AIR QUALITY RESEARCH PROGRAM

Texas Commission on Environmental Quality
Contract Number 582-15-50047
Awarded to The University of Texas at Austin

Quarterly Report

December 1, 2016 through February 28, 2017

Submitted to

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Texas Air Quality Research Program

Quarterly Report

December 1, 2016 – February 28, 2017

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.

PROGRAM ACTIVITIES FOR THE QUARTER

Between December 1, 2016 and February 28, 2017, the AQRP Program Administration executed the final contractual agreements with the entities performing research projects. The focus then turned to ensuring that all project investigators were informed of, and met all reporting requirements, both technical and financial. Once the final Work Plans were approved, the Project Managers worked with the Investigators to ensure that all project activities were underway. They also assisted with ensuring all technical reporting requirements were being met.

At the end of the previous quarter, Master Agreements, defining the general terms and conditions of contracting with The University of Texas at Austin under the AQRP, had been executed with each of the universities and business that were awarded research projects. Eight of the ten research projects were authorized to begin work, although two of the eight had Task Orders (project specific contractual documents that outline the period of performance, budget, and scope of work to be performed) that were not yet fully executed. In December, one additional Work Plan (project Statement of Work, Budget and Budget Justification, and Quality Assurance Project Plan (QAPP)) was approved and a Task Order was issued. All three of these Task Orders were fully executed by the end of December. In January, the final project Work Plan was approved and the Task Order was issued, signed, and fully executed by the end of the month.

During this quarter, projects began invoicing and the Program Administration worked with each institution to ensure that the invoices were complete and all expenses were allowable. This will continue throughout the term of the projects.

In February the Program Administration also began a redesign of the AQRP website. This will be completed during the next quarter.

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).

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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.
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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 July 29, 2015 for the 2016-2017 biennium. Consistent with the provisions in HB 1796, up to 10% of the available funding is to be used for program administration; the remainder (90%) of the available funding is to be used for research projects, individual project management activities, and meeting expenses associated with an Independent Technical Advisory Committee (ITAC).

RESEARCH PROJECT CYCLE

The Research Program is implemented through a 9 step cycle. The steps in the cycle are described from project concept generation to final project evaluation for a single project cycle.

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, the Council and the TCEQ, develop research priorities; the research priorities are released along with a Request for Proposals.

2.) Project proposals relevant to the research priorities are solicited. The Request for Proposals can be found at http://aqrp.ceer.utexas.edu/ .

3.) The Independent Technical Advisory Committee (ITAC) performs a scientific and technical evaluation of the proposals.

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.

5.) The recommendations from the ITAC and the TCEQ are presented to the Council and the Council selects the proposals to be funded. The Council also provides comments on the strategic research priorities.

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

7.) Funded projects are assigned an AQRP Project Manager at UT-Austin and a Project Liaison at TCEQ. The AQRP Project Manager 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 AQRP Project Manager has responsibility for documenting progress toward project measures of success for each project. The AQRP Project Manager works with the researchers, and the TCEQ, to create an approved work plan for the project.

   The AQRP Project Manager also works with the researchers, TCEQ and the Program's Quality Assurance officer to develop an approved Quality Assurance Project Plan (QAPP) for each project. The AQRP Project Manager reviews monthly, annual and final reports from the researchers and works with the researchers to address deficiencies.

8.) The AQRP Director and the AQRP Project Manager for each project describe progress on the project in the ITAC and Council meetings dedicated to on-going project review.

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

Steps 7 and 8 are in progress for the quarter being reported.

RESEARCH PROJECTS

FY 2016 – 2017 Projects

Project 16-008	**STATUS: Active – Sept. 22, 2016**

High Background Ozone Events in the Houston-Galveston-Brazoria Area: Causes, Effects, and Case Studies of Central American Fires

University of Houston – Yuxuan Wang

AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Doug Boyer

Funded Amount: $191,366

Abstract
A significant fraction of surface ozone in Texas comes from regional background originating from outside the state. Background ozone is particularly variable over the Houston-Galveston-Brazoria (HGB) region due to its unique geographical location and meteorology. Prior analyses of the HGB background ozone have focused predominantly upon averages, not high concentration days or exceptional events. To bridge this gap, the objectives of this project are to identify high background ozone events across the HGB area over the past 16 years (2000-2015), characterize meteorological conditions and anomalous emissions that cause these events, and understand their effects on ozone exceedances. With regard to emission anomalies, the focus will be on fire events from Mexico and Central America, a large fire region globally of unique importance to Texas air quality in springtime and summer whose impact on Texas background ozone has not been quantified.

Integrated analyses of observations and modeling will be conducted to achieve the project objectives. Daily HGB background ozone estimated by researchers at the Texas Commission on Environmental Quality (TCEQ) will be used as the data source to identify high background ozone days. Different types of meteorological events which may be potentially associated with high background ozone (e.g., cold fronts and thunderstorms) or high local photochemical production (e.g., heat waves and stagnation) will be identified based on the analysis of meteorology data. The relationship between high background ozone days and the meteorological ‘event days’ will be characterized, e.g., in terms of their overlapping (or the lack of it), and background ozone difference between meteorological ‘event days’ and ‘non-event days’ will be evaluated. Anomalies in fire emissions leading to high background ozone will be mapped through spatiotemporal sampling of the Fire INventory from NCAR (FINN) along background trajectories of air masses affecting the HGB area prior to and during the selected high background ozone days. The GEOS-Chem global chemistry transport model, with the FINN inventory implemented, will be used to simulate a number of case studies of large Central American fires and estimate the perturbations caused by ozone precursor emissions from those fires on background ozone concentrations in Texas and the HGB area. Finally, we will develop a quantitative estimate of the effects of background ozone versus local production on ozone exceedance cases in the HGB area and the dependence of such effects on meteorology and Central America fire emissions.

Project Update

The following progress has been made towards project goals:

Distributions of MDA8 and background ozone mixing ratios during heatwave and stagnation event days were investigated (Figure 1). Stagnation events (green curves in Fig 1) were always associated with higher MDA8 and background ozone in HGB, not only leading to higher means of the ozone distribution but also higher tails. As heatwaves occurred irregularly from year to year and month to month, its effects on HGB ozone were not as clear or robust because the sampling may have missed some of the events. Three different methods of selecting 15% highest ozone days were tested and compared. The top 15% in a single month is the most "stable" method to select the highest ozone days to minimize the impact of large month-to-month and year-to-year variability in ozone. However, this method missed some high ozone days during the heatwave years (e.g. 2011); in these cases, using a fixed threshold (e.g. 70 ppbv) may be better in capturing all the high ozone days.

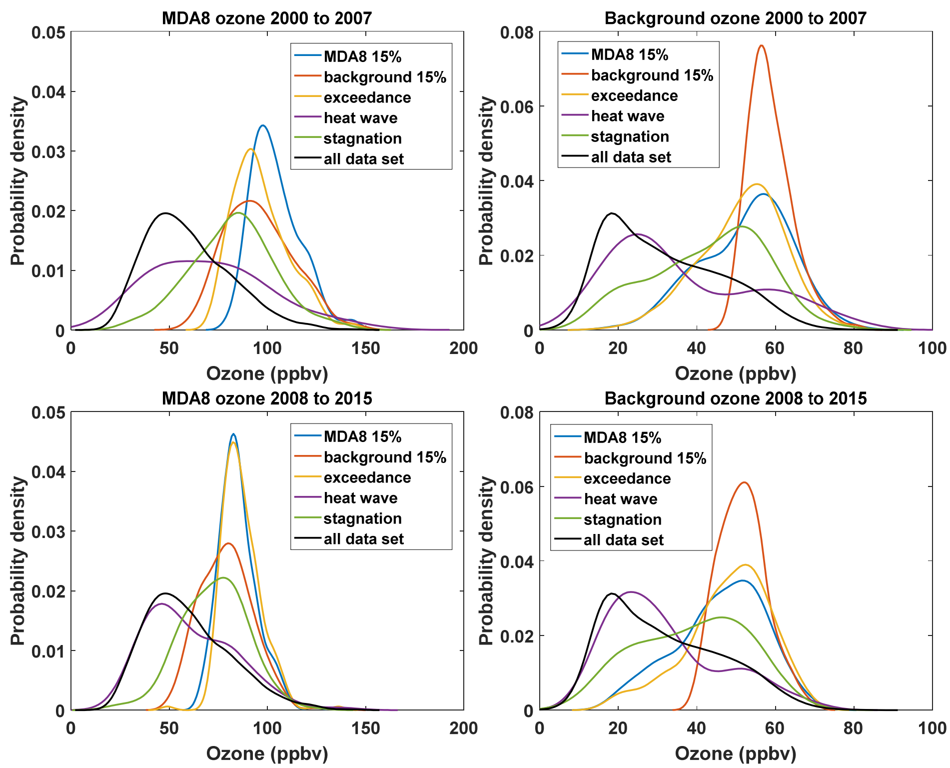

Figure 1. MDA8 (left column) and background (right column) ozone mixing ratios during weather events and high ozone days 2000-2007 (upper row) versus 2008-2015 (lower row).

