AIR QUALITY RESEARCH PROGRAM

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

Annual Report

September 1, 2010 through August 31, 2011

Submitted to

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Texas Air Quality Research Program

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OVERVIEW

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

(i) to support scientific research related to Texas air quality, in the areas of emissions inventory development, atmospheric chemistry, meteorology and air quality modeling,

(ii) to integrate AQRP research with the work of other organizations, and

(iii) to communicate the results of AQRP research to air quality decision-makers and stakeholders.

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

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

BACKGROUND

Section 387.010 of HB 1796 (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 was implemented through an 8 step cycle. The steps in the cycle are described from project concept generation to final project evaluation for a single project cycle. During the first quarter of AQRP operation, steps 1-5 were completed for the first project cycle. During the second quarter, sub-agreements for most projects were established and Task Orders began to be initiated (step 6 and parts of step 7). In the third quarter, the final sub-agreements were executed and Task Orders were initiated for the majority of the projects. In the fourth quarter, Task Orders were finalized for the remaining Projects and work was in progress on every Project. During the fifth quarter, work progressed on all projects, including the DFW Field Study. On August 31, 2011, six (6) projects were completed and the remaining projects were issued a 90-day contract extension.

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

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

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

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

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

6.) All Investigators are notified of the status of their proposals, 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 each project and s/he continues to have ongoing contact with his/her PIs. TCEQ has assigned a TCEQ Project Liaison to each project.

8.) The AQRP Director and the Project Manager for each project describes progress on the project in the ITAC and Council meetings dedicated to on-going project review. Six projects have been completed, having met project objectives, as of August 31, 2011. All projects were reviewed by the ITAC at a meeting held in Austin on September 27 and 28, 2011. The AQRP Director will ensure that any comments made by the ITAC in the September 2011 meeting are responded to in the final project deliverables of the remaining active projects.

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

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.

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

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

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

September 2010: Program quarterly report due to TCEQ

December 2010: Program quarterly report due to TCEQ

March 2010: Program quarterly report due to TCEQ

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

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

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

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

September 27 & 28, 2011: AQRP Data Workshop

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

Independent Technical Advisory Committee (ITAC)

The AQRP funding is used primarily for research projects, and one of three groups responsible for selecting the projects is the Independent Technical Advisory Committee (ITAC). The ITAC, composed of up to 15 individuals with scientific expertise relevant to the Program, is charged with recommending technical approaches, and establishing research priorities. Initially, the ITAC was to meet at least twice per year at locations rotating between Austin, Dallas and Houston. As the Program proceeded, it was more efficient for the ITAC to meet once in Austin and as needed via conference call/webinar. One of the meetings each year is dedicated to new project review. A second meeting each year is dedicated to reviewing progress on funded projects and review of the Program's strategic plan.

Members of the ITAC consist of the TCEQ Project Director (or designee), representatives with air quality expertise from research institutions with extensive expertise in air quality research in Texas. The members of the ITAC are drawn from Texas universities active in air quality research, national laboratories that have participated in air quality studies in Texas, and institutions that have expertise not available in Texas and that have participated in air quality studies in Texas. The members of the ITAC are listed in Table 1. Dr. Thomas Ho, of Lamar University was selected to fill the position left by the death of George Talbert in February 2011.

As the ITAC membership is intentionally drawn from air quality researchers who have experience in Texas; these researchers and their colleagues will likely have interest in responding to the requests for research proposals issued by the AQRP. This raises potential confidentiality and conflict of interest issues, and the contract between TCEQ and the University of Texas requires that the AQRP shall maintain and implement an appropriate written policy on conflict of interest. Specifically for the ITAC, all members are required to certify:

> *Confidentiality:* As a member of ITAC I understand that I will have access to proposals submitted to the Air Quality Research Program. Subject to any legal requirements, I agree to keep the information in these proposals confidential until the selection process is completed and it is appropriate to release information to the public. I understand that there may be certain information that comes to me in my role as a member of ITAC that retains its confidential nature even after the process is concluded. I also understand that I will review said proposals and may have access to the reviews made by other ITAC members. I agree to keep these reviews and the identity of the reviewers confidential until such time as this information is released to the public. (NOTE: For the reviews and reviewers, this information may never be released.)
> *Conflict of Interest:* As a member of ITAC, I agree that I will not evaluate, comment on, or vote on proposals in which I or my home institution is involved, including but not limited to, any financial interest, or in which I have another form of conflict of interest. I understand that ITAC members with conflicts of interest must leave the meeting room or the conference line when a proposal with which they have a conflict is discussed, voted on or otherwise being considered. I understand that I must recuse myself from participating in or attempting to influence at any time the ITAC's or the AQRP Council's consideration or decision concerning such proposals. I agree to bring any issues concerning a possible conflict of interest to the attention of the Director of the Air Quality Research Program or the TCEQ Project Director. If there is a question of interpretation regarding whether a conflict of interest exists, I agree that the decision regarding whether a conflict of interest

exists will be made by the Director of the Air Quality Research Program or the TCEQ Project Director.

All members of the ITAC agreed to abide by these conflict of interest and confidentiality provisions prior to participating in the review of proposals.

Table 1: Members of the Independent Technical Advisory Committee

Name	**Title**	**Organization**
David Allen	Gertz Regents Professor in Chemical Engineering	The University of Texas at Austin
Peter Daum	Head, Atmospheric Science Division	Brookhaven National Lab
Mark Estes	Senior Air Quality Scientist Air Modeling and Data Analysis Section	Texas Commission on Environmental Quality
Fred Fehsenfeld	Senior Scientist, Cooperative Institute for Research in Environmental Sciences	Colorado University
Robert Griffin	Associate Professor, Civil and Environmental Engineering	Rice University
Kuruvilla John	Professor of Mechanical and Energy Engineering Associate Dean for Research and Graduate Studies	University of North Texas
Barry Lefer	Assistant Professor, Department of Earth and Atmospheric Sciences	The University of Houston
Jim Meagher	Deputy Director, Chemical Science Division, Earth Systems Research Laboratory	National Oceanic and Atmospheric Administration
J. David Mobley	Deputy Director, Atmospheric Modeling and Analysis Division, Office of Research and Development	U.S. Environmental Protection Agency
John Nielsen-Gammon	Professor and Texas State Climatologist The Center for Atmospheric Chemistry and the Environment	Texas A&M University
Tho (Thomas) Ching Ho	Chairman, Dan F. Smith Department of Chemical Engineering	Lamar University
Jay Turner	Associate Professor of Energy, Environmental and Chemical Engineering	Washington University in St. Louis
William Vizuete	Assistant Professor, Gillings School of Global Public Health	The University of North Carolina at Chapel Hill
Christine Wiedinmyer	Scientist II, Atmospheric Chemistry Division	Nation Center for Atmospheric Research
Greg Yarwood	Principal	Environ

TCEQ Relevancy Review

Once the ITAC has reviewed and ranked research project proposals according to technical merit, they are submitted to the TCEQ for a relevancy review. The TCEQ reviews proposals for relevancy to the State's air quality research needs. TCEQ approval is required for a project to receive funding from the Program.

Advisory Council

The final group responsible for selecting AQRP research projects is the Advisory Council. The Council serves as a Board of Directors for the Program and consists of up to 11 members, all residents of the State of Texas. Two Council members with relevant scientific expertise are nominated by the TCEQ. As defined in the AQRP contract, up to four members of the Council can be county judges from the Houston-Galveston-Brazoria (HGB) and Dallas-Fort Worth (DFW) non-attainment counties. Additional members include government officials from Texas Near-Non-Attainment Areas active in air quality management. The purpose of the Council is to give final approval to projects recommended by the ITAC and TCEQ, and to provide guidance on the Strategic Plan. The Council meets twice per year. One meeting is dedicated to new project selection. A second meeting each year will be dedicated to providing summaries of on-going projects and review of the strategic plan.

Table 2: Members of the Advisory Council

Name	Title	Organization
Ramon Alvarez	Senior Scientist	Environmental Defense Fund
Daniel Baker	Senior Consultant in Air Quality	Shell Global Solutions
Sam Biscoe	County Judge	Travis County
Jeff Branick	County Judge	Jefferson County
Edward M. Emmett	County Judge	Harris County
Ralph B. Marquez	Former TCEQ Commissioner	Environmental Strategies and Policy
Keith Self	County Judge	Collin County
Kim Herndon	Assistant Director Air Quality Division	Texas Commission on Environmental Quality
TCEQ 2	Pending appointment by TCEQ	

Table 3 below provides a list of the top two-thirds of the projects that were recommended by the ITAC and forwarded to the TCEQ and Advisory Council for review. The column titled Funding Awarded by Council shows the amounts approved; changes are shown in the notes. Some projects were able to reduce their budget slightly as the Scopes of Work and QAPPs were refined.

