Quality Assurance Project Plan

Project 14-024
Sources of Organic Particulate Matter in Houston: Evidence from DISCOVER-AQ data Modeling and Experiments

Lea Hildebrandt Ruiz
Center for Energy and Environmental Resources
The University of Texas at Austin
Austin, Texas 78758
lhr@che.utexas.edu
512-471-1050

Ying Xu
Center for Energy and Environmental Resources
The University of Texas at Austin
Austin, Texas 78758
xuying@mail.utexas.edu
512-471-6507

Greg Yarwood
Bonyoung Koo
ENVIRON

Gookyoung Heo
The University of California, Riverside

Summary of Project

QAPP Category Number: III
Type of Project: Measurements and Data Evaluation

QAPP Requirements: This QAPP requires descriptions of project description and objectives; organization and responsibilities; scientific approach; sampling and measurements procedures; quality metrics; data analysis, interpretation, and management; reporting; and references.

QAPP Requirements:
Audits of Data Quality: 10% Required
Report of QA Findings: Required in final report

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1. PROJECT DESCRIPTION AND OBJECTIVES

1.1 Process and/or environmental system to be evaluated.

The United States Environmental Protection Agency recently lowered the annual National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ from 15 to 12 μg m^{-3} (US EPA, 2013). This new annual standard brings the Houston region to near non-attainment for $PM_{2.5}$, underlining the importance of understanding the composition and sources of $PM_{2.5}$ in Houston. The University of Texas at Austin (UT-Austin) under the leadership of PI Lea Hildebrandt Ruiz recently collected air-quality measurements in the Houston region as part of Texas Air Quality Research Program (AQRP) project 12-012, including measurements of PM concentration and composition, as well as the concentrations of gas-phase species (Hildebrandt Ruiz & Yarwood 2013). Preliminary data analysis indicates that the majority – up to 70% – of fine PM measured in Conroe, TX (~ 70 km North of the urban center) was composed of organic material (Hildebrandt Ruiz & Yarwood 2013). This is consistent with studies conducted during the last decade, which have also found that a significant fraction of fine PM in Texas is composed of organic material (Allen 2005; Bahreini et al. 2009). An improved understanding of Houston organic aerosol is therefore essential and will directly benefit the Texas Commission on Environmental Quality (TCEQ) in understanding how to manage Houston's air quality.

Traditionally, organic aerosol (OA) has been classified as primary or secondary OA (POA or SOA). In this classification, POA refers to compounds that are emitted as particles and have not reacted in the atmosphere. SOA is formed when gas-phase compounds undergo one or more chemical transformations in the gas phase, forming less volatile compounds that then partition between the gas and particle phase (Donahue et al. 2006; Pankow et al. 2001). These gas-phase precursors of SOA are classified (in decreasing order of vapor pressure/volatility) as volatile organic compounds (VOC), intermediate volatility organic compounds (IVOC) or semivolatile organic compounds (SVOC). Sources of OA in Houston include POA and SOA from urban anthropogenic activity, the petrochemical industry and fires, as well as SOA from biogenic VOC. Understanding the sources and formation of OA is therefore very complex, and significant uncertainties remain.

1.2 Purpose of the project and objectives

This work will focus on improving our understanding of the contributions of IVOC, specifically large alkanes and polycyclic aromatic hydrocarbons (PAHs) to SOA, because these contributions have not received much attention, the emissions of IVOC are expected to be high in Houston, and the contributions of IVOC to SOA appear to be important but underestimated (Robinson et al. 2007; Shrivastava et al. 2008). Our work will include analysis of the recently collected ambient data during DISCOVER-AQ, new environmental chamber experiments and photochemical modeling of the Houston region. For the formation of SOA from VOC and IVOC precursors the photochemical model will use a new state of the art approach based on the Volatility Basis Set (VBS) (Donahue et al. 2006) which has recently been implemented in CAMx (and also CMAQ) to account for important aspects of OA formation such as the semi-volatile nature of POA and NOx-dependent yields for SOA (Koo et al., 2013). This new scheme accounts for systematic variations in both volatility and oxidation state (O:C ratio) and is referred to as a 1.5-dimensional (1.5D) VBS.