The HGB background ozone data were categorized by air mass origins calculated with 72-hour back trajectories (Figure 2). Compared with the Gulf-clean category, which represents the clean maritime background without being directly influenced by emissions from land, the impact of Yucatan fires on HGB background ozone is estimated to be 4.26 ppbv on average and that of Central Mexico fires is 12.81 ppbv. The different level of contributions between Yucatan and Central Mexico fires can be explained by the distance of transport and emissions from different sources.

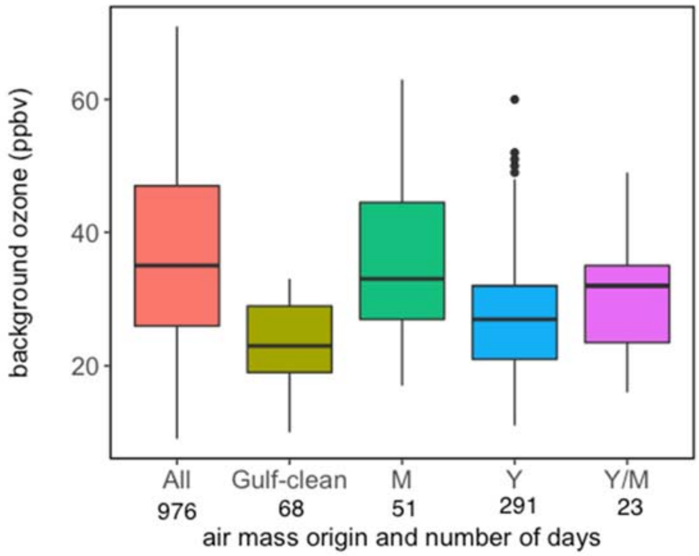

Figure 2. The boxplot of HGB background ozone in April and May 2000-2015 in each group of air mass origins: M indicates Mexico, Y indicates Yucatan, and Y/M indicates both Mexico and Yucatan. The numbers on the x-axis are the number of days in each group.

GEOS-Chem model simulations with the resolution of 0.5°x 0.667° for two case studies were conducted. These two cases were on April 26-27, 2011 and May 9-11, 2008, which have been reported by literatures. Two runs with and without fire emissions for each case were conducted to test the impact of Central American fires. Figure 3 shows the maps of surface ozone simulated by GEOS-Chem on April 27 2011. The plume caused by the fires in Yucatan was clearly shown in Figure 3. The contribution of the Yucatan fires on HGB surface ozone was around 3-5 ppbv in the model results, which was consistent with the observation data shown in Figure 2.

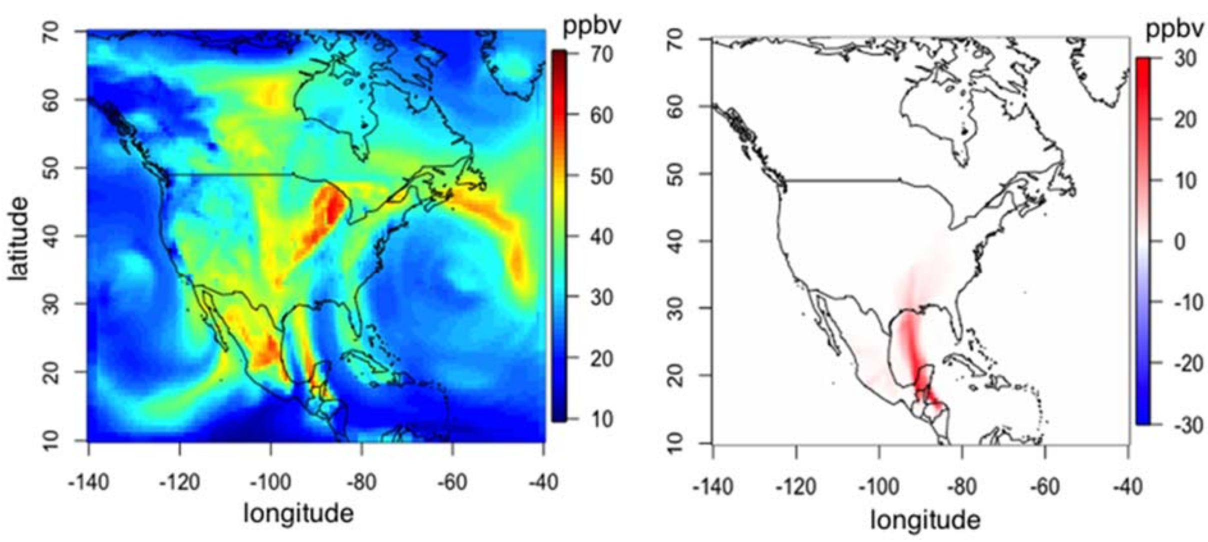

Figure 3. Left: The simulated surface ozone on April 27 2011. Right: The differences of surface ozone concentration with and without Central American fires on April 27 2011.

There are no delays or other issues to report at this time.

Project 16-010	STATUS: Active – Oct. 20, 2016

MOVES-Based NOx Analyses for Urban Case Studies in Texas

Sonoma Technology, Inc. – Stephen Reid

AQRP Project Manager – Gary McGaughey
TCEQ Project Liaison – Chris Kite

Funded Amount: $69,075

Abstract

Emissions inventories are an important component of air quality planning and a key input to photochemical grid models that support air quality assessments. Findings from recent studies suggest that nitrogen oxides (NOx) emissions may be overestimated in the U.S. Environmental Protection Agency's (EPA) National Emissions Inventory (NEI), perhaps by as much as a factor of two. This overestimate has generally been attributed to the mobile source sector (e.g., on-road motor vehicles), for which emission estimates are prepared using EPA's MOVES model. A number of potential issues have been identified with MOVES, including reliance on the model's default input data rather than more representative local inputs.

The overall goals of this project are to examine MOVES emission estimates at the local scale and identify which input parameters have the greatest influence on NOx emission estimates. Specifically, we will use a well-established emissions reconciliation technique to quantitatively compare MOVES emission results with ambient near-road monitoring data. These analyses will be performed for case studies in three Texas metropolitan areas: Dallas-Fort Worth, Houston, and El Paso. In addition, we will perform sensitivity analyses comparing MOVES emission results using default vs. local data to identify key parameters that have substantial influence on NOx emissions. The results of this work will support emissions inventory development and air quality management efforts in Texas by providing information on the accuracy of current MOVES emission estimates and MOVES input parameters, for which local data are critical.

Project Update

Over this quarter (December 2016 to February 2017), the project team followed the project plan and continued work on Task 1 Emissions Reconciliation Analyses. The team assessed the analysis areas and collected pollutant concentration data for three near-road monitoring sites in Houston, Fort Worth, and El Paso; the team also collected local MOVES modeling data from TCEQ (Texas Commission on Environmental Quality), NCTCOG (North Central Texas Council of Government), and HGAC (Houston-Galveston Area Council). Using the collected data, the team performed quality assurance and continued work to (1) process the concentration data to calculate ambient-based CO/NO_x ratios for each site; (2) conduct MOVES modeling runs with local inputs; and (3) compare ambient-based and emissions-based CO/NO_x ratios.

Over the next quarter, work will focus on completing the emissions reconciliation analysis with processing monitoring air quality data from the selected near-road and background sites, conducting MOVES scenario runs, and comparing ambient-based and emission-based pollutant ratios. The project team will also start work on MOVES sensitivity analyses in the next quarter.

There were no delays or issues related to the project during this reporting time period. The project team intends to use all funds allocated to the project by 8/31/2017 to complete the planned work tasks.

Project 16-011	STATUS: Active – Oct. 6, 2016

A Next Generation Modeling System for Estimating Texas Biogenic VOC Emissions

Ramboll Environ US Corporation – Gregory Yarwood

AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Doug Boyer

Funded Amount: $158,134

Abstract

The exchange of gases and aerosols between the Earth's surface and the atmosphere is an important factor in determining atmospheric composition and regional air quality. Emissions of reactive gases from the earth's surface drive the production of ozone and aerosol and other atmospheric constituents relevant for regional air quality. Emissions of some compounds, including biogenic volatile organic compounds (BVOCs), are highly variable and can vary more than an order of magnitude over spatial scales of a few kilometers and time scales of less than a day. This makes estimation of these emissions especially challenging and yet accurate quantification and simulation of these fluxes is a necessary step towards developing air pollution control strategies and for attributing observed atmospheric composition changes to their causes.

The overall goal of Project 16-011 is to improve numerical model predictions of regional ozone and aerosol distributions in Texas by reducing uncertainties associated with quantitative estimates of BVOC emissions from Texas and the surrounding region. Although there have been significant advancements in the procedures used to simulate BVOC emissions, there are still major uncertainties that affect the reliability of Texas air quality simulations. This includes significant gaps in our understanding of BVOC emissions and their implementation in numerical models including 1) isoprene emission factors, 2) missing compounds, and 3) and unrepresented processes including canopy heterogeneity and stress induced emissions. In this project, we will develop new emission factors and incorporate missing BVOC compounds and unrepresented BVOC emission processes into the Model of Emissions of Gases and Aerosols from Nature (MEGAN) framework. To accomplish this, we will develop a transparent and comprehensive approach to assigning isoprene and monoterpene emission factors and will update MEGAN to include additional BVOC and processes including stress induced emissions and canopy heterogeneity. We will evaluate MEGAN BVOC emission inventories for Texas and surrounding regions using surface and aircraft observations and a photochemical model.