Table 3: Project Selection

AQRP Project Number	Title	Principal Investigator	Institutions represented	ITAC 1st Tier	ITAC 2nd Tier	Funding Awarded by Council	Notes
6	Quantification of Industrial Emissions of VOCs, NO_2 and SO_2 by SOF and Mobile DOAS	Johan Mellqvist	Chalmers Univ. of Technology & Univ. of Houston	x		$498,644	Actually funded at $484,662.
8	Factors Influencing Ozone-Precursor Response in Texas Attainment Modeling	Daniel Cohan	Rice, & Environ	x		$190,966	Actually funded at $178,796.
9	Additional Flare Test Days for TCEQ Comprehensive Flare Study	Vincent Torres	UT-Austin	x		$591,332	
14	Quantifying Emission Estimates from Biogenic and Oil and Gas Production Sources in Texas	Christine Wiedinmyer	UCAR/NCAR	x		$595,173	Unable to agree to contractual terms – Project not awarded.
15	An Assessment of Nitryl Chloride Formation Chemistry and its Importance in Ozone Non-attainment areas in Texas	James Roberts	NOAA, Environ	x		$201,306	Unable to agree to contractual terms with NOAA as PI. Changed Environ to Lead PI and reduced NOAA's Scope to specific task deliverables. Actually funded at $201,280.
20	NO_x Reactions and Transport in Nighttime Plumes and Impact on Next-Day Ozone	Steven Brown	NOAA, Environ	x		$202,498	Unable to agree to contractual terms with NOAA as PI. Changed Environ to Lead PI and reduced NOAA's Scope to specific task deliverables.
21	Dry Deposition of Ozone to Built Environment Surfaces	Richard Corsi	UT-Austin	x		$248,830	Actually funded at $248,786.
22	Development of Speciated Industrial Flare Emission Inventories for Air Quality Modeling in Texas	Daniel Chen	Lamar Univ.		x	$150,000	

26	Biogenic VOC Flux Measurements in East Texas	Gunnar Schade	Texas A&M		x	$200,000	After funding was announced PI withdrew, during Work Plan development.
29	Wind Modeling Improvements with the Ensemble Kalman Filter	John Neilson-Gammon	Texas A & M	x		$80,108	
32	SHARP Data Analysis: Radical Budget and Ozone Production	Barry Lefer	Univ. of Houston, Penn State, Univ. of New Hampshire, Univ. of Miami, & UCLA	x		$248,652	
34	Dallas Measurements of Ozone Production	Barry Lefer	Univ. of Houston & Penn State	x		$195,054	
42	Environmental Chamber Experiments to Evaluate NOx Sinks and Recycling in Atmospheric Chemical Mechanisms	Greg Yarwood	Environ, UC-Riverside, & Smog Reyes	x		$237,481	
45	Quantification of Hydrocarbon, NOx, and SO2 emissions from Petrochemical Facilities in Houston: Interpretation of the 2009 FLAIR dataset	Jochen Stutz	UCLA, UNC, Aerodyne, & Washington State	x		$398,401	Actually funded at $398,042
Contingency Projects							
24	Surface Measurements and One-Dimensional Modeling Related to Ozone Formation in the Suburban Dallas-Fort Worth Area	Robert Griffin	Rice, Univ. of New Hampshire, NCAR, Univ. of Michigan, & Univ. of Houston		x	To Be Determined up to $511,878 if funding available	Funding awarded at $458,957. NCAR's portion of the project had to be removed due to contractual issues.
44	Airborne Measurements to Investigate Ozone Production and Transport in the Dallas/Fort Worth (DFW) Area During the 2011 Ozone Season	Maxwell Shauck	Univ. of Houston		x	Up to $380,261, depending on funding available	Funding Awarded at $279,642.

Not Selected for Funding by Council						Funding Requested	
2	Measurement of Atmospheric Nitrophenols in the HGA and DFW Areas	Purnendu Dasgupta	UT-Arlington & Univ. of Houston		x	$270,798	
12	Attribution of Ozone and Ozone Precursors in Texas based Upstream Source regions and Emission Control Regulations using a Source-Oriented Air Quality Model	Qi Ying	Texas A&M & Molina Center for Strategic Studies in Energy and the Environment		x	$94,411	
18	Evaluating Texas Emissions and Land Use with Models and Observations	Michael Trainer	NOAA		x	$200,555	
19	Impact of aerosol-activated chlorine on tropospheric ozone production	Alexei Khalizov	Texas A&M		x	$226,261	
23	Investigation of the Importance of Heterogeneous Reactions of Nitric Acid as a Source of Radical Precursor Nitrous Acid	Robert Griffin	Rice, Aerodyne, & Univ. of New Hampshire		x	$174,982	
31	Evaluating and Improving Transport Algorithms in the CAMx Grid Model	Chris Emery	Environ		x	$149,881	
36	Tropospheric Ozone Pollution Project's Ozonesonde Network in Texas (TOPP's ON IT)	Gary Morris	Valparaiso & Univ. of Houston		x	$273,746	
40	Assessment of Estimates of Radical Sources from Recent Field Measurements in a Box Model and Regulatory Air Quality Model	William Vizuete	UNC-Chapel Hill & UCLA		x	$389,283	

PROGRAM ADMINISTRATION

This Section summarizes activities performed during the current Program year, beginning in September 2010.

During September through November 2010, Program Administration was focused on establishing the systems and procedures that would be required to manage the Program once the Research Projects were underway. The contracting mechanism, which was implemented in two parts, was completed. PIs were notified of their project award status, and Project Managers were assigned to funded projects. Work began on the Project Work Plans (Scope of work, Budget, and QAPP).

In order to maintain more direct control of the expenditures of all of the research partners in any given project, it was decided that UT would strictly limit the number of subcontracts that it would allow. Instead of having a single prime contract and multiple sub-contracts issued by the prime contractor, each entity that made up a component of a project contracted individually with UT for their portion of the Work Plan. Because of the array of projects that were awarded, this meant that some institutions would be awarded multiple contracts. To deal with this most efficiently, the first part of the contracting mechanism was a blanket agreement with each institution that defined basic terms and conditions.

These were issued to the institutions in September and October, and required significant negotiation. UT was unable to agree to terms with Federal agencies and Federally Funded Research Centers, due to the indemnity and insurance language required in the contract. Because of this, the projects with NCAR had to be dropped and the NOAA projects were reorganized so that they no longer led the project and a much larger role was played by their partner, Environ International, Inc. Many of the other institutions also took issue with the indemnity and insurance clauses, and well as with the Warranty, Publication, and Intellectual Property clauses. One PI decided not to continue with the research project, but this was unrelated to the contract negotiations.

By the end of October, the umbrella portion of the contract had been agreed to by most institutions, and Work Plan development began. As the Work Plans were approved by the Project Managers and the TCEQ Liaisons, often after multiple revisions, Task Orders, the second part of the contract mechanism, were issued to each separate entity taking part in the Project. This process took several months and was the primary activity through February.

In December, when it was determined that two of the projects would not have Task Orders issued, UT contacted the Council and began negotiations with the lead PIs of the two (2) projects that had been selected as contingency projects. Because of the timing of the notifications, these projects were the last to begin.

The individual contracting entities for each Project executed the Task Orders, work began and Program Administration efforts turned to the review and payment of invoices. Monthly invoices were carefully reviewed to ensure that all charges were allowable and allocable. This effort was especially time consuming when the institutions involved in the DFW Field Study began submitting invoices and often required working directly with the PIs and institutional accounting offices to produce payable invoices.

In early spring, the AQRP website was modified to reflect the Research Projects and provide information for those interested in learning more about the Program. A page was set up for each Project providing project information, an executive summary, and monthly technical reports.

In April and May, the Program Administration worked with the PI of the DFW Site Set-up Committee to ensure that all permissions were in place for the field study teams to use the Eagle Mountain Lake site (Site). This included working with the property owner to secure site access, and putting a site access agreement in place with each institution that would be operating at the Site.

In June, the Flair Project, under the direction of Jochen Stutz, held a data workshop at the Pickle Research Campus of UT. The Program Administration assisted with the logistical arrangements for this meeting, including securing a location for the meeting, securing a block of hotel rooms at the state rate, and ensuring that TCEQ personnel were informed of and invited to the Workshop.

In this same month, UT-Austin received a Contract Extension for the AQRP. This extension continues the program through the end of the 2012/2013 biennium, and allows the AQRP to utilize the FY 10 funds through April 30, 2012, and the FY 11 funds through April 30, 2013. The extension enabled the AQRP to allow the Research Projects to request contract extensions and part of August was spent providing amendments to those who requested them. More details on this are provided under the Research Project section of this report.

Each month a Financial Status Report/Invoice from UT to TCEQ has been produced. As the projects began, these invoices became much more complex. In an effort to meet the requirements of the TCEQ and to make the invoices easier to review, UT has developed an organized system for reporting Program activities and Project progress as it relates to expenditures.

Throughout the entire Program, UT and the TCEQ have communicated frequently on a variety of topics including notification of research project activities, program activities, preferences for reporting information, and other topics, as needed. In a continuing effort to transmit information from the Program and Projects, a Data Workshop and ITAC meeting will be held September 27 and 28, 2011, at the UT Pickle Research Campus. All research projects will be required to present at the Workshop which is being organized by the AQRP Program Administration. TCEQ personnel will be notified of and invited to the event.

Program Administration Financial Information

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

Fringe benefits for the Administration of the AQRP are 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 are 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. 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 through August 31, 2011 are included in the spreadsheet below.

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.

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

Table 4: AQRP Administration Budget

Administration Budget (includes Council Expenses)

Budget Category		**FY10**	**FY11**	**Total**	**Expenses**	**Pending Expenses**	**Remaining Balance**
Personnel/Salary		$195,100	$148,755	$343,855	$281,894.52		$61,960.48
Fringe Benefits		$38,082	$32,726	$70,808	$51,271.43		$19,536.57
Travel		$500	$7,500	$8,000	$346.85		$7,653.15
Supplies		$24,015	$2,744	$26,759	$12,802.66		$13,956.34
Equipment		$0	$0	$0			$0
Other			$4,007	$4,007			$4,007.00
Total Direct Costs		$257,697	$195,732	$453,429	$346,315.46	$0	$107,113.54
Authorized Indirect Costs		$19,510	$14,876	$34,386	$28,189.46		$6,196.54
10% of Salaries and Wages							
Total Costs		**$277,207**	**$210,608**	**$487,815**	**$374,504.92**	**$0**	**$113,310.08**
Fringe Rate		22%	22%		18%		

PROJECT MANAGEMENT

Once the awards were announced, each Research Project was assigned a Project Manager (PM). The PM worked with the PIs to accomplish project goals and ensure that all reporting requirements were met. Initially, this focused on the development of the Project Work Plan and a detailed QAPP (Quality Assurance Project Plan). The amount of effort required on the part of the PM depended on the Project requirements, as well as the PI's prior experience developing a Work Plan and QAPP. Two PMs were assigned to review the QAPP for all Projects to ensure a consistent level of detail and rigor.