Task 0. Sharing of DISCOVER-AQ Data – UT Austin

Data collected during DISCOVER-AQ will be shared between the PIs of projects 14-009, 14-0024 and 14-029 (Drs. Griffin, Hildebrandt Ruiz and Sheesley, respectively). Tasks 4, 5, 6 and 7 of this project (14-024) will be performed on the combined dataset including all shared data. Tasks 1, 2 and 3 of this project do not depend on previously collected data.

The sharing of data is planned to occur according to the following schedule:

June 2014:

- Dr. Hildebrandt Ruiz (14-024) will share preliminary data collected during DISCOVER-AQ at the Conroe stationary measurement site with the aerosol chemical speciation monitor (ACSM), Scanning Electric Mobility System (SEMS), and High Resolution Time of Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS). ACSM data include bulk concentration of PM_1 sulfate, ammonium, nitrate and organics, the fraction of organic PM_1 due to molecular fragments at a mass to charge ratio (*m/z*) 44 (f_{44}), used as a proxy for organic PM_1 oxidation state, as well as the ratio of nitrate mass at *m/z* 30 and *m/z* 46, which is indicative of whether observed nitrate is due to inorganic or organic nitrate. SEMS data will include PM_1 size distributions measured throughout the campaign as well as integrated particle volume. The data will still be preliminary at this point as final quality assurance will depend on potential adjustments based on filter analysis (Task 5) and comparison to data analyzed as part of projects 14-009 and 14-029. HR-ToF-CIMS data shared will include concentrations of Cl_2, HCl, $ClNO_2$, N_2O_5, alpha-pinene and isoprene measured throughout the DISCOVER-AQ campaign.

- Dr. Griffin (14-009) and research team will share data collected during mobile and stationary measurements by their high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS). HR-ToF-AMS data shared will include bulk concentration of PM_1 sulfate, ammonium, nitrate and organics, the oxidation state of organic PM_1 estimated from elemental analysis of molecular fragments, and the concentrations of the NO^+ and NO_2^+ fragment, which provides information on whether observed nitrate is due to inorganic or organic nitrate. HR-ToF-AMS data collected at the Conroe measurement site will be used in this project for comparison with ACSM data (Task 5). Data collected at other stationary measurement sites will be used for comparison to modeled concentrations (Task 7).

- Dr. Sheesley (14-029) and research team will share data on the concentrations of organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ filters collected at the Moody Tower, Manvel Croix, Conroe and La Porte stationary measurement sites.

September 2014:

- Dr. Hildebrandt Ruiz (14-024) will share finalized DISCOVER-AQ data from the ACSM, SEMS and HR-ToF-CIMS as explained in more detail above, as well as the results of the filter analysis (Task 5), i.e. concentrations of inorganic ions in $PM_{2.5}$.

February 2015:

- Dr. Hildebrandt Ruiz (14-024) will share results from PMF analysis (Task 6).

- Dr. Sheesley (14-029) and research team will share data on the concentrations of water-soluble organic carbon (WSOC) in $PM_{2.5}$ filters collected at the Moody Tower, Manvel Croix, Conroe and La Porte stationary measurement sites.

March 2015

- Dr. Sheesley (14-029) will share results from radiocarbon analysis of filter samples, focusing on the final week of the September campaign.

Task 1. Inventory Analysis - ENVIRON

IVOC (volatility range 10^4 to 10^6 μg m^{-3} in saturation concentration) includes organic compounds such as long-chain alkanes (C_{12} and greater) and PAHs. These species are too volatile to be captured by conventional POA emission measurements and are typically missing from VOC inventories. However, they can contribute to a significant fraction of SOA production (Lim & Ziemann