The overall benefit of this project will be more accurate VOC emission estimates for the Texas air quality simulations that are critical for scientific understanding and the development of regulatory control strategies that will enhance efforts to improve and maintain clean air.

Project Update

During the December 2016 - February 2017 quarter, work was carried out on Tasks 1- 3 and Task 5.

Task 1: Development and Application of a Transparent Approach for Estimating BVOC Emission Factor Distributions

During December, Dr. Guenther revised the model framework for calculating BVOC emission factors based on discussions with Ramboll Environ and TCEQ staff (Figure 1). Ramboll Environ then explored various database options for system development and arrived at a Python/SQLite database platform in consultation with TCEQ and Dr. Guenther. In January, Ramboll Environ developed a draft BVOC emission factor database and implemented a schema of database tables and queries in Python/SQLite. Ramboll Environ prepared a detailed Readme file that provides a list of required packages and information on how to install them and use the BVOC database system. In February, Dr. Guenther began review and testing of the draft database system.

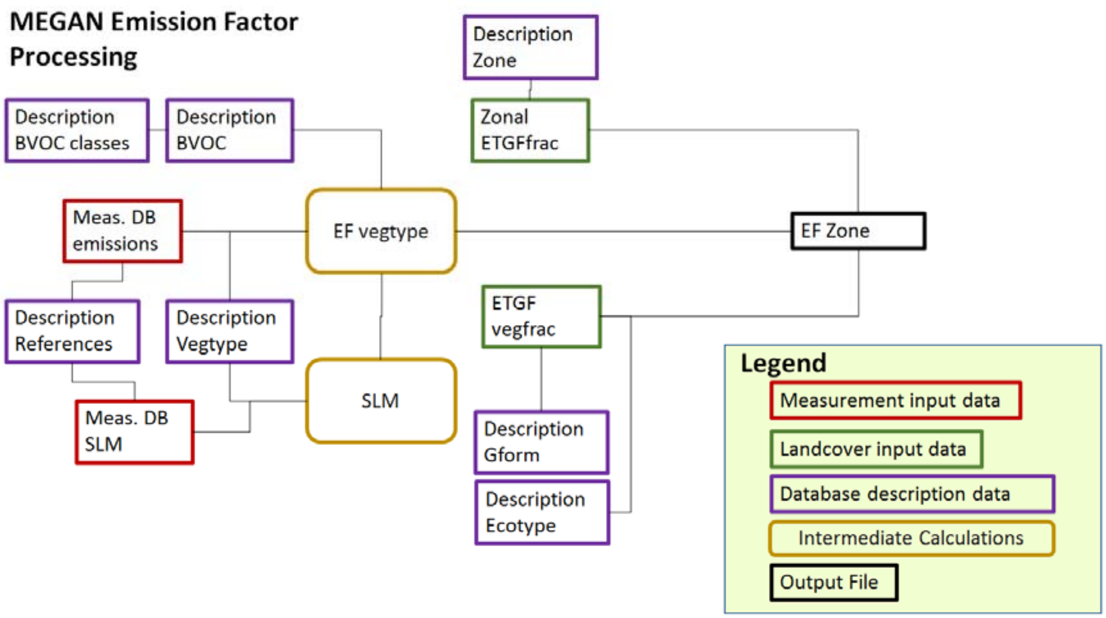

Figure 1. Schematic of MEGAN emission factor processing.

Task 2: Emission Factor Development

Task 2 was initiated in December. Dr. Guenther populated the emission measurement and specific leaf mass database with results summarizing more than 500 published studies. Dr. Guenther compiled above-canopy flux measurements from aircraft and tower flux studies and integrated them into the emission measurement database. Emission factors used in MEGAN2.1 and BEIS for the Texas region were assessed and compared with other data in the emission factor database to initiate the process of reconciling various observations and emission factor data.

Task 3: Development of MEGAN3

The MEGAN emission category approach was updated by adding additional compounds and by revising the emission categorization. The scheme was integrated into the emission factor processor developed under Task 1.

Approaches for clarifying/improving the MEGAN code were developed and documented by Alex Guenther and provided to Ramboll Environ to be implemented in the MEGAN code. Dr. Guenther defined the MEGAN3 overall structure and specific programing tasks for new model features (e.g., stress induced emissions) and communicated it to Ramboll Environ for implementation. Ramboll Environ made several improvements and clarifications to the existing MEGAN code to address concerns noted by users and began the development of MEGAN3 code.

Dr. Guenther and Ramboll Environ collaborated on the MEGAN3 programming and overall structure. Ramboll Environ prepared a draft package of MEGAN3 source code with job scripts, input/output data, log files, etc. Dr. Guenther examined the structure of the draft MEGAN3 code and tested the code. Additional modifications (canopy environment model improvements, update of existing parameters, and clarification of existing code) were implemented.

Task 4: MEGAN Evaluation and Sensitivity Study

Task 4 has not yet been initiated.

Task 5: Project Management and Reporting

This task is ongoing. Dr. Guenther began compiling information for the final report.

The project team anticipates that all funds allocated for the project will be utilized by August 31, 2017.

Project 16-019	STATUS: Active – Sept. 30, 2016

The Influence of Alkyl Nitrates from Anthropogenic and Biogenic Precursors on Regional Air Quality in Eastern Texas

University of Texas at Austin – Elena McDonald-Buller
Ramboll Environ US Corporation – Gregory Yarwood

AQRP Project Manager – David Sullivan
TCEQ Project Liaison – Jim Smith

Funded Amount: $180,641
($118,019 UT Austin, $62,622 Ramboll Environ)

Abstract
Mono and multifunctional alkyl nitrates (ANs) are formed from the oxidation of biogenic or anthropogenic volatile organic compound (VOC) precursors and serve as a reservoir or sink of nitrogen oxides (NO_x). Alkyl nitrates have sufficiently long atmospheric chemical lifetimes (hours to days), such that they can influence tropospheric ozone and secondary organic aerosol (SOA) formation over regional to global spatial scales. Their functionalities, yields, and fates are known to depend upon the size and structure of the VOC. Depending on their structure, ANs can be transported, chemically processed, removed by deposition to vegetation and other surfaces, or undergo partitioning to and from the aerosol phase where hydrolysis is thought to be a loss mechanism. Although knowledge gaps still exist, recent laboratory and field studies have provided new insights on these processes for ANs formed from biogenic and anthropogenic hydrocarbon precursors. An ongoing need will be to incorporate these findings into the chemical mechanisms of photochemical models used to assess regional air quality. The objectives of this work are to apply the findings of ongoing experimental studies examining alkyl nitrates formed from the OH-initiated oxidation of C8-C11 alkanes at the University of Texas at Austin in addition to those of new publications that have focused on other hydrocarbon precursor classes relevant to Texas emissions inventories to improve how ANs are represented in the version 6 of the Carbon Bond mechanism (CB6). Revision 4 of CB6 (CB6r4) will soon be available in version 6.32 of the Comprehensive Air quality Model with extensions (CAMx v6.32). Sensitivity tests with CAMx will evaluate the formation and fate of ANs in central and southeastern Texas, the influence of ANs on regional ozone by recycling NO_x, and dependencies on organic aerosol concentrations.

Project Update
The project consists of three tasks: (1) develop modifications to the CB6r4 mechanism in CAMx, (2) evaluate the CB6r4 updates in CAMx modeling during the time period of the DISCOVER-AQ campaign through sensitivity studies that evaluate the formation and fate of ANs in central and southeastern Texas, the influence of ANs on regional ozone by recycling NO_x, and dependencies on organic aerosol concentrations, and (3) disseminate results through reporting, publications, and presentations. Project activities began in October 2016. Progress to date is described below. We anticipate that all funds allocated for the project will be utilized by August 31, 2017.

Task 1: Refinements to the CB6r4 Mechanism in CAMx

Work on Task 1 this quarter has focused on establishing and running the CAMx base case and planning for updates to the CB6r4 chemical mechanism. The project leverages a CAMx episode for the DISCOVER-AQ time period (August 18-September 30, 2013) developed for AQRP Project #14-024. It has several important updates including expansion of the 4-km domain to include all of eastern Texas, updates to more recent data for land use/land cover and leaf area index (LAI), and use of CAMx 6.40 and the gas-phase chemical mechanism, CB6r4.

Two algorithms are available in CAMx 6.40 to describe organic gas-aerosol partitioning and oxidation: the hybrid 1.5-dimensional (1.5-D) Volatility Basis Set (VBS) or Secondary Organic Aerosol Partitioning (SOAP) schemes. SOAP has been recently updated with the latest information on SOA yields, saturation concentrations, and water solubility; the most recent version, SOAP2, is available in CAMx 6.40. Although we initially proposed to use the 1.5-D VBS approach in the evaluation of the chemical mechanism updates for the project, the Texas Commission on Environmental Quality (TCEQ) has approved the application of the SOAP2 scheme instead, as it is expected it to be more widely used. Results with VBS are being compared to those with SOAP2 as a sensitivity study. However, all other CAMx sensitivity studies with the mechanism updates (Task 2) will use the SOAP2 scheme. Emissions estimates for intermediate volatile organic compounds (IVOCs) were prepared for the VBS scheme and then mapped to species for SOAP2.