Once Task Orders were issued, the PM ensured that all reporting requirements were met, and acted as a liaison between the PI and TCEQ for any issues requiring special attention. This included getting permission for the purchase of equipment, budget amendments, and other procedural matters. The PM also reviewed each invoice to ensure the level of effort matched the activities described in the Monthly Technical Report, and that all purchases were allocable to the project. Finally, the PMs acted as a liaison between the Program Administration and the PIs.

Project Management Financial Information

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

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

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

Table 5: Project Management Budget

Project Management Budget

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

RESEARCH PROJECTS

After projects were selected by the Council in August, 2010, (see Table 3 for a list of funded projects) Project Managers and TCEQ Project Liaisons were assigned to each of the projects and the Principal Investigators (PIs) began putting together project Work Plans, which include the Statement of Work, a detailed budget, and a Quality Assurance Project Plan (QAPP). Work on the Research Projects began after Agreements were put in place, Work Plans were approved, and Task Orders were issued.

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

The projects that made-up the DFW Field Study were:

- 10-006 – Quantification of Industrial Emissions of VOCs, NO2, and SO2 by SOF and Mobile DOAS (PI – John Mellqvist, Chalmers University)
- 10-024 – Surface Measurements and One-Dimensional Modeling Related to Ozone Formation in the Suburban Dallas-Fort Worth Area (PI – Robert Griffin, Rice University)
- 10-034 – Dallas Measurements of Ozone Production (PI – Barry Lefer, University of Houston)
- 10-044 - Airborn Measurements to Investigate Ozone Production and Transport in the Dallas Fort Worth (DFW) Area During the 2011 Ozone Season (PI – Max Schauk, University of Houston)

The funding for the DFW Field Study was discussed in the Project Management section of this report. A summary of the activities for this, and all other Projects, can be found in the Appendix.

As of August 31, 2011, six projects were complete and the others remained active. Table 6 on the following 2 pages illustrates the funding awarded to each project and the total expenses reported on each project as of August 31, 2011. Please note that this reflects expenses that have posted to the UT-Austin accounting system as of August 31, 2011. There may be additional expenses pending that will not post until the following month.

At this time, all funding for research projects has been allocated to the projects or to the DFW Field Study. As discussed earlier in this report, projects 10-021, 10-DFW, and 11-DFW are complete, though a final invoice has not yet been received for any of the projects; 30-day contract extensions have been granted to projects 10-008, 10-024, and 10-045, to allow travel expenses associated with the AQRP Data Workshop to be charged; and 90-day contract extensions have been granted to all remaining projects.

Table 7 shows the funds that are estimated to be returned to the AQRP from each project upon completion. At this time, it is estimated that $38,200 of FY10 funds will be returned, and $7,954 of FY 11 funds will be returned. Also, all of the funds that were moved from Project Management to Project 11-DFW will be returned.

Per the agreement with TCEQ, FY 10 funds must be fully expended from the categories as budgeted by April 30, 2012. As such, UT has developed a plan for expending the $38,200 of FY 10 funds. The first step will be to increase the budget for the 10-DFW project and move all expenditures out of the 11-DFW project to the 10-DFW project. This will move expenditures totaling $29,262 from FY 11 to FY 10. The remainder of the funds will be used to fulfill a contractual requirement that all project data be stored in an accessible, yet protected location for 3 years after the project ends. The AQRP has contracted with the Texas Advanced Computing Center (TACC) for that data storage at a cost of $10,000. This will fully expend the FY 10 funds and leave approximately $35,000 in FY 11 funds. The AQRP will have until April 2013 to fully expend those funds.

At this time, the AQRP, with input from the TCEQ, is considering using the remaining FY 11 funds for the development of a State of the Science Assessment. The purpose of this Assessment will be to provide a summary of prior air quality research activities and their results, and provide a roadmap for the direction of future air quality research activities.

Table 6: 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	$96,765	$32,086
10-008	Environ International	$49,945	$46,670	$3,275
10-009	UT-Austin	$591,332	$590,747	$585
10-021	UT-Austin	$248,786	$244,068	$4,718
10-022	Lamar University	$150,000	$9,631	$140,369
10-032	University of Houston	$176,314	$2,589	$173,725
10-032	University of New Hampshire	$23,054	$0	$23,054
10-032	UCLA	$49,284	$14,195	$35,089
10-034	University of Houston	$195,054	$34,913	$160,141
10-042	Environ International	$237,481	$156,574	$80,907
10-045	UCLA	$149,773	$65,026	$84,747
10-045	UNC - Chapel Hill	$33,281	$28,711	$4,570
10-045	Aerodyne Research Inc.	$164,988	$88,707	$76,281
10-045	Washington State University	$50,000	$31,591	$18,409
10-DFW	UT-Austin	$37,857	$37,857	$0
FY 10 Total Contractual Funding Awarded		$2,286,000		
FY 10 Contractual Funding Remaining to be Awarded		$0		
FY 10 Contractual Funds Expended to Date*			$1,448,044	
FY 10 Contractual Funds Remaining to be Spent				$837,956

FY 11 Contractual Funding		**$1,736,063**		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
10-006	Chalmers University of Tech	$262,179	$118,651	$143,528
10-006	University of Houston	$222,483	$146,892	$75,591
10-015	Environ International	$201,280	$107,044	$94,236
10-020	Environ International	$202,498	$130,290	$72,208
10-024	Rice University	$225,662	$50,855	$174,807
10-024	University of New Hampshire	$70,747	$37,779	$32,968
10-024	University of Houston	$64,414	$19,212	$45,202
10-024	University of Michigan	$98,134	$16,477	$81,657
10-029	Texas A&M University	$80,108	$54,136	$25,972
10-044	University of Houston	$279,642	$12,973	$266,669
11-DFW	UT-Austin	$50,952	$29,262	$21,690
FY 11 Total Contractual Funding Awarded		$1,758,099		
FY 11 Contractual Funding Remaining to be Awarded		-($22,036)		
FY 11 Contractual Funds Expended to Date*			$723,571	
FY 11 Contractual Funds Remaining to be Spent				$1,034,528
Total Contractual Funding		$4,022,063		
Total Contractual Funding Awarded		$4,044,099		
Total Contractual Funding Remaining to be Awarded		-($22,036)		
Total Contractual Funds Expended to Date*			$2,171,615	
Total Contractual Funds Remaining to be Spent				$1,872,484

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

Table 7: Research Funds Estimated to be Returned to AQRP (Estimates as of September 30, 2011)

Funds Estimated to be Returned			
FY 10 Contractual Funding		**$2,286,000**	
Project Number		Amount Awarded (Budget)	Amount Estimated to be Returned
10-008	Rice University	$128,851	$3,200
10-008	Environ International	$49,945	$0
10-009	UT-Austin	$591,332	$0
10-021	UT-Austin	$248,786	$0
10-022	Lamar University	$150,000	$22,000
10-032	University of Houston	$176,314	$6,000
10-032	University of New Hampshire	$23,054	$1,000
10-032	UCLA	$49,284	$0
10-034	University of Houston	$195,054	$1,000
10-042	Environ International	$237,481	$0
10-045	UCLA	$149,773	$5,000
10-045	UNC - Chapel Hill	$33,281	$0
10-045	Aerodyne Research Inc.	$164,988	$0
10-045	Washington State University	$50,000	$0
10-DFW	UT-Austin	$37,857	$0
FY 10 Contractual Funds Estimated to be Returned			$38,200
FY 11 Contractual Funding		**$1,736,063**	
Project Number		Amount Awarded (Budget)	Amount Estimated to be Returned
10-006	Chalmers University of Tech	$262,179	$0
10-006	University of Houston	$222,483	$0
10-015	Environ International	$201,280	$0
10-020	Environ International	$202,498	$0
10-024	Rice University	$225,662	$0
10-024	University of New Hampshire	$70,747	$0
10-024	University of Houston	$64,414	$3,000
10-024	University of Michigan	$98,134	$3,800
10-029	Texas A&M University	$80,108	$1,500
10-044	University of Houston	$279,642	$0
11-DFW	UT-Austin	$28,916	($346)
FY 11 Contractual Funds Estimated to be Returned			$7,954
Total Contractual Funds Estimated to be Returned			$46,154

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 was 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.

The following tables show the budget and cumulative expenditures for each piece of the AQRP for FY 10 and FY 11, as well as a total Financial Status Report by fiscal year. Expenditures are reported as of August 31, 2011.

Table 8: Program Administration Financial Summary

Administration Budget (includes Council Expenses)

FY 2010

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

Administration Budget (includes Council Expenses)

FY 2011

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

Table 9: ITAC Financial Summary

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**

Table 10: Project Management Financial Summary

Project Management Budget

FY 2010

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

Project Management Budget

FY 2011

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

Table 11: AQRP Financial Summary – FY 10

AQRP Budget

FY 2010

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

Table 12: AQRP Financial Summary – FY 11

AQRP Budget

FY 2011

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

Appendix

Research Project Summaries

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

End Date Extended to November 30, 2011

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

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

Funding Awarded: $484,662
($262,179 Chalmers, $222,483 UH)

Annual Project Update:

A measurement study was performed from April 6 – June 18, 2011, in southeast Texas, with the aim to study direct emission of volatile organic compounds (VOCs), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and formaldehyde from refineries and petrochemical industries. The substances above are key species for the formation of photochemical smog. Several techniques were used, i.e. Solar Occultation Flux (SOF), mobile Differential Optic Absorption Spectrometry (DOAS) and thermal Fourier Transform Infrared (FTIR) and canister sampling.

