**$210,608**	**$487,815**	**$296,263.68**	**$25,171.10**	**$166,380.22**
Fringe Rate		22%	22%				

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 December and January are included in the spreadsheet above. February 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. In addition, a computer was purchased to serve as a data server for AQRP project data, and a color printer with toner was purchased for report preparation.

Indirect costs for the months of March and April are included in Table 1. May indirect costs have not posted as of the writing of this report.

At the initiation of the AQRP, funds were budgeted and expenses were projected based on assumptions made with the information known at that time. As the AQRP has progressed, spending decisions and staffing allocations have been made to most efficiently meet the needs of the program. Since the program started later than anticipated, the contracting and other program start-up activities have been pushed into FY 11 and concentrated into a shorter period of time. Thus the amount of time (FTE) spent on the program in FY 10 was reduced and the amount of time (FTE) those individuals working within the Administrative roles are spending on necessary program start-up functions has increased in FY 11. Their original percent time was estimated and divided between FY 10 and FY 11. As stated above, these tasks still need to be completed within FY 11 and thus the increase of FTE within FY 11

As these start-up activities are essential, 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.

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							
Total Costs		**$18,864**	**$19,400**	**$38,264**	**$9,239.83**	**$0.00**	**$29,024.17**

Project Management

Project Managers (PMs) have been assigned to each of the research projects. During the period from March 1, 2011 through May 31, 2011, PMs have worked with PIs to complete project Work Plans and begin the Monthly Technical Reporting as projects became active. At the end of the current reporting period all projects were active and the role of the PM evolved to helping the PIs accomplish project goals and ensuring 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.

Currently, all of the expenses relating to the DFW Field Study Site preparation have been allocated to the Project Management account. Per direction from the TCEQ, in June the AQRP will establish two separate Research Projects for the DFW Field Study Site, one in the FY 10 account and one in the FY11 account. The expenses currently charged to Project Management will be moved to these new accounts. It is anticipated that the expenses related to the DFW Field Study Site will fully utilize the unallocated Research Project funds in FY 10 and FY 11.

Table 3: Project Management Budget

Project Management Budget

Budget Category		FY10 Budget	FY11 Budget	Total Budget	Expenses	Pending Expenses	Remaining Balance
Personnel/Salary		$139,653	$101,011	$240,664	$137,080.58	$10,430.64	$93,152.78
Fringe Benefits		$30,725	$22,223	$52,948	$23,322.49	$3,230.15	$26,395.36
Travel		$4,000	$5,200	$9,200	$3,055.82		$9,200.00
Supplies		$1,657	$1,465	$3,122	$2,241.95		$880.05
Equipment							
Other							
Contractual							
Total Direct Costs		$176,035	$129,899	$305,934	$165,700.84	$13,660.79	$126,572.37
Authorized Indirect Costs		$13,965	$10,101	$24,066	$11,600.21		$12,465.79
10% of Salaries and Wages							
Total Costs		**$190,000**	**$140,000**	**$330,000**	**$177,301.05**	**$13,660.79**	**$139,038.16**

Research Projects

As of May 31, 2011, all projects are 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 May 31, 2011.

The projects that have the Cumulative Expenditures and Remaining Balance shadowed have not yet submitted their initial invoices.

At this time, it is anticipated that all funding for research projects will be allocated to the projects listed above or to the DFW Field Study. It is still early in the Program, but it is anticipated that all Program funds will also be used.

Table 4: Contractual Expenses

Contractual Expenses				
FY 10 Contractual Funding		**$2,286,000**		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
10-008	Rice University	$128,851	$71,023	$57,828
10-008	Environ International	$49,945	$44,790	$5,155
10-009	UT-Austin	$591,332	$510,276	$81,056
10-021	UT-Austin	$248,786	$152,082	$96,704
10-022	Lamar University	$150,000		
10-032	University of Houston	$176,314		
10-032	University of New Hampshire	$23,054		
10-032	UCLA	$49,284		
10-034	University of Houston	$195,054	$5,837	$189,217
10-042	Environ International	$237,481	$133,042	$104,439
10-045	UCLA	$149,773	$27,290	$122,483
10-045	UNC - Chapel Hill	$33,281	$3,615	$29,667
10-045	Aerodyne Research Inc.	$164,988	$57,566	$107,422
10-045	Washington State University	$50,000	$7,356	$42,644
FY 10 Total Contractual Funding Awarded		$2,248,143		
FY 10 Contractual Funding Remaining to be Awarded		$37,857		
FY 10 Contractual Funds Expended to Date*			$1,012,876	
FY 10 Contractual Funds Remaining to be Spent				$1,273,124

FY 11 Contractual Funding		$1,736,063		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
10-006	Chalmers University of Tech	$262,179	$21,240	$240,939
10-006	University of Houston	$222,483	$64,732	$157,751
10-015	Environ International	$201,280	$5,501	$195,779
10-020	Environ International	$202,498	$15,006	$187,492
10-024	Rice University	$225,662		
10-024	University of New Hampshire	$70,747		
10-024	University of Houston	$64,414		
10-024	University of Michigan	$98,134	$6,227	$91,907
10-029	Texas A&M University	$80,108	$31,708	$48,400
10-044	University of Houston	$279,642		
FY 11 Total Contractual Funding Awarded		$1,707,147		
FY 11 Contractual Funding Remaining to be Awarded		$28,916		
FY 11 Contractual Funds Expended to Date*			$144,413	
FY 11 Contractual Funds Remaining to be Spent				$1,591,650
Total Contractual Funding		$4,022,063		
Total Contractual Funding Awarded		$3,955,290		
Total Contractual Funding Remaining to be Awarded		$66,773		
Total Contractual Funds Expended to Date*			$1,157,290	
Total Contractual Funds Remaining to be Spent				$2,864,773