On-going experiments and a literature review are informing the planning for updates to the CB6r4 mechanism. The updates have had three areas of focus:

(a) Organic Nitrates from Anthropogenic Alkane and Alkene Precursors
Chamber experiments at the University of Texas at Austin, under the sponsorship of the Texas Air Research Center (TARC), are examining the gas-particle partitioning and particle-phase hydrolysis of organic nitrates from alkane and alkene precursors of differing sizes and structures that typically originate from anthropogenic emission sources. Experiments are characterizing the dependence of particle-phase hydrolysis loss rates of organic nitrates on relative humidity and aerosol pH. Updates are planned to modify the CB6r4 surrogate species for C4+ alkanes (named PAR) into two species to better differentiate organic nitrate yields and their tendency to partition to the aerosol phase where they can be hydrolyzed.

(b) Organic Nitrates from the Nitrate-Radical Initiated Oxidation of Monoterpenes
Recent environmental chamber experiments and measurements in the southeastern U.S. as part of the Southern Oxidant and Aerosol Study (SOAS) and Southeastern Center for Air Pollution and Epidemiology (SCAPE) studies have provided new insights on the effects of nitrate radical-initiated oxidation of monoterpenes on organic nitrate and secondary organic aerosol (SOA) formation and fate. Characterizations of organic aerosol species in the southeastern U.S., as well as during DISCOVER-AQ in southeastern Texas, have indicated that less-oxygenated organic aerosol (LO-OOA), which peaks at night, is correlated with the nitrate functionality from organic nitrates. Its prevalence indicates the important contribution of monoterpene organic nitrates to total organic aerosol in both regions. SOA yields and the ability of organic nitrates formed from NO_3+monoterpene chemistry to serve as permanent or temporary NO_x sinks vary with

monoterpene precursors. The CB6r4 mechanism will be modified to differentiate the single surrogate species for all terpenes (named TERP) into two species based on α-pinene and β-pinene as surrogates.

(c) pH-Dependent Hydrolysis of Organic Nitrates
Hydrolysis of organic nitrates in the aerosol phase at elevated relative humidity can act as a NO_x sink, influencing NO_x and O_3 transport. Recent experimental work has examined the effects of solution acidity on hydrolysis rates of simple alkyl nitrates and an organic nitrate derived from α-pinene oxidation by hydroxyl radical. Hydrolysis rate constants increased with solution acidity for all organic nitrates studied. Implementation of pH-dependent hydrolysis rates using aerosol pH derived by the inorganic thermodynamic model ISORROPIA in CAMx is planned.

Task 2. Evaluating CB6r4 Updates in CAMx Modeling for DISCOVER-AQ
Not yet initiated.

Task 3. Project Reporting and Presentation
On-going per requirements.

Project 16-031	STATUS: Active – Oct. 18, 2016

Condensed Chemical Mechanisms for Ozone and Particulate Matter Incorporating the Latest in Isoprene Chemistry

University of North Carolina – Chapel Hill – William Vizuete

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

Funded Amount: $225,000

Abstract
Isoprene, the most emitted non-methane hydrocarbon on the planet, is known to influence ozone (O_3) formation in Houston, Texas. Eastern Texas and northern Louisiana feature some of the largest biogenic emission sources of isoprene in the United States. It is also now known that the photochemical oxidation of isoprene, when mixed with anthropogenic emissions from urban areas like those found in Houston, can produce significant yields of fine particulate matter ($PM_{2.5}$) through acid-catalyzed multiphase chemistry of isoprene epoxydiols (IEPOX) that leads to secondary organic aerosol (SOA) formation. Next-generation regulatory models in Houston will attempt to capture this recent discovery even though there exists great uncertainty in both gas-phase isoprene oxidation and SOA formation chemistry. This work will produce a fully updated condensed gas-phase mechanism based on SAPRC-07 and PM formation parameters suitable for use in a regulatory air quality model. The updated parameters will be evaluated against an archive of UNC smog chamber experiments, including new isoprene SOA experiments that investigate the effect of organic coatings/mixtures on the acid-catalyzed multiphase chemistry of IEPOX.

Our previously funded Air Quality Research Program (AQRP) work has directly derived the multiphase kinetics of IEPOX only on pure inorganic aerosols. In the atmosphere, however, IEPOX will more likely encounter mixed particles containing both pre-existing organics and acidic sulfate. As a result, there is a need to constrain the impact of pre-existing organics within acidic sulfate aerosol on the kinetics of IEPOX multiphase chemistry. We will also produce a regulatory air quality modeling episode focused on Houston to test these new updates in a simulated urban environment. This work directly addresses the stated priority area of improving the understanding of O_3 and PM formation and the interaction with PM precursors. Further, the regulatory air quality modeling system developed by this work can begin to address the stated priority of quantifying the impacts of uncertainty due to the treatment of atmospheric chemical processes by condensed models.

Project Update
The following progress has been made towards project goals:

Task 1 Updated SAPRC-07 and Aerosol Module for Isoprene Oxidation

<u>Data Collected</u>
We have completed the collection of our archived digital files of the experimental data needed for the evaluation of updates in the SAPRC-07 mechanism. We have completed the training of

the GRA on the software needed to complete the task. We have also conducted several discussions with Dr. William Carter concerning the evaluation of the latest version of SAPRC. Dr. Carter has agreed to let us analyze a pre-release version of SAPRC-16 for evaluation against our chamber data. Specifically he is looking for guidance on the isoprene oxidation chemistry.

Goals and Anticipated Issues for the Succeeding Reporting Period
We will complete training on the software needed to visualize the modeling results to provide meaningful analysis. We will also begin the process of integrating the SAPRC-16 chemical mechanism into our modeling system.

Detailed Analysis of the Progress of the Task Order to Date
The progress on the task is on schedule.

Task 2 Chamber Experiments: Interplay of Particle-Phase Composition, Phase, and Viscosity on IEPOX Multiphase Chemistry

Preliminary Analysis
Given that our measurement equipment was out of operation we were unable to make any progress. We feel, however, that instrument should be ready in March and our progress will remain on schedule.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments
Both the CIMS and ACSM instruments need to be repaired before further chamber experiments can proceed.

Goals and Anticipated Issues for the Succeeding Reporting Period
We will be tweaking certain aspects of our experimental approach to better constrain the uptake kinetics in the chamber. Potential Aerosol Mass (PAM) Oxidation Flow Reactor (Aerodyne Research, Inc) will be used to generate monodisperse organic aerosols, which will then be fed into the indoor chamber until targeting particle concentration is attained prior to IEPOX uptake. Two differential mobility analyzers are used to select aerosols by size, one for acidified sulfate aerosols entering the PAM and one for the organic aerosols output from PAM. With this approach, the coating thickness and size of the aerosol are in theory evenly distributed across aerosol population and therefore the modeled uptake coefficient can better represent the heterogeneous reaction probability with respect to the thickness and type of the organic layers enwrapping the acidified sulfate seeds. The PAM is expected to arrive in March.

Detailed Analysis of the Progress of the Task Order to Date
The progress on the task is on schedule.

Project 17-007	STATUS: Active – Nov. 3, 2016

Evaluating Methods for Determining the Vapor Pressure of Heavy Refinery Liquids

University of Texas at Austin – Vincent Torres

AQRP Project Manager – Gary McGaughey
TCEQ Project Liaison – Russell Nettles

Funded Amount: $205,500

Abstract

During the last five years, crude oil and natural gas production and petroleum refinery operations have seen an increased focus on their emissions of volatile organic compounds (VOCs), hazardous air pollutants (HAPS) and greenhouse gases (GHGs), especially those from storage tanks. These actions have been taken by the United States Environmental Protection Agency (US EPA) "because EPA and state investigations have identified Clean Air Act compliance concerns regarding significant emissions from storage vessels, such as tanks or containers at onshore oil and natural gas production facilities" and to "collect information on processing characteristics, crude slate, emission inventories, and limited source testing to fill information gaps". State and federal laws require certain facilities to design, install, operate and maintain effective pollution control measures to minimize the emissions of VOCs and HAPs. For example, the federal New Source Performance Standards for Crude Oil and Natural Gas Production "requires that new, reconstructed or modified storage vessels with the potential for VOC emissions of equal to or greater than six tons per year reduce VOC emissions by at least 95%." The Texas Commission on Environmental Quality (TCEQ) funded two projects recently to better understand the composition and properties of heavy refinery liquids and the most appropriate method of determining their true vapor pressure (TVP).

The purpose of this research is to improve the estimates of VOC emissions from storage tanks holding heavy refinery liquids. These tanks are found at storage terminals and refineries and are frequently heated in order to reduce the viscosity of their contents and make them pumpable. Evidence is mounting that the emissions from these tanks are underreported and may explain some of the VOC inventory gap in parts of Texas.