In addition, measurements of methane, ethane, propane, carbon monoxide (CO), nitric oxide (NO) and other VOCs were made in the Fort Worth area, to study emission from natural gas production. The techniques used here were mobile extractive FTIR and tracer correlation combined with canister sampling. In addition, SOF measurements were carried out.

In the sites surveyed with SOF and mobile DOAS in previous studies i.e. Houston Ship Channel (HSC), Mt Belvieu and Texas City we have measured emissions of alkanes, alkenes, SO_2, NO_2 and formaldehyde. The general emission patterns are the same in 2011 as in previous campaigns in 2006 and 2009, although there are differences.

The Beaumont and Port Arthur area was surveyed for the first time with SOF in this campaign. Alkane emissions as summed from seven individual plant areas, averaged about 6700 kg/h. This is slightly more than half of the alkane emissions measured from the HSC area in 2011. In terms of alkenes four plants in the Beaumont Port Arthur area contributed with 148 kg/h of ethene emissions on average, whereas no major propene emissions were observed. At one plant also emissions of 1,3 butadiene and 1-butene was observed. The adjacent petrochemical site in Orange was measured to have ethene emissions of on average 197 kg/h. A major alkene source was found in Longview, also surveyed for the first time with SOF. The site showed an ethene emission of 452 kg/h and a propene emission 282 kg/h.

In the Fort Worth study we find that the largest continuous sources are the treatment facilities and the large compressor stations emitting up to 100 kg/h of methane, 5 kg/h of ethane and other species. Another source is well pads emitting about 1 kg/h of methane and about 2-5% by mass of ethane. Due to the large amount of well pads, this constitutes a major source. There are reports in the literature claiming that regeneration of drying liquid from well pads may constitute a large source. It is believed that this occurred during one of our measurements from a well pad. Here emissions of 2 kg/h of ethane and 0.4 kg/h of ethene was measured by meFTIR and canister sampling; noteworthy is the importance of the latter species for ozone formation.

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

End Date Extended to September 30, 2011

Factors Influencing Ozone-Precursor Response in Texas Attainment Modeling

Rice University – Daniel Cohan
ENVIRON International – Greg Yarwood

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

Funding Awarded: $178,796
($128,851 Rice, $49,945 ENVIRON)

Annual Project Update:

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

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

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

Bayesian Monte Carlo analysis was then applied to weight the relative likelihood of alternate structural and parametric scenarios, based on model performance in simulating observed concentrations within the Dallas-Fort Worth (DFW) region during the June 2006 episode. Metric 1 evaluated model performance on high-ozone days at three DFW monitors, while Metric 2 considered average 8-hour ozone concentrations across all DFW monitors on each episode day. A non-Bayesian metric for assigning weights based on standard model performance statistics (Metric 3) was also developed and was applied to produce alternative weightings of the Monte Carlo scenarios.

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

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

End Date Extended to November 30, 2011

Additional Flare Test Days for TCEQ Comprehensive Flare Study

University of Texas at Austin – Vincent Torres

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

Funding Awarded: $591,332

Annual Project Update:

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 TCEQ's 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 were compared to the extractive measurement results. A final report (*TCEQ 2010 Flare Study Final Report)* for this task is now posted on the TCEQ website at http://www.tceq.texas.gov/airquality/stationary-rules/flare_stakeholder.html

Task 2 - The goal of the modeling project (Task 2) is to be able 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. Two types of models were 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. One modeling approach (Multivariate Image Analysis or MIA) uses feature variables extracted from the spectral information of the flare images on the video recordings from the tests. This complements the predictive capability of the computational fluid dynamics (CFD) model, which uses first principles to model the full-scale flares used in the Task 1 tests. The CFD model will predict flare performance, i.e., combustion efficiency and destruction and removal efficiency, while at the same time predicting emissions produced at different operating conditions.

In the MIA approach (Task 2.1) for the steam-assisted flare, 8 tests were usable (the flame was visible), while there were 13 usable tests for the air-assisted flare. Different training/validation approaches were examined:

(1) Use half the images from each test as a training set, and the other half to validate the model.

(2) Use data from some of the tests as a training set, and use all the sets to validate.

Other variables recorded for each test included lower heating value of fuel stream, assist gas flow rate, air to fuel ratio in combined assist/fuel stream, and crosswind velocity. These variables were used along with the feature variables in the regression. The best results were obtained when odd-numbered images were used to train the model and even-numbered images were used as the validation set. When building a model with the goal of making predictions about previously unseen flares, a wide range of training data is required. In this case, combustion efficiency from analytical equipment such as FTIR will be needed to train the image analysis model. Then the MIA model could be used for real-time adjustment of steam flow to a flare.

In Task 2.2, a CFD model was used to model a flare and calculate the combustion efficiency for use in MIA. However, It takes a long time (hours) to obtain a result from CFD, so this approach could not be used to analyze on-line measurements. Fitting of the CFD model to the data was needed due to the uncertainty of the reaction kinetics mechanism for propylene combustion, so one parameter is adjusted to match the field data, which provides a reasonably accurate fit for both steam and air-assisted flare tests. In Task 2.3, the Combustion Zone Heating Value (CZHV), or the heating value of the combined assist gas and fuel stream, is related to the combustion efficiency. We have concluded that the correlation is not strong enough to make accurate predictions (± 20% in some cases).

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

End Date Extended to November 30, 2011

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

ENVIRON International – Greg Yarwood

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

Funding Awarded: $201,280

Annual Project Update:
The primary goals of this project are to analyze nitryl chloride formation in urban areas utilizing the existing field campaign data sets and to implement this chemistry in photochemical grid models to aid the Texas SIP development.

Background

Results from the 2006 TexAQS-II/Gulf of Mexico Atmospheric Composition and Climate Study (TexAQS-II for short) in Houston showed that reactions at night between ozone (O_3), nitrogen oxides (NOx), hydrogen chloride (HCl) and particulate matter (PM) gave rise to nitryl chloride ($ClNO_2$). This finding was confirmed by other studies and is significant because $ClNO_2$ undergoes rapid photolysis in the morning and can influence photochemistry and O_3 formation at the start of the day. Sea salt PM is an important source of chloride in coastal regions but $ClNO_2$ also has been observed far from the ocean (in Boulder, Colorado) indicating that other sources of chloride can give rise to $ClNO_2$ and that its influence on photochemistry may not be limited to coastal regions.

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

Assessment of Nitryl Chloride Formation in Urban Areas

Observations during the 2006 TexAQS-II study brought up a number of questions about whether or not the $ClNO_2$ chemistry was self-consistent, how the chemistry depended on N_2O_5 uptake, and aerosol chloride concentration, if there was enough soluble chloride to produce the observed $ClNO_2$, and how these aspects of the chemistry could be incorporated into regional air quality models that describe ozone production in non-attainment areas. To answer these questions, the project team further examined the ambient data set acquired during the TexAQS-II study and

assessed the data sets from the Study of Houston Atmospheric Radical Precursors (SHARP) in 2009, and the CalNex study conducted in the Los Angeles area in May and June of 2010. Several approaches were used to estimate N_2O_5 uptake rate and $ClNO_2$ conversion efficiencies from ambient measurements: the odd-nitrogen budget of isolated nighttime plumes, and box modeling of the few reactions that govern N_2O_5 formation and N_2O_5 to $ClNO_2$ conversion. In addition, gas phase HCl, HNO_3 and particle nitrate and chloride measurements for these three studies were analyzed to assess the importance of sea salt acidification as a source of soluble aerosol chloride, and the adequacy of aerosol measurements in providing the information necessary to model $ClNO_2$ formation.

Three-Dimensional Photochemical Grid Modeling

The CAMx photochemical grid model was updated to include a parameterization of the ClNO2 chemistry and applied to a summer 2006 ozone and PM modeling episode using the EPA's nationwide 12-km grid modeling database. The reactive chlorine and particle chloride emission inventories in the EPA's modeling database were extended to include additional chlorine/chloride emission sources, e.g., swimming pools, sea salt and wildfires.

The simulation results were compared with two ground site measurement datasets, the CalNex 2010 LA site at Pasadena and the SHARP 2009 Moody Tower site near downtown Houston. At the Pasadena site, CAMx significantly underestimates HCl and PCl while overestimating HNO_3 which may indicate a shortfall in the amount of chloride in the emission inventory. The missing chloride could be sea salt or additional chlorine and/or chloride emission categories that are missing in the current emission inventory. At this site, almost all of the total chloride resides in the gas phase, which could also result in less chloride available to form $ClNO_2$ because HCl is efficiently removed from atmosphere by deposition process. Another possible explanation for the discrepancy between the model and observation is that there exist abundant sea salts deposited on the surface which release HCl by acid displacement following HNO_3 deposition. CAMx underpredicts HCl and N_2O_5 at the Moody Tower site, but predicts similar to or higher $ClNO_2$ concentrations than the measurements. The observed $ClNO_2$ concentrations at this site are quite low compared to measurements made on board the NOAA R/V Ron Brown during the TexAQS-II 2006 campaign. On average, the Pasadena site observed lower HCl + PCl concentrations but higher $ClNO_2$ than the Houston site.