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

Appendix

Financial Reports by Fiscal Year

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

Administration Budget (includes Council Expenses)
FY 2010

Budget Category		FY10 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$173,100	$163,740.49	$6,615.00	$2,744.51
Fringe Benefits		$38,082	$30,852.02	$3,071.54	$4,158.44
Travel		$8,500	$346.85		$8,153.15
Supplies		$34,215	$12,418.77		$21,796.23
Equipment		$6,000			$6,000.00
Other					
Contractual					
Total Direct Costs		$259,897	$207,358.13	$9,686.54	$42,852.33
Authorized Indirect Costs		$17,310	$16,344.33		$965.67
10% of Salaries and Wages					
Total Costs		**$277,207**	**$223,702.46**	**$9,686.54**	**$43,818.00**

Administration Budget (includes Council Expenses)
FY 2011

Budget Category		FY11 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$148,755	$58,244.36	$13,846.00	$76,664.64
Fringe Benefits		$32,726	$9,190.61	$1,638.56	$21,896.83
Travel		$7,500			$7,500.00
Supplies		$2,744			$2,744.00
Equipment					
Other		$4,007			$4,007.00
Contractual					
Total Direct Costs		$195,732	$67,434.97	$15,484.56	$112,812.47
Authorized Indirect Costs		$14,876	$5,126.25		$9,749.75
10% of Salaries and Wages					
Total Costs		**$210,608**	**$72,561.22**	**$15,484.56**	**$122,562.22**

ITAC Budget
FY 2010

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

ITAC Budget
FY 2011

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

Project Management Budget
FY 2010

Budget Category		FY10 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$139,653	$129,868.60	$5,125.64	$4,658.76
Fringe Benefits		$30,725	$23,322.49	$3,054.23	$4,348.28
Travel		$4,000	$3,055.82		$944.18
Supplies		$1,657	$2,241.95		($584.95)
Equipment					
Other					
Total Direct Costs		$176,035	$158.488.86	$8,179.87	$9,366.27
Authorized Indirect Costs		$13,965	$11,600.21		$2,364.79
10% of Salaries and Wages					
Total Costs		**$190,000**	**$170,089.07**	**$8,179.87**	**$11,731.06**

Project Management Budget
FY 2011

Budget Category		FY11 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$101,011	$7,211.98	$5,305.00	$88,494.02
Fringe Benefits		$22,223		$175.92	$22,047.08
Travel		$5,200			$5,200.00
Supplies		$1,465			$1,465.00
Equipment					
Other					
Total Direct Costs		$129,899	$7,211.98	$5,481.92	$117,206.10
Authorized Indirect Costs		$10,101			$10,101.00
10% of Salaries and Wages					
Total Costs		**$140,000**	**$7,211.98**	**$5,481.92**	**$127,307.10**

AQRP Budget

FY 2010

Budget Category		FY10 Budget	Cumulative Expenditures	Pending Expenditures	Remaining Balance
Personnel/Salary		$173,100	$163,740.49	$6,615.00	$2,744.51
Fringe Benefits		$38,082	$30,852.02	$3,071.54	$4,158.44
Travel		$8,500	$346.85	$0.00	$8,153.15
Supplies		$34,215	$12,418.77	$0.00	$21,796.23
Equipment		$6,000	$0.00	$0.00	$6,000.00
Other		$0	$0.00	$0.00	$0.00
Contractual		$2,286,000	$1,012,876.48	$0.00	$1,273,123.52
ITAC		$18,864	$9,239.83	$0.00	$9,624.17
Project Management		$190,000	$170,089.07	$8,179.87	$11,731.06
Total Direct Costs		$2,754,761	$1,399,563.51	$17,866.41	$1,337,331.08
Authorized Indirect Costs		$17,310	$16,344.33	$0.00	$965.67
10% of Salaries and Wages					
Total Costs		**$2,772,071**	**$1,415,907.84**	**$17,866.41**	**$1,338,296.75**

AQRP Budget

FY 2011

Budget Category		**FY10 Budget**	**Cumulative Expenditures**	**Pending Expenditures**	**Remaining Balance**
Personnel/Salary		$148,755	$58,244.36	$13,846.00	$76,664.64
Fringe Benefits		$32,726	$9,190.61	$1,638.56	$21,896.83
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		$1,736,063	$144,413.10	$0.00	$1,591,649.90
ITAC		$19,400	$0.00	$0.00	$19,400.00
Project Management		$140,000	$7,211.98	$5,480.92	$127,307.10
Total Direct Costs		$2,091,195	$219,060.05	$20,965.48	$1,851.169.47
Authorized Indirect Costs		$14,876	$5,126.25	$0.00	$9,749.75
10% of Salaries and Wages					
Total Costs		**$2,106,071**	**$224,186.30**	**$20,965.48**	**$1,860,919.22**