During the course of this project, the most accurate, reliable, convenient, and reasonably priced means of measuring the TVP of heavy refinery liquids stored in tanks will be identified. Identifying an appropriate means of measuring the TVP of these heavy refinery liquids is important because direct measurement of VOC emissions from storage tanks is inherently inexact and expensive, so equations are used to estimate emissions from storage tanks. The value used for the TVP in these equations has a profound impact on the results. The results of this research will facilitate efforts being made by the US EPA, TCEQ, and agencies in other states to better understand, more accurately estimate, and manage emissions from tanks holding heavy refinery liquids.

Project Update

The project team (PT) continued to pursue the acquisition of a mini-method instrument for making vapor pressure measurements of the heavy liquids, in particular those that will be tested during the project. Surrogate samples were sent to two manufacturers of mini method instruments for confirmation that these instruments can measure the vapor pressure of typical heavy liquids. Preliminary results from these measurement look promising that there may be one instrument from two different manufacturers to choose from. A decision will be made and a plan developed to acquire the instrument(s) in the next quarter.

The PT also identified most of the suppliers for the samples materials to be measured and began ordering those sample materials that have sources acceptable (price, sample documentation, and availability) to the PT. The remaining sources will be determined early in the next quarter. The composition of the material sample with known vapor pressure as predicted by the UNIFAC model was selected and chemicals to blend this sample were purchased.

The PT purchased most of the components for the sample dispensing system and began assembly of it when they came in. The remaining components will be purchased in March and the system should be completed by early May.

The PT has now identified at least one laboratory that can make measurements of vapor pressure using the ASTM test methods prescribed by the project. Final selection of the labs will be made in the next quarter.

The project team did not have any delays or issues related to the project during the reporting period.

Project 17-024	STATUS: Active – Oct. 17, 2016

Improving the Modeling of Wildfire Impacts on Ozone and Particulate Matter for Texas Air Quality Planning

Atmospheric and Environmental Research, Inc. – Matthew Alvarado

AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Erik Gribbin

Funded Amount: $170,039

Abstract
Fires can have a large impact on ozone and particulate matter concentrations, and thus air quality, in Texas. Current air quality models (also called chemical transport models) take estimates of the primary emissions from biomass burning (such as forest and grass fires) and unphysically dilute them, which can lead to incorrect estimates of the impact of biomass burning on air quality. Smaller scale models like AER's Aerosol Simulation Program allow us to examine the chemical and physical transformations of trace gases and aerosols within biomass burning plumes and to develop new methods for accurately including this aging process in standard air quality models. In this project, we will improve our understanding of the impacts of local and out-of-state fires on air quality in Texas by implementing an improved approach for modeling the near-source chemistry of biomass burning plumes into the CAMx (Comprehensive Air Quality Model with Extensions) model used in Texas air quality planning. This improved approach will allow CAMx to better represent the impact of forest and grass fires on air pollutants such as ozone and fine particulate matter ($PM_{2.5}$). We will also investigate the impact that long-range transport of wildfire smoke has on air quality in Texas. This project thus addresses two strategic topics of the Texas Air Quality Research Program: "Improving the understanding of ozone and particulate matter (PM) formation [and] the interactions of ozone and PM precursors" and "Investigating global, international, and regional transport of pollutants using data and modeling analyses."

Project Update
The overarching goal of this project is to use an advanced smoke plume chemistry model (AER's Aerosol Simulation Program, or ASP) to improve understanding of the formation of O_3 and $PM_{2.5}$ in biomass burning (BB) plumes, and improve estimates of the impacts of in-state and out-of-state biomass burning on Texas air quality. The project is split into the following two tasks:

- To develop and evaluate an improved sub-grid scale parameterization of biomass burning for CAMx based on ASP coupled with the large eddy simulation model SAM (SAM-ASP) and an analysis of O_3 and SOA production in fire plumes observed during BBOP.
- To explore the impact of BB plumes on the boundary conditions used for CAMx and the resulting impact on Texas air quality with ASP coupled with the Lagrangian particle dispersion model STILT (STILT-ASP).

The progress to date and challenges encountered for each task are discussed below. We currently estimate that we will use all of the funds allocated to this project by 08/31/2017.

Task 1: Develop improved parameterization and assess the impact on Texas air quality

Preliminary runs of the coupled SAM-ASP model were performed and the formation of O_3 and other pollutants in these simulations were evaluated against the box model simulations of the Williams fire performed by Alvarado et al. (2015). These preliminary results were presented at the AGU Fall Meeting (Lonsdale et al., 2016). In this reporting period we continued our evaluation tests to try to understand why the horizontal dispersion of the plume is underestimated, even though the dilution-corrected loss rate of NO_x ($\Delta NO_x/\Delta CO_2$) looks reasonable (see Figure 1). Depending on the results of this investigation, we may try to force the horizontal dispersion in the model to a more reasonable value for the parameterization.

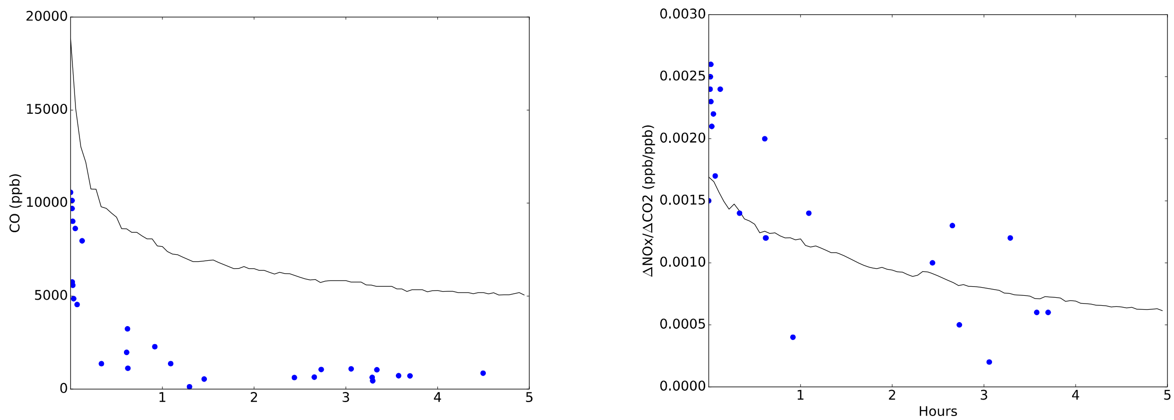

Figure 21: Preliminary SAM-ASP simulation of CO (left) and $\Delta NO_x/\Delta CO_2$ (right) for the Williams Fire (black line) versus observations (blue dots).

In this reporting period we also used the previous parameterization of Lonsdale et al. (2014) to develop a Gausian Emulator Model (GEM). This was done both to test the process to ensure we can build the final GEMs for this project, as well as to help identify which of the input variables account for most of the variance in the outcome of the parameterization. Based on this analysis, we expect that fuel type, staring zenith angle, and temperature will be the most critical input variables to the parameterization. Further work will determine if adding other variables, such as fire mass flux, fire size, dispersion rate, overhead ozone column, result in significant improvements in the parameterization performance.

In this reporting period we also began test CAMx simulations using the TCEQ 2012 modeling episode during this reporting period and verified we were able to reproduce previous results. We also began incorporating fire emissions into the CAMx model via the plume-in-grid module.

Task 2: Investigate the impact of long-range transport of BB pollution on Texas air quality

In this period we identified several periods where fires from Mexico were impacting CO concentrations along the border of the modeling domain used for the May and June 2012 TCEQ modeling episodes. This was first done by examining each edge of the GEOS-Chem boundary grid and calculating the total number of 3-hour observations exceeding a 120 ppbv threshold.

In order to determine whether or not remote wildfires impacted the grid, the STILT model was then run for a selection of cases to calculate the 1-week air flow history for the city of Austin, as shown in Figure 1. We identified three periods where fires were significantly impacting the southern border of the TCEQ modeling domain during the May and June 2012 TCEQ modeling episode: May 5th, 11th, and 25th. We ran STILT-ASP for a receptor in Austin for these periods. Example results are shown in Figure 3. We see that during the evening (when the impact of the fires on the border of the domain is greatest), there is relatively little impact of fires on CO and O_3 during this episode, but a non-negligible impact on $PM_{2.5}$ of ~5 μg m^{-3}. We are extending these analyses to cover the full day, and adding runs for receptors along the southern border to look at possible issues with numerical diffusion in the estimate of biomass burning impacts from GEOS-Chem. We plan to present preliminary results of this work at the 8th International GEOS-Chem meeting in May.