Conclusions

The results of ambient data analyses have illustrated several key features of the $ClNO_2$ chemistry. The highest $ClNO_2$ concentrations were observed when N_2O_5 uptake coefficient was high but N_2O_5 to $ClNO_2$ conversion efficiencies were fairly modest. Episodes when high N_2O_5 was observed, but $ClNO_2$ was very low corresponded to low N_2O_5 uptake and there was very low conversion. Relative humidity appears to be one of the more important parameters controlling N_2O_5 uptake, but high aerosol organic fraction may also suppress uptake.

Photochemical grid modeling showed that the model significantly underpredicted HCl and PCl. Several hypotheses were proposed and tested to explain the discrepancies between the model and observations. The test results are expected to provide valuable insights to improve our understanding of nitryl chloride formation in the region.

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

End Date Extended to November 30, 2011

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

ENVIRON International – Greg Yarwood

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

Funding Awarded: $202,498

Annual Project Update:

Background

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 (NO_x) emissions that occur at night will influence their availability to participate in next day O_3 formation. During the second Texas Air Quality Study in 2006 (TexAQS II), the NOAA P-3 aircraft measured a wide suite of atmospheric species at high temporal resolution during a series of nighttime flights, including flights downwind of several Texas power plants. The primary objective of AQRP Project 10-020 was to take advantage of the P-3 data collected during the nighttime plume intercepts of two power plants to understand and simulate the fate of emissions from these plants during the night and the implications for next-day ozone formation. The two plants are the Oklaunion plant in north Texas, near the Oklahoma border and the city of Wichita Falls, TX, and the W.A. Parish plant, located on the southwest side of the city of Houston.

The AQRP project consists of three main components:

- Data analysis and empirical modeling analysis of night-time chemistry and mixing in NO_x plumes from power plants
- Deterministic modeling of night-time power plant plumes using a reactive plume model (SCICHEM) and a three-dimensional chemical transport model (CAMx)
- Data analysis of night-time vertical profiles in the Houston boundary layer

Analysis of Chemistry and Mixing in NO_x Plumes from Large Point Sources

The aim of the analyses was to understand: 1) nighttime NO_x plume widths and depths in order to characterize nighttime plume mixing; 2) the mass balance of ozone and total nighttime odd oxygen to measure the conversion of nitrogen oxides into both reservoir and reactive compounds; and 3) direct measurement and/or estimates of nighttime nitrogen containing species that result from heterogeneous N_2O_5 reactions, such as HNO_3. An assessment of the impact of NO_x emission control technology on nighttime NO_x transport and loss was also conducted.

The analysis showed that mixing of intense point source NO_x plumes with background air is inefficient at night, and the chemistry within these plumes is spatially confined. The plume NO_x has the potential to completely consume the background O_3, effectively shutting off further NO_x

oxidation through the formation of NO_3 and N_2O_5 since these species cannot co-exist with the excess NO present in a fully O_3-titrated plume. Overnight NO_x transport without oxidation or conversion to soluble species such as HNO_3 is more efficient if full titration of background O_3 occurs. The hypothetical control analysis showed that plumes with selective catalytic reduction control (SCR) are more likely to have insufficient NO_x to titrate background O_3 and thus undergo rapid oxidation, while those without such controls transport non-oxidized NO_x overnight.

A draft manuscript detailing this analysis is currently under review by co-investigators at both NOAA and ENVIRON. The draft manuscript has also been submitted to AQRP for review. The manuscript will be submitted to a peer-reviewed journal after incorporating revisions arising from the reviews.

SCICHEM and CAMx Modeling of the Oklaunion Night-time Plume

The reactive plume model, SCICHEM (Second-order Closure Integrated puff model with CHEMistry), and the Comprehensive Air quality Model with extensions (CAMx) were used to simulate the Oklaunion power plant plume during the night of October 10, 2006. SCICHEM was able to capture many of the observed features of the aircraft plume measurements by restricting horizontal and vertical plume growth, increasing puff resolution (in time and space) and using aircraft measurements of wind speed, direction, and temperature.

The CAMx simulations were conducted with two configurations to simulate the Oklaunion plume: a Plume-in-Grid (PiG) configuration with five reactors in each PiG puff to capture the chemical inhomogeneity across the plume; and a high-resolution flexi-nest with 200 m grid spacing downwind of the power plant. The results with the latter approach were in better agreement with the aircraft measurements than those from the PiG approach. With the PiG approach, the modeled plume was significantly wider than the observed plume. The wider modeled puffs were attributed to the large shear in the model wind fields, and a sensitivity study in which shear-induced growth was set to zero resulted in narrower plumes. The PiG approach also could not capture the variations in chemistry across the plume as well as the flexi-nest approach.

Analysis of Night-time P-3 Profiles of the Houston Urban Boundary Layer

This analysis is still ongoing.

Project 10-021	**STATUS: Active – October 11, 2010**
	Project Complete: August 31, 2011

Dry Deposition of Ozone to Built Environment Surfaces

University of Texas at Austin – Richard Corsi

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

Funding Awarded: $248,786

Annual Project Update:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

End Date Extended to November 30, 2011

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

Lamar University – Daniel Chen

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

Funding Awarded: $150,000

Annual Project Update:

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) 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-assisted and steam-assisted flares under open-air conditions. This project (1) predicts the performance of Tulsa testing flares by using CFD modeling, and (2) further compares with the measured flare performance data and speciated volatile organic compound (VOC) concentrations. This modeling tool has the potential to help TCEQ's on-going evaluation on flare emissions and to serve as a basis for a future State Implementation Plan (SIP) revision.

The 50-species combustion mechanism is reduced from the combined GRI and USC mechanisms with the goal of allowing NOx formation and handling light hydrocarbon combustion. This optimized Lamar mechanism has been validated against methane, ethylene, and propylene experimental data. Further, NO_2 is added to the existing mechanism and is shown in good agreement with the full mechanism. FLUENT models (Species, Turbulence-Chemistry, Viscous, and Numerical Solution), model parameters, and boundary conditions have been selected.

The main operating, design, and meteorological data of the flare test campaign were provided by the University of Texas (UT) including Combustion Efficiency (CE), Destruction & Removal Efficiencies (DRE). Both Probability Density Function (PDF) and Eddy Dissipation Concept (EDC) turbulence-chemistry interaction approaches have been adopted to run Tulsa flare test cases. Two air-assisted flare test cases and one steam-assisted flare test case have been run and compared with the measured DRE/CE data. Even though the PDF approach was verified with University of Alberta wind tunnel data and was shown in good agreement; the more simplistic PDF model tends to predict somewhat higher flare efficiencies than the measured ones. The more rigorous EDC model, however, tends to give low DRE/CE due to the low fuel flow rates and low fuel heating values. The EDC approach is also sensitive to the inclusion of the pilot flame. More time is needed to resolve the aforementioned CFD simulation issues; consequently, no-cost contract extension to November 30, 2011 has been requested and approved for the project.

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

End Date Extended to September 30, 2011

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

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

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

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

Annual Project Update:

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 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) are investigating this hypothesis through performance of an air quality sampling campaign and subsequent data analyses.

The Rice, UH, and UNH team installed several additional pieces of air quality monitoring equipment at the Eagle Mountain Lake Texas Commission on Environmental Quality monitoring site for a one-month period from May 30 to June 30, 2011. Eagle Mountain Lake is located approximately 40 kilometers to the northwest of downtown Forth Worth. This location was chosen for several reasons: a wealth of natural gas activity, wind that predominantly blows from the direction of the DFW metropolitan area, and monitoring that has noted 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 included not only the concentrations of O_3, NO_x, and VOCs but also values for other relevant chemical and physical variables, including meteorological parameters. In addition, a group from the University of Michigan conducted computational modeling used in conjunction with the data generated from these measurements to determine the VOC emissions, atmospheric reactions, and meteorological conditions that lead to O_3 formation in the DFW region.

The first round of data analyses indicate that the air quality at the Eagle Mountain Lake site is determined by being a receptor of aged and processed air from the DFW metropolitan area. However, there are strong indications that intermittent local sources influence air quality at the site. Future analyses will focus on deconvolving the relative influences of local and distal sources and on determining how the mixing of aged air and fresh emissions affects pollutant concentrations at Eagle Mountain Lake.

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

End Date Extended to November 30, 2011

Wind Modeling Improvements with the Ensemble Kalman Filter

Texas A&M University – John Nielsen-Gammon AQRP Project Manager – Gary McGaughey
TCEQ Project Liaison – Bright Dornblaser

Funding Awarded: $80,108

Annual Project Update:
Introduction

Computer-based simulations of the atmosphere are a vital component of a comprehensive air quality research program. Scientists and regulators use simulations to help understand the causes and sources of high levels of air pollution and to test various strategies for reducing air pollution levels. The Environmental Protection Agency requires that State Implementation Plans to reduce air pollution include computer simulations demonstrating that the proposed strategy will actually do the job.

It is essential that the simulation be accurate, that it not only reproduce the observed pattern of air pollution during a given episode (to within specified tolerances) but also correctly simulate the processes leading to the particular observed pattern. Otherwise, regulations might be proposed to reduce emissions from one set of sources when the pollution is actually being caused by a different set of sources.

Most air pollution modeling systems consist of three essential components:

- the emission inventory and models, which specify which pollutants enter the atmosphere where, as a function of time of day, day of week, and meteorological conditions;
- the meteorological model, which simulates the wind, temperature, moisture, cloud, and rainfall; and
- the photochemical model, which uses the output from the emission inventory and meteorological model to simulate the transport and mixing of pollutants and the chemical reactions that take place among them.

Errors in the meteorological model output, or met model output for short, harm the air pollution simulation in several ways. For example, winds that are too strong will produce pollution concentrations that are too weak and in the wrong place. Winds that are from the wrong direction will produce pollution concentrations in the wrong place. Too much cloud cover or precipitation will reduce pollution concentrations. Too much vertical mixing of pollutants will reduce pollution concentrations and allow them to be more easily dispersed at night.

Many of these errors can be reduced or eliminated by incorporating available data into the met model simulation. Wind observations, for example, can be "assimilated" into the met model so that the simulation closely matches the observations. For other errors, the best solution is to improve the model itself.

This is especially true for vertical mixing. Vertical mixing is important because it affects horizontal wind speeds as well as vertical dispersion of pollutants. Direct observations of vertical mixing are rare and are difficult to incorporate into a met model. Furthermore, met models do not directly simulate vertical mixing. Instead, they estimate it on the basis of the simulated vertical profiles of wind and temperature. The estimation scheme, called a "parameterization", is based on measurements of the atmosphere in very simple situations that may not directly apply to a particular urban area.

Observations during field programs show that met models handle vertical mixing poorly, and that these errors can lead to a factor of two difference in surface concentrations of various pollutants. Thus, it is important to reduce these parameterization errors.

Project Overview

The purpose of this project is to improve and refine a vertical mixing parameterization scheme used by a standard met model known as WRF. The idea behind the project is to combine two sources of information to accomplish this task. The first set of information is the set of differences between the met model output and observations. The second set of information is a set of differences between met model outputs from models whose parameterizations have been altered slightly. This latter set of met model output contains information on which changes to the parameterization produce which changes in the output. By combining the two sources of information, it is possible to determine which changes to the parameterization would help the model reduce the differences between the met model output and observations.

The basic technique used for this task is called the Ensemble Kalman Filter (EnKF). Earlier work has demonstrated that this particular use of the EnKF can improve the accuracy of met simulations and forecasts, but the testing was conducted on a single ozone episode. This project is designed to obtain firmer conclusions regarding improved model performance by testing the procedure on other ozone episodes, examining how many different aspects of the parameterization should be changed at one time, and determining whether the parameterization gets modified in the same way in different simulations.

Summary of Progress and Results

Because the EnKF system had been designed for older versions of the WRF model, the focus of the project so far has been to lay the groundwork for future simulations and ultimate adoption by TCEQ. The EnKF software system has been documented and a description of scientific papers describing the evolution and testing of the EnKF has been prepared. Because the EnKF system has been written by several different individuals over the course of several years, part of the project has been devoted to refining the system and making it more robust. Meanwhile, the WRF modeling system has been upgraded to the current version (version 3.3), and testing is underway to work through any issues with compatibility with the computer system used for this project.

To date, the preparation work is nearing completion, and future work during the next few months will focus on running the test cases and analyzing the results.

Project 10-032 **STATUS: Active - February 9, 2011**
End Date Extended to November 30, 2011

SHARP Data Analysis: Radical Budget and Ozone Production

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

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

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

Annual Project Update:

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 by Objective:
The PI team has been working on the preparation of the mechanism schemes (RACM2, CB05, MCM, SAPRC07, and LaRC) for the SHARP data analysis. Input files for these mechanisms have been created and the model mechanisms have been updated to the available constrained chemical and meteorological parameters. Almost all model simulation runs have been run, and the analysis of the SHARP data and the various 0-D and 1-D box modeling simulations is underway. The preliminary model results have been shared with all members of the PI team to help their data analyses. Initial results for each of the project objectives are summarized below:

Objective 1. Identify the variation of measured HOx and HO_2/OH with NOx and VOCs and compare to the model prediction. (UMiami and Penn State)

Objective 1A: Comparison of observed and modeled HOx

The measured and modeled OH and HO_2 exhibit similar diurnal and day-to-day variations, with maxima in the early afternoon and minima at night. The median daytime observed-to-modeled OH ratio is 1.08 with a correlation coefficient, r, of 0.68. The median daytime observed-to-modeled HO_2 ratio is 1.34 with a correlation coefficient, r, of 0.87.

Two oxidation pathways can contribute to nighttime HOx in the planetary boundary layer: (1) O_3 can react with alkenes to produce a significant amount of OH and HO_2, and (2) NO_3 can produce HOx directly via reaction with HCHO or indirectly after conversion of the RO_2 that is initially produced by VOCs+NO_3. These processes become more important for the nighttime HOx production because daytime HOx photolytic sources vanish at night. At night, the modeled HO_2 agrees reasonably well with the measurements during nighttime, with a median measured-to-modeled ratio of 1.41, which is within the combined uncertainties of measured and modeled HO_2. However, nighttime OH is significantly under-predicted, with a median measured-to-modeled ratio of 6.2. This difference indicates that the RACM mechanism fails to capture the processes that create nighttime OH in this urban environment.

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

The observed-to-modeled OH and HO_2 ratios can test our understanding of the HOx photochemistry because the cycling between OH and HO2 is very fast and the photochemical equilibrium among OH and HO_2 is closely tied to the interconversion of NO to NO_2 in the troposphere. Both the measured and modeled HO2/OH ratios decrease with increasing NO. This

decrease occurs because NO shifts HOx into OH by reacting with HO_2. However, when NO is lower than a few hundred pptv, the modeled HO_2/OH ratios are significantly higher than the measured. The agreement of measured and modeled HO_2 to OH ratios is good when NO is around a few hundred pptv. The slope of measured HO_2/OH as a function of NO is significantly less than the modeled slope. This difference is consistent with measured OH being greater than modeled OH at low NO, while measured HO_2 is much greater than modeled HO_2 at high NO.

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

Calculated HOx production is dominated by photolysis of HONO in the early morning and by O_3 photolysis in the midday, and is mainly from O_3 reactions with alkenes a night. On average, the daily HOx production rate was 23.8 ppbv day^{-1}, of which 31% is from O_3 photolysis, 23% from HONO photolysis, 12% from HCHO photolysis, and 14% from O_3 reactions with alkenes. For HOx loss, the clearly dominant process was the OH reaction with NO_2, while the self-reactions between OH, HO_2, RO_2 become important in the afternoon when their concentrations are the highest.

Objective 3. Examine the significance of nighttime OH and to determine the importance of both the reaction of O_3 + alkenes and NO_3 chemistry as nighttime OH sources. (UMiami)

Objective 3A. Nighttime OH

The median measured nighttime OH concentration is 0.038 pptv or $9.4x10^5$ molecules cm^{-3}, while the modeled nighttime OH concentration is 0.009 pptv or $2.1x10^5$ molecules cm^{-3}. The median measured nighttime HO_2 on is 5.9 pptv, while the modeled nighttime HO_2 concentration is 3.9 pptv. This indicates that OH and HO_2 may also play important roles in the nighttime oxidation chemistry. The model underpredicts both nighttime OH and HO_2. The median measured-to-modeled HO_2 ratio at night is 1.54, which is within the combined uncertainty of measured and modeled HO_2. The median measured-to-modeled OH ratio at night is 6.2, which is significantly beyond the combined uncertainty of the measured and modeled OH. This difference indicates that the RACM2 mechanism fails to capture the processes that create nighttime OH in this urban environment.

Objective 3B. Importance of the O_3 + alkene reactions and NO_3 chemistry as nighttime HOx sources

Modeling results show that typical diurnal variations of HOx production from these two pathways were calculated. HOx production from O_3 + alkene reactions peaks in the midday when O_3 concentration reaches highest, while HOx production from NO_3 chemistry peaks at night because of low NO_3 concentration during the day due to its fast photolysis. In general, NO_3 chemistry contributes less HOx production than O_3 + alkene reaction, except for a few nights (e.g., the night of May 20 and 21) when NOx concentrations were high and NO titrated O_3 to very low levels while the reaction of NO_2 with O_3 produced high concentrations of NO_3 on these nights. Modeled NO_3 concentrations are used in the calculation due to the low data coverage in the DOAS NO_3 measurements. In general the modeled NO_3 is in good agreement with observed NO_3, with the modeled NO_3 lower than the observed NO_3, but within the

uncertainty of the observed NO_3. On average, O_3 + alkene reactions contribute about two thirds (~68%) of nighttime HOx production while the other one third comes from NO_3 chemistry.

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

Compared to the OH and HO_2 measurements in other two cities in Mexico City and New York City, the measured OH concentrations in Houston during SHARP are comparable to the OH measurements in the other two cities. However, the peak HO_2 concentration in Mexico City is the highest, while the HO_2 concentrations in New York City are the lowest, simply because of the high NOx concentrations in New York City throughout the day.

Objective 5. Investigate the instantaneous O_3 production and deviations of the NOx 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. (UH).

To assess the impacts of changes in actinic flux on ozone production and loss rates, the LaRC 0-D photochemical box model was run with photolysis rates from both measured and modeled actinic fluxes. The reduction in measured photolysis rates relative to modeled rates are quantified by taking the ratio of SAFS derived photolysis rates to the CFM rates generated by TUV, defined as the j-value impact factor (JIF). The median JIF for 6 cloud free days was 0.98, while the median JIF for the remaining 42 days was 0.83. For JIFs of 1±0.15, O_3 production can reach instantaneous rates greater than 50 ppbv/hour. While other factors besides j-values were also regulating ozone production during SHARP (wind speed & direction, boundary layer height, emissions, etc.), reductions in $j(NO_2)$ correspond to reduced net O_3 production rates with a nearly one-to-one relationship, albeit of much smaller net O_3 production rates below JIFs of 0.85.

For all days of the SHARP, the median O_3 destruction terms are nearly an order of magnitude smaller than the formation rates. During the SHARP campaign, clouds and aerosols reduced the net O_3 production during the campaign by an average of ~3.1 ppbv/hour out of 10.4 ppbv/hour. On high ozone days there was a 9% reduction in ozone production (average of 1.3 out of 14.3 ppbv) ozone per hour which was primarily due to aerosol reductions in solar UV radiation.