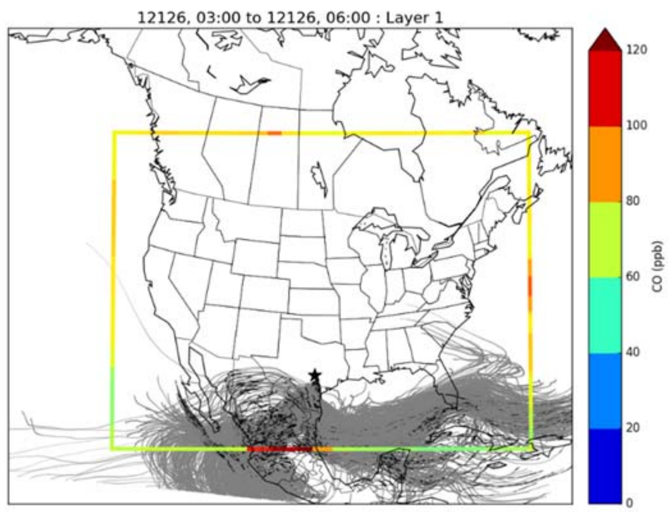

Figure 32: STILT run for May 5th, 2012 for the Austin, TX site. Note the southerly flow, indicating the possibility that wildfires in Mexico may impact the Austin site.

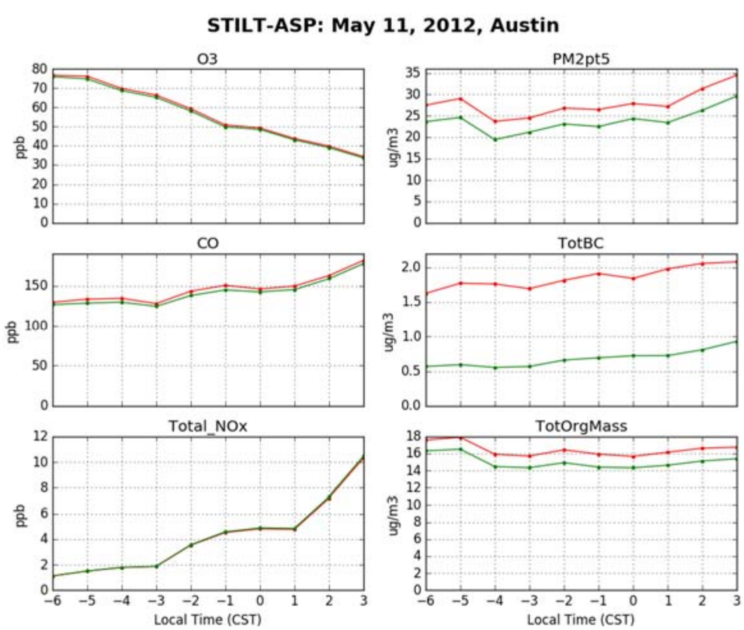

Figure 43: STILT-ASP results for Austin, Texas on May 11, 2012 without fire emissions (green line) and with fire emissions (red line).

Alvarado, M. J., C. R. Lonsdale, R. J. Yokelson, S. K. Akagi, H. Coe, J. S. Craven, E. V. Fischer, G. R. McMeeking, J. H. Seinfeld, T. Soni, J. W. Taylor, D. R. Weise, and C. E. Wold (2015), Investigating the Links Between Ozone and Organic Aerosol Chemistry in a Biomass Burning Plume from a Prescribed Fire in California Chaparral, *Atmos. Chem. Phys.*, 15, 6667–6688, doi:10.5194/acp-15-6667-2015.

C. R. Lonsdale, M. J. Alvarado, R. J. Yokelson, K. R. Travis, and E. V. Fischer (2014), A sub-grid scale parameterization of biomass burning plume chemistry for global and regional air quality models, presented at the 2014 Community Modeling and Analysis System (CMAS) Conference, Chapel Hill, NC, 27-29 Oct.

Lonsdale, C. R., C. Brodowski, M. Alvarado, J. Henderson, J. R. Pierce, and J. Lin (2016), Regional Modeling of Biomass-Burning Aerosol Impacts, Abstract GC51E-1225, presented at the 2016 AGU Fall Meeting, San Francisco, CA, Dec. 12-16.

Project 17-032	STATUS: Active – Dec. 6, 2016

Spatial Mapping of Ozone Formation near San Antonio

Drexel University – Ezra Wood

AQRP Project Manager – Gary McGaughey
TCEQ Project Liaison – Mark Estes

Funded Amount: $59,000

Abstract
Ozone (O_3) is the main component of smog and causes adverse effects on human health, especially to sensitive groups such as children and the elderly. Unlike "primary" pollutants which are emitted directly from vehicles and industrial processes, ozone is formed in the atmosphere from photochemical reactions involving volatile organic compounds (VOCs) and nitrogen oxides ("NO_x"). In order for San Antonio to comply with the new National Ambient Air Quality Standard for ozone of 70 ppb, regulators will need to make science-based decisions on effective mitigation strategies, including emission reduction programs. Such decisions will require knowledge of the amount of ozone that is transported into the city from upwind regions (usually located southeast of San Antonio), the absolute rates of ozone formation in and around San Antonio, the relative importance and interaction of emissions from various sources (e.g., upwind oil and gas activity and urban emissions from the city itself), and when and where ozone formation occurs under "NO_x-limited" or "VOC-limited" conditions. In contrast to Houston and Dallas, little is known about ozone formation in San Antonio. This research project will address this major shortcoming and elucidate the mechanisms and rates of ozone formation that affect air quality in San Antonio using novel measurements of peroxy radicals aboard a mobile supersite during a 3-week field project during late spring of 2017. Instantaneous ozone production rates $P(O_3)$ will be quantified aboard the Aerodyne Mobile Laboratory using new but tested measurements of total peroxy radicals. These measurements will be used to "map" the rate of ozone formation upwind, downwind, and inside of the urban core of San Antonio. Measurements of organic nitrates will also be used to investigate the role of alkanes and organic nitrate formation as a terminator of ozone chemistry.

The main goals of the project are to quantify how much ozone is produced inside the city compared to upwind, and to quantify the role of alkanes in ozone formation.

Project Update
During the December 2016 – February 28 quarter, the PI successfully interviewed, recruited, and hired a post-doc who will be working on this project almost 50% time between mid-February and the end of the project (8/31/2017). Dr. Daniel Anderson recently completed his Ph.D. from the University of Maryland, where he conducted research on ozone formation in biomass burning plumes, aircraft-based formaldehyde measurements, and NOx emissions from the US vehicle fleet. Dr. Anderson started in early February, and is spending the other 50% of his time on a project on atmospheric chemistry in forests, which uses the same analytical equipment.

During this quarter, the PI completed acquiring the materials needed to "re-construct" the peroxy radical sensor which will be used to quantify ozone production rates during the San Antonio measurements. These materials/equipment include mass flow controllers (replacing those that the PI was unable to take with him during his move from U. Massachusetts) and new solenoid valves (used for controlling gas flows for the peroxy radical sensor). The PI has also started an improvement to the thermal dissociation instrument which will be used to quantify alkyl nitrates in San Antonio. This improvement will lead to better, automated temperature control of the thermal dissociation quartz tubes in which organic nitrates are thermally converted into NO_2 which is ultimately measured by the “CAPS” sensor.

The PI has also participated in several planning calls with collaborators from Aerodyne Research, Inc. (S. Herndon) and the University of Houston (J. Flynn).

This project experienced slight delays related to the move of the PI from U. Massachusetts to Drexel U., but is on track and no delays that could negatively affect the project are anticipated.

All funds are anticipated to be spent by 8/31/2017 (the end of the project period).

Project 17-039	STATUS: Active – Nov. 16, 2016

Use of Satellite Data to Improve Specifications of Land Surface Parameters

University of Alabama - Huntsville – Richard McNider

AQRP Project Manager – Elena McDonald-Buller
TCEQ Project Liaison – Bright Dornblaser

Funded Amount: $149,227

Abstract

It is the purpose of this proposal to continue a process to evaluate and improve the performance of the land surface models used in WRF by the use of satellite skin temperatures to better specify physical parameters associated with land use classes. Improved temperature performance impacts biogenic emissions, thermal decomposition (chemical chain lengths and slopes of ozone/NOy curves) and thermally driven winds. Also, land surface parameters control surface deposition which impacts the efficacy of long-range transport. Physical parameters such as heat capacity, thermal resistance, roughness, surface moisture availability, albedo etc. associated with a land use class are actually used in the land surface model. Many of the land use class associated parameters such as surface moisture availability are dynamic and ill-observed depending on antecedent precipitation and evaporation, soil transport, the phenological state of the vegetation, irrigation applications etc. Other parameters such as heat capacity, thermal resistance or deep soil temperature are not only difficult to observe they are often unknowable *a priori*. Despite the difficulty in specifying these parameters they are incredibly important to model predictions of turbulence, temperature, boundary layer heights and winds.

This proposal is directed toward the Meteorology and Air Quality Modeling and Biogenic Emissions Priority. Biogenic emissions are highly sensitive to temperature. Improvement in temperature predictions in conjunction with improved radiation inputs into biogenic emission model (MEGAN or BEIS) should increase the quality of biogenic emissions. The proposal is responsive to three areas in the Meteorology and Air Quality Modeling Priority- (1) boundary layer performance can impact local circulations driven by thermal gradients and the strength of low level jets is controlled by nighttime surface cooling rates; (2) boundary layers can impact clouds both boundary layer topped cumulus and clouds in sea breeze convergence zones; (3) dry deposition of ozone and nitrogen species is often controlled by stomatal uptake which depends on soil moisture.