Objective 6. Study the sensitivity of O_3 production to NOx and VOCs. (UMiami)

The ozone production sensitivity to NOx or VOCs has a similar behavior for TexAQS2000, TRAMP2006 and SHARP2009; it is VOC sensitive in the early morning and late afternoon but NOx-sensitive throughout the afternoon. This behavior is typical of US urban areas. These results are independent of the differences between the measured and modeled OH and HO_2. Note that in the afternoon the ozone sensitivity in SHARP2009 has a longer NOx-sensitive period than TexAQS2000 and TRAMP2006, indicating that NOx control is an efficient approach for the O_3 control in springtime.

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

Initial results indicate that the reaction of OH + NO is unimportant as a source of HONO in this campaign, and thus the PI team did not correct the OH formation from HONO photolysis by the rate of this back-reaction. These calculations were based on UCLA's LP-DOAS observations of O_3, HCHO, and HONO mixing ratios at three light paths nominally at 40-70 m, and 70-150 m

and 150-300 m above ground. In general, HONO photolysis dominates in the lowest and middle light path in the morning. Morning HONO photolysis in the upper height interval is about equally important as HCHO, and sometimes O_3, photolysis. At around 10:00 CST ozone photolysis becomes the most important OH source. However, both HCHO and HONO photolysis remain important. It is interesting to note that OH formation from ozone and HCHO photolysis show little altitude dependence, although it appears that O_3 photolysis is slightly higher aloft. In contrast, OH formation through HONO photolysis shows very distinct gradients, with higher rates near the surface. In the lower two height intervals HONO photolysis is the second most important OH source after 10:00 CST. In the upper interval HCHO photolysis is equally or even more important than HONO photolysis. In the later afternoon HONO photolysis again becomes the dominant OH source in the lowest two height intervals.

Objective 9. Investigate the processes creating strong correlations between HNO_3 and gas phase chloride, and their implications for coupled Cl and NOx chemistry in Houston. (UNH).

Gaseous nitric acid (HNO_3) and gas phase soluble chloride (Cl^-) were highly correlated on short (minutes to hours) time scales throughout the SHARP campaign. This correlation between soluble Cl^- and HNO_3 was discovered during the early days of SHARP campaign and re-analysis of the 2006 TRAMP data revealed that is also phenomenon also occurred during that project. Peak mixing ratios of soluble Cl^- occurred during transport from south (i.e., clean conditions) with lower mixing ratios occurring in polluted from the north and east. Overall the opposite conditions resulted in peak HNO_3 mixing ratios yet there is a remarkably strong correlation between HNO_3 and soluble Cl^- from sample to sample and diurnally were observed regardless of wind direction. During intervals with sustained northerly flow (relatively low Cl^-) daytime maxima routinely exceeded 1 ppbv. Similar observations made during TexAQS 2006 on the Moody Tower and the NOAA vessel Ronald H. Brown indicate that abundant soluble Cl^-, linked with HNO_3 by processes not yet understood, is characteristic of the Houston-Galveston Bay region during both spring and summer.

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

End Date Extended to November 30, 2011

Dallas Measurements of Ozone Production

University of Houston – Barry Lefer

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

Funding Awarded: $195,054

Annual Project Update:

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 (February 2001 – August 2011):

Task 1 was to purchase and fabricate the various components of the MOPS instruments. A new design adds a bit more complexity to the instrument, but this new method is significantly faster and more importantly provides a better measure of the "background" ozone production for the MOPS system.

Task 2 was to identify CAMS sites with help of AQRP and TCEQ for MOPS instrument deployments. The PI team selected and received permission from the City of Fort Worth and TCEQ to setup MOPS instruments at the Eagle Mountain Lake (C75) and Fort Worth Northwest (C13) sites for summer and fall of 2011.

Task 3 was to deploy two MOPS instruments for an extended period of time in the DFW area. The MOPS team installed the 1st MOPS instrument at the Eagle Mountain Lake (C75) site during the first week of August 2011. The second MOPS system was installed at the Fort Worth Northwest (C13) site during the 3rd week of August

During the last two weeks of August the MOPS instruments have been working consistently; with intermittent problems. The MOPS PI team is currently evaluating the August MOPS data, a month with a number of DFW ozone exceedances. Specifically for the month of August, the MOPS System at Eagle Mountain Lake (MOPS-C75) has deployed for a total of 26 days, with the cover working for 9.5 days (36%); the cover was open for 3 days (11%); and offline for 13.5 days (52%). The (MOPS-C13) was deployed for the last 17 days of the month with the cover working for 4 days (23%); the cover open for 2.5 days (18%); cover closed for 1 day (7%); and instrument off-line for 7.5 days (53%). With fixes to the communication string that UH has made the last week of August the time off-line has shrunk to less than 4%.

Data collection will continue in September and October.

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

End Date Extended to November 30, 2011

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

ENVIRON International – Greg Yarwood

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

Funding Awarded: $237,481

Annual Project Update:

Introduction

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 performed new environmental chamber experiments to characterize NOx sinks and sources for VOCs that are poorly understood. New experiments were performed using the aromatic hydrocarbon toluene and its degradation products, the biogenic hydrocarbon isoprene, and several nitrogen-containing organic compounds that are prototypical of compounds found in the atmosphere. In addition, data were obtained from chamber experiments performed in Europe that have not been utilized in the US for developing chemical mechanisms. The data obtained have been 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.

Experiments Performed

A total of 33 dual reactor environmental chamber experiments were performed for this AQRP project at the University of California at Riverside (UCR). Because of the dual reactor design, each successful experiment provides data for two separate reactor irradiations, each of which can be treated as a separate experiment for modeling purposes. Modeling input and experimental output data were obtained for a total of 55 such reactor irradiations (runs). The experiments may be divided into 3 groups: NOx sink experiments, NOx source experiment and chamber characterization experiments needed to support interpretation of the former.

NOx sink experiments added a test compound to an alkene-NOx mixture and measured the resulting change in ozone and other compounds. Because alkene-NOx experiments inherently have strong radical production and weak NOx sinks they are sensitive to NOx sinks introduced

by the test compound. Experiments were carried out for toluene, o-cresol, furan (a precursor to the aromatic fragmentation product 2-butene-1,4-dial), and isoprene. Several isoprene-NOx experiments with low initial NOx concentrations were also performed to support interpretation of the NOx sink experiments for isoprene. The NOx sink experiments demonstrated that all of the compounds tested inhibited ozone formation by mixtures of ethene and NOx because the test compounds have strong NOx sinks that convert NOx to inactive forms.

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

Chemical Mechanism Development

The TCEQ is using the CB6 mechanism for ozone SIP modeling and mechanism improvements will benefit the reliability of SIP planning. The new experiments conducted at UCR, combined with experiments retrieved from the European EUPHORE chamber for this project, have been used to improve the Carbon Bond 6 (CB6) mechanism. The revised mechanism is to be called CB6r1.

The results of NOx sink experiments conducted with toluene, o-cresol, furan (a precursor to 2-butenedial) and isoprene are shown in Figure 1. The effect on ozone and NO_2 of adding the test compound was simulated very well for o-cresol and isoprene and fairly well for toluene and furan. These results suggest that CB6r1 is performing well in representing the strengths of the NOx-sinks present for toluene, o-cresol, and isoprene. The results for furan are complicated by the fact that furan is not the compound of interest but rather was used as a precursor to make 2-butenedial (the compound of interest) during the chamber experiment. Results from a EUPHORE experiment (not shown) that was performed using 2-butenedial directly are being used to complement results from the experiment with furan shown in Figure 1.

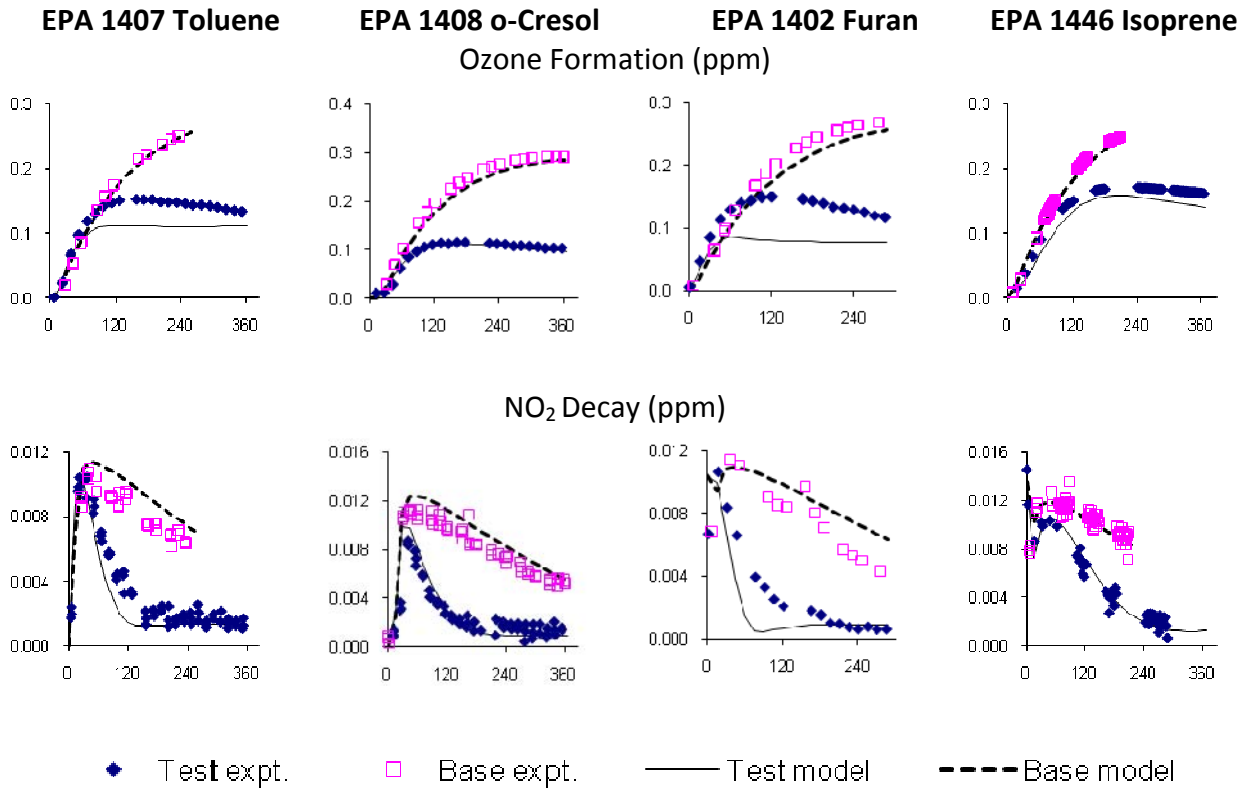

Figure 1. Model simulations with CB6r1 of NOx sink experiments with toluene, o-cresol, furan and isoprene added to a base mixture of ethene and NOx .