The proposal will continue and expand activities under a 2015 funded AQRP project using satellite observed skin temperatures. That project was a late selected reduced scope project. Despite some initial issues with a NOAA skin temperature data set, the project ended up showing improvement in model performance for skin temperatures and in wind performance. However, the improvements were not as large as in previous uses of skin temperature data. Part of this may be due to following the Pleim-Xiu air temperature approach in the project, in which absolute differences between model and observed skin temperatures were used rather than skin temperature tendencies. Differences between the model and satellite skin temperatures not related to the boundary layer parameters such as emissivity or atmospheric correction in the satellite product might be an issue. Under this activity skin temperature tendencies will be tested

instead which avoids such problems. The DISCOVER AQ period of 2013 was an unusually cloudy and windy period over most of the Eastern U.S. and not characteristic of the conditions usually associated with ozone episodes in Texas. While significant effort went into QA for the skin temperature data set, cloud contamination in the skin temperatures may still be an issue. Under the current activity alternative skin temperature products such as MODIS data will used in conjunction with the tendency method that may reduce cloud contamination issues. Also, in consultation with TCEQ additional periods such as TEXAQS 2006 or the 2012 SIP period will be examined. Finally, the work on the previous project included emphasis on the large 12-km domain. Under this activity a greater emphasis will be given to fine scale model performance around Houston and Dallas. Particular attention will be given to wind changes due to changes in boundary layer parameters including changes in sea breezes and low level jets.

Project Update

The progress to date and challenges encountered are discussed below.

Additional Model Evaluation Period: As noted in the proposal for this project, the Discover AQ period was not a particularly representative period for air quality concerns. Many active fronts and pervasive cloudiness dominated the period. Thus, as part of this year's effort an additional modeling period was to be chosen in conjunction with TCEQ. After discussion with TCEQ it was decided that the period of July 1, 2012 – August 31, 2012 would be the new period. The drier 2012 year is a contrast to the 2013 Discover AQ period. This period may coincide with potential SIP work in in Texas. Skin temperatures from GOES and MODIS have been processed for this period.

Skin Temperature anomalies: Also under this task the team has revisited an issue with the previous Pleim-Xiu use of skin temperatures to adjust moisture. There appears to be some temporal patterns to the error. In looking at the source of this error the satellite observed skin temperatures may have different values relative to view angles and sun angles primarily related to shading effects in canopies. Using tendencies rather than absolute values avoids these issues. However, use of anomalies rather than absolute values can reduce this effect. Thus, we plan to re-run September 2013 (since we already have the previous results to compare with) using anomalies.

Surface Radiative Energetics: In reviewing the errors in the 2013 period, there is concern that cloud/land surface radiative energetics may not have been fully accounted. A re-run of the 2013 case indicates the need to include both satellite derived insolation and satellite albedo. In the previous 2013 runs satellite albedo was not used. The re-run with satellite albedo shows a reduced error compared to the prior runs.

Cloud Concerns in the Pleim-Xiu Scheme: There is concern that in using absolute differences rather than tendencies in the Pleim-Xiu scheme that errors in radiative forcing (clouds and albedo) may be attributed to moisture errors. For the next run of 2013 an aggressive scheme will be implemented to ensure that moisture assimilation is not carried out when either clouds are present in the satellite data or clouds are present in the model. While this will reduce the amount of data to be assimilated, it may improve performance.

Funds: Charges and time devoted the project during the first 2 months was below targets in part due to some competing projects and set up of accounts. However, charges will accelerate in the coming months so that charges will meet project targets.

Project 17-053	STATUS: Active – Jan. 10, 2017

Identifying and Apportioning Ozone Producing VOCs in Central American Fires

Aerodyne Research, Inc. – Scott Herndon

AQRP Project Manager – Gary McGaughey
TCEQ Project Liaison – Mark Estes

Funding Amount: $185,193

Abstract
Aerodyne Research, Inc. will conduct measurements using a mobile laboratory as a portable photochemistry super site to study ozone production and the emission sources that ultimately impact air quality in central Texas. Work will be done at locations upwind, downwind and lateral to San Antonio. The suite of instrumentation has been selected to quantify key oxygenated volatile organic carbon species (OVOC) and nitrogen containing species (e.g. alkyl nitrates) to pinpoint and apportion ozone within broad categories of VOC emission sectors. The instrument payload will also directly quantify the instantaneous production rate of ozone to determine whether the chemical regime is NOx limited or VOC limited. An additional component of this research project will be to characterize emission sources associated with oil and natural gas production in the Eagle Ford Shale play, including active medium to large processing flares, as well as oil and condensate tanks at wellpads.

The project will provide scientific insight into the VOCs that are contributing to the ozone in central Texas. The effectiveness of mitigation strategies will be informed by these results. This work will isolate ozone production due to VOC oxidation from biogenic sources, refinery emissions, emissions from oil producing well pads and emissions from natural gas production. The dataset will inherently contain regional transport of emissions and processed air. The project will quantify local ozone production rates and evaluate the ozone sensitivity regime.

Project Update
This report discusses the progress from January 10th to February 28th, 2017. It includes updates related to identification of measurement site locations, instrument readiness, integration scheduling, and steps taken to ensure the scientific objectives will be met. Each topic will be discussed and summarized below.

Site selection

The science objectives dictate that a few different sites be visited during the measurement campaign. It will also be important to allow the measurement plan to adapt to changes in dominant wind direction. This need for flexibility and multiple sites must be balanced with logistical concerns like the need for electrical power, the cost to rent a location (if any), travel distances, the advance notice required to stay at a site, and so forth.

The University of Texas at San Antonio has been chosen as a core measurement site. This could be an ideal location to sample photochemical processed air during the periods of flow from the southeast. Scientific teams from other University of Texas campuses will be performing parallel measurement campaigns during the same spring time frame. These scientists will be able to serve as liaisons with the UT San Antonio campus, greatly facilitating planning and logistics.

In searching for additional candidate measurement sites, a list of suitable RV parks located in the source emission regions has been drafted. RV parks are ideal because they are set up with electrical power hookups. Initial telephone calls have been made. One challenge, however, is that any RV sites need to be rented with advance notice and firm date commitments. Significant additional planning is required on this front the next two weeks.

A final option that is being investigated is the possibility of renting a construction generator. This option would give the mobile laboratory control over its own power when it is away from the UT San Antonio site, and could allow for more flexibility in site choice.

Instrumentation readiness and scheduling

During this first reporting period, the availability of trace gas instrumentation has been assessed for the Spring of 2017. All required instruments and equipment will be available in time for this campaign.

A number of these instruments are Aerodyne Research, Inc. brand laser spectrometers (referred to as TILDAS instruments hereafter), and can be configured to measure different gases depending on the application. The various configuration options have been discussed and a plan has been made that prioritizes the measurements that are most important to the science goals, while minimizing the amount of instrument reconfiguration required.

The springtime campaign will involve the deployment of 5 TILDAS instruments in the mobile laboratory (a box truck). The space budget for the truck will require that these instruments be mounted one above the other in the truck's cargo bay. An existing mounting system is capable of accommodating the two largest of the 5 instruments. The plans for a second similar mounting system have been decided. This second mounting system will be capable of accommodating the remaining 3 TILDAS instruments. It will consist of a standard 19-inch rack (such as those used in computer server rooms) attached to the vehicle with heavy duty springs in order to protect the delicate equipment from damage during cross-country transit. The 19-inch rack has been purchased and is in-house.

The recently constructed Aerodyne Long Time of Flight Aerosol Mass Spectrometer (LToF-AMS) combines the sensitivity typically associated with operating in one ion flight path (V mode) with the resolution obtained by a separate ion flight path (W mode) with the conventional High Resolution Time of Flight Mass Spectrometer (HR-ToF-AMS). This negates the previous need to switch modes and cycle between optimum sensitivity and optimum resolution; with the LToF-AMS, both are optimized at the same point in time. Less measurement time is needed for good data. Consider, for example, an unexpected plume that lasts 8 seconds, which is a fairly common occurrence when sampling in a mobile environment. 1 second data points are usually acquired in such environments, so the conventional HR-ToF-AMS would be run in V mode and would not have time to switch ion flight modes in this 8-second-long unforeseen plume. This conventional instrument also has comparibile sensitivity to the LToF-AMS, but a resolution that is a factor of 2 worse. With the LToF-AMS and its single mode operation, there is no need to switch the modes, the measurement will have optimum sensitivity and resolution in the brief plume.

The gas chromatograph coupled to a time of flight detector (GC-TOF) is functioning with sample loop injection system. A multicomponent adsorbent (Graphsphere 1016 and Carboxen 1000) sample pre-concentration method has been selected, based upon Tanner et al., 2006. The adsorbent pre-concentrator hardware and new instrument rack are currently being designed. Labview-based command and control software is under development. A pair of primary gas standards are in-house, and instrument calibration will begin after the pre-concentrator has been constructed.

The Ethane Chemical Amplifier (ECHAMP) for detection of HOx and ROx radicals will ship to Aerodyne for integration into the mobile laboratory in mid/late April.

The chemical ionization mass spectrometer using the iodide-reagent ion (I^- CIMS) will be available to be tested and integrated in the mobile laboratory in mid-April 2017. Preliminary tests will need to evaluate the overall instrument performance on a mobile platform. Once the location of the I^- CIMS in the mobile lab is decided, a rack with shock mounts to absorb vibrations, especially during the transit to Texas will need to be designed and built. The optimal inlet configuration options are being discussed with the goal of reducing losses; this is particularly important for gas phase molecules with low volatility that the instrument is capable of measuring. Finally, a dilution system has been planned for use with the atmospheric sample if necessary. This same system will also deliver clean air to the water and methyl iodide reservoirs used to create I^- ions, in order to minimize the level of sample contamination.

One challenge in measuring regional photochemistry is the potential for sources near to the measurement site to interfere with the regional measurement. An example would be exhaust from the rental car used to transport scientists to and from the mobile laboratory. Extending the sampling inlet up high has the potential to mitigate these effects. A tall mast has been found that can be raised at each measurement site. Tubing and a strong fan will turbulently pull down air from the inlet tip, and the instruments can subsample from this flow. Elevating the inlet will have the advantage of desensitizing the sample footprint to immediately local emissions at the ground. Feasibility calculations are in progress to determine whether the production rate of ozone can be determined with adequate sensitivity using this sampling concept.

Science Discussion

Recent discussions have refined how to use Alkyl-nitrates to identify the VOC precursor for observed ozone. Several data products have been identified that will be useful in providing scientists with an understanding of the results live, as they are acquired. A plan has been made to integrate the computation of OH reactivity into the acquisition, display and analysis software running in the mobile lab. Finally, a live computation of the production rate of ozone, $p(O_3)$, based on data from the ECHAMP and NO instruments has been discussed. This data product will be useful when combined with the matrix of VOCs that will be quantified.

FINANCIAL STATUS REPORT

Initial funding for fiscal years 2016 and 2017 was established at $1,000,000 each, for a total award of $2,000,000 for the FY 2016/2017 biennium. The 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 (per Fiscal Year)
This category includes all staffing, materials and supplies, and equipment needed to administer the overall AQRP. It also includes the costs for the Council meetings.

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

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

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

Program Administration

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

During the reporting period several staff members were involved, at various levels of effort, in the administration of the AQRP. Dr. David Allen, Principal Investigator and AQRP Director, is responsible for the overall administration of the AQRP. Maria Stanzione, AQRP Program Manager, with Terri Mulvey, Melanie Allbritton, and Susan McCoy each provided assistance with program organization and financial management. Denzil Smith is responsible for the AQRP Web Page development and for data management.

Fringe benefits for the administration of the AQRP were initially budgeted to be 24% of salaries and wages across the term of the project. It should be noted that this was an estimate, and actual fringe benefit expenses are reported for each month. The fringe benefit amount and percentage fluctuate each month depending on the individuals being paid from the account, their salary, their FTE percentage, the selected benefit package, and other variables. For example, the amount of fringe benefits is greater for a person with family medical insurance versus a person with individual medical insurance. Actual fringe benefit expenses to date are included in the spreadsheets below.

In December the Program Administration rebudgeted FY 2016 funds within the category in order to use the funds more efficiently. The Supply and Travel budgets were reduced, and the Salary, Fringe, and IDC budgets were increased. Since this did not exceed the 10% threshold, TCEQ approval was not needed to make this change.

Table 1: Administration Budget

Administration Budget (includes Council Expenses)
FY 2016/2017

Budget Category		**FY16 Budget**	**FY17 Budget**	**Total**	**Expenses**	**Remaining Balance**
Personnel/Salary		$73,895.00	$70,040.00	$143,935.00	$92,241.45	$51,693.55
Fringe Benefits		$17,731.00	$16,806.00	$34,537.00	$22,860.94	$22,860.94
Travel		$34.00	$150.00	$184.00	$34.00	$150.00
Supplies		$950.00	$6,000.00	$6,950.00	$60.39	$6,889.61
Equipment						
Total Direct Costs		$92,610.00	$92,996.00	$185,606.00	$115,196.78	$70,409.22
Authorized Indirect Costs		$7,390.00	$7,004.00	$14,394.00	$9,224.15	$5,169.85
10% of Salaries and Wages						
Total Costs		**$100,000.00**	**$100,000.00**	**$200,000.00**	**$124,420.93**	**$75,579.07**

ITAC

All ITAC expenses for FY 2016 were accounted for by the end of September 2016. No changes were made to the ITAC budget and no expenditures occurred during the reporting period.

Table 2: ITAC Budget

ITAC Budget
FY 2016/2017

Budget Category		**FY16 Budget**	**FY17 Budget**	**Total**	**Expenses**	**Remaining Balance**
Personnel/Salary						
Fringe Benefits						
Travel		$4,900.00	$10,000.00	$14,900.00	$4,076.57	$10,823.43
Supplies		$1,100.00	$5,000.00	$6,100.00	$1,079.20	$5,020.80
Total Direct Costs		$6,000.00	$15,000.00	$21,000.00	$5,155.77	$15,844.23
Authorized Indirect Costs						
10% of Salaries and Wages						
Total Costs		**$6,000.00**	**$15,000.00**	**$21,000.00**	**$5,155.77**	**$15,844.23**

Project Management

FY 2016 Project Management funds were rebudgeted within the category in order to better utilize the funds. Supplies and Travel were reduced and Salary, Fringe and IDC were increased. Since this did not exceed the 10% threshold, TCEQ approval was not needed to make this change. Currently, Project Management funds are budgeted at 8.22% of Contractual/Research Project funds, below the 8.5% threshold.

Table 3: Project Management Budget

Project Management Budget
FY 2016/2017

Budget Category		FY16 Budget	FY17 Budget	Total	Expenses	Remaining Balance
Personnel/Salary		$50,182.00	$44,000.00	$94,182.00	$53,763.31	$40,418.69
Fringe Benefits		$12,083.00	$10,600.00	$22,683.00	$11,661.55	$11,021.45
Travel		$0.00	$500.00	$500.00	$0.00	$500.00
Supplies		$500.00	$5,500.00	$6,000.00	$38.13	$5,961.87
Other		$2,000.00	$5,000.00	$7,000.00	$0.00	$7,000.00
Total Direct Costs		$64,765.00	$65,600.00	$130,365.00	$65,462.99	$64,902.01
Authorized Indirect Costs		$5,019.00	$4,400.00	$9,419.00	$5,376.33	$4,042.67
10% of Salaries and Wages						
Total Costs		**$69,784.00**	**$70,000.00**	**$139,784.00**	**$70,839.32**	**$68,944.68**

Research Projects

A total of $1,630,000.00 was originally budgeted for research projects. In previous quarters those funds were increased by $9,216, due to the reduction in funds allocated to Other and ITAC. A total of ten (10) projects were selected for funding out of fifty four (54) proposals submitted to the AQRP RFP for the 2016-2017 biennium. $1,593,175.00 was allocated to the 2016-2017 research projects. Table 4 on the following page shows the distribution of the projects across the fiscal years and the cumulative expenditures to date.

Table 4: Contractual/Research Project Budget

Contractual Expenses				
FY 16 Contractual Funding		**$815,000**		
FY 16 Contractual Funding Transfers		**$9,216**		
FY 16 Total Contractual Funding		**$824,216**		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
16-008	University of Houston	$191,366	$17,129.19	$174,236.81
16-010	Sonoma Technology, Inc.	$69,075	$21,062.25	$48,012.75
16-011	Ramboll Environ	$158,134	$41,302.82	$116,831.18
16-019	Univ. of Texas - Austin	$118,019	$48,396.58	$69,622.42
16-019	Ramboll Environ	$62,622	$7,127.29	$55,494.71
16-031	UNC - Chapel Hill	$225,000	$0.00	$225,000.00
FY 16 Total Contractual Funding Awarded		$824,216		
FY 16 Contractual Funds Expended (Init. Projects)			$135,018.13	
FY 16 Contractual Funds Remaining to be Spent				$689,197.87
FY 17 Contractual Funding		**$815,000**		
FY 17 Contractual Funding Transfers		**$0**		
FY 17 Total Contractual Funding		**$815,000**		
Project Number		Amount Awarded (Budget)	Cumulative Expenditures	Remaining Balance
17-007	Univ. of Texas - Austin	$205,500	$39,826.59	$165,673.41
17-024	Atmospheric and Environmental Research, Inc.	$170,039	$70,694.51	$99,344.49
17-032	Drexel University	$59,000	$0.00	$59,000.00
17-039	Univ. of Alabama - Huntsville	$149,227	$2,136.71	$147,090.29
17-053	Aerodyne Research, Inc.	$185,193	$0.00	$185,193.00
FY 17 Total Contractual Funding Awarded		$768,959		
FY 17 Contractual Funding Expended (Init. Projects)			$112,657.81	
FY 17 Contractual Funds Remaining to be Spent				$702,342.19
Total Contractual Funding		$1,639,216		
Total Contractual Funding Awarded		$1,593,175		
Total Contractual Funding Remaining to be Awarded		$46,041		
Total Contractual Funds Expended to Date			$247,675.94	
Total Contractual Funds Remaining to be Spent				$1,391,540