The NOx source experiments with alkyl nitrates (isopropyl nitrate and isobutyl nitrate) demonstrate formation of NOx when organic nitrates undergo photolysis and reaction with OH. The evidence is stronger for photolysis than OH reaction because photolysis dominated the decay of the organic nitrates in the experiments performed. Figure 2 shows results of NOx source experiments and simulations with CB6r1. The yields of NO_2 (and O_3) are simulated very well by CB6r1 for experiments with isopropyl nitrate and isobutyl nitrate.

Simulations of experiments with 2-nitrophenol are shown in Figure 2. Simulations using several test mechanisms confirm that 2-nitrophenol decayed rapidly by photolysis and this reaction needed to be added to CB6r1. Formation of NO_2 from 2-nitrophenol was observed and CB6r1 simulates the NO_2 formation fairly well. Formation of O_3 was observed although the measurement suffers from strong interference (i.e., UV absorption) by 2-nitrophenol and the apparent good agreement for the final O_3 may be misleading. The NOx source experiments for 2-nitrophenol provided important evidence for photolysis of nitrophenols accompanied by formation of NOx and this process has been included in CB6r1 for nitrophenols and nitrocresols formed from aromatic hydrocarbons.

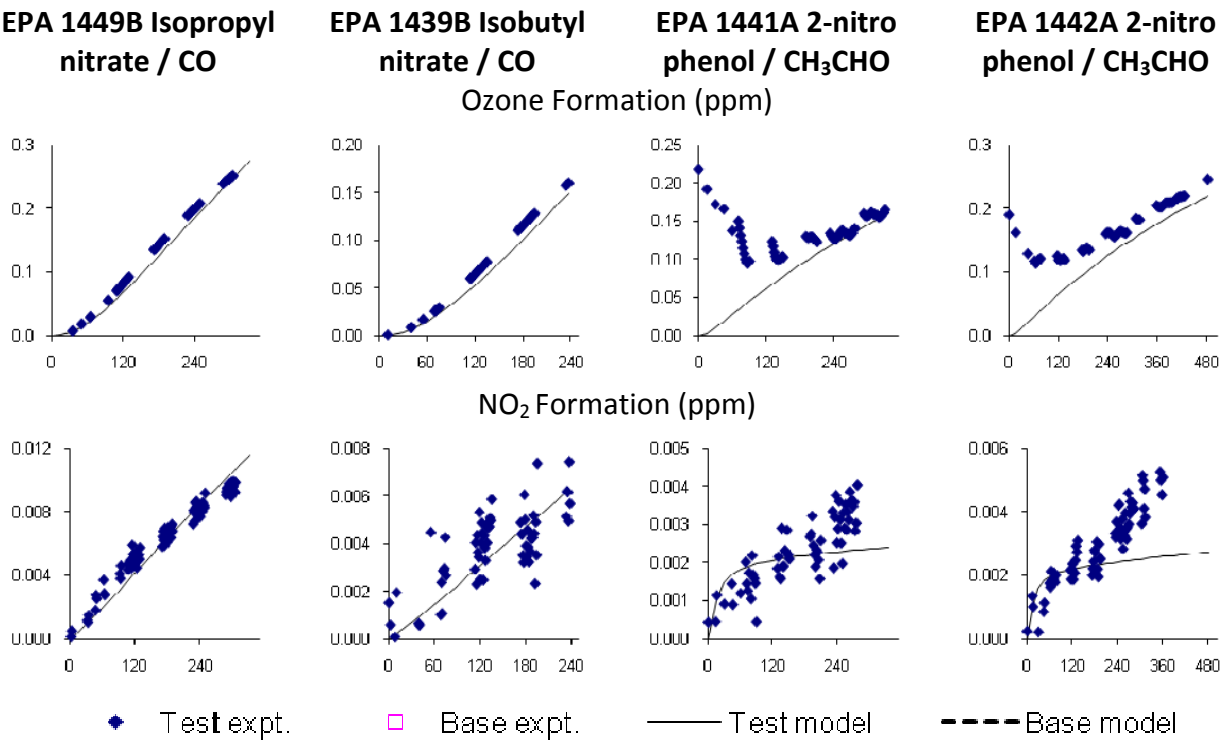

Figure 2. Model simulations with CB6r1 of NOx source experiments with organic nitrates added to mixtures of CO and H_2O_2 or CH_3CHO and H_2O_2.

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

End Date Extended to November 30, 2011

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

University of Houston – Maxwell Shauck

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

Funding Awarded: $279,642

Annual Project Update:
The University of Houston (UH) aircraft-based Air Quality Monitoring Team participated in an air quality field study in the Dallas Fort Worth (DFW) area during the 2011 ozone season. This study, administered by the Air Quality Research Program (AQRP), was conducted in coordination with ground based air quality measurements performed by UH and other institutions.

Airborne air quality measurements enable investigators to better understand the mechanisms associated with the transport of precursors and their contribution to ozone formation under specific meteorological conditions.

A twin-engine Piper Aztec aircraft equipped with a full complement of instrumentation was utilized. Both aircraft and instruments were extensively modified for the purpose of air quality monitoring.

The aircraft sampling data complemented the ground based measurements to enhance the understanding of atmospheric chemistry processes, meteorology, spatial distribution and transport of pollutants of interest in and around the DFW area. The campaign included 50 flight hours flown during the latter part of June and early part of July. The primary objectives of the program addressed the characterization of the air quality, the transport of ozone and ozone precursors and the potential contribution of emissions associated with natural gas production in the vicinity of gas wells and compressor stations located in the Barnett Shale region.

Detailed flight plans were developed in coordination with AQRP that provided identification of emission sources and objectives for each measurement flight. The UH Aztec collected airborne samples on five science flights measuring ozone (O_3), nitrogen oxides (NOx), sulfur dioxide (SO_2), formaldehyde (HCHO), reactive alkenes, volatile organic compounds (VOC), and meteorological parameters.

The meteorological conditions were quite consistent during the measurement period with steady southerly synoptic flows, sunny and hot conditions. Thus, it was possible to collect data under very similar conditions. The study focused on Barnett Shale and the DFW downwind conditions during photochemically active daytime periods.

Major results of the project include the following observations:

- Regional DFW Metroplex: Upwind ozone levels (i.e. in this case south of the DFW Metroplex) typically range between 30-50 ppbv and largely agree with ozone background levels determined in other studies in Texas. Highest secondary pollutants occur in the downwind area of the urban DFW Metroplex. Typically, maximum ozone values may be enhanced by a factor 2-2.5 compared with the values obtained in the upwind area on the same day.

- Urban DFW area: the urban plume is characterized by enhanced NOy and CO. Levels of NO, NO_2 and reactive alkenes remain modest in the downwind area of the DFW Metroplex indicating photochemically aged air masses.

- Barnett Shale area: at times HCHO and reactive alkenes correlate in the Barnett Shale area, while ozone and NOy are not that well correlated with reactive alkenes.

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

End Date Extended to September 30, 2011

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

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

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

Funding Awarded: $398,401
($150,132 UCLA, $33,281 UNC, $164,988 Aerodyne, $50,000 Washington State)

Annual Project Update:

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

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

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

The destruction removal efficiency, DRE, and combustion efficiencies, CE, from in-use flares were also quantified using ground-based in situ measurements. Uncertainty in knowledge of the vent gas leads to uncertainties in the DRE but not the CE values. A range of DRE and CE values

were observed for in-use flares – ranging from 0 (unlit) to 0.7 (steaming) to 0.999 (presumably operating as intended).

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

Analysis of the emission inventory in Texas City, as well as triangulation and wind field analysis revealed that the most likely source of HCHO is a FCCU regeneration unit. The 2006 ozone non-acid rain inventory reports 2.6 kg/h of HCHO emissions from this FCCU unit. The 2006 base case reg 10 emission inventories shows that the area around this unit emits 3.3 – 4.3 kg/h of formaldehyde-like compounds (designated in inventory as FORM). All reported HCHO emission rates are considerably smaller than those found in our observations. It is not clear at this point if units of this type in other refineries would also emit HCHO.

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

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

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

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

Project 10-DFW & 11-DFW	**STATUS: Active - February 1, 2011**
	Project Complete: August 31, 2011

Dallas – Fort Worth Field Study

UT-Austin – Vincent Torres

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

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

Executive Summary:
Due to the fact that there 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). Expenditures for the project were dedicated to making the DFW field site ready for the measurement teams, including arranging access agreements, preparing the site, and arranging for power, communications and site security.

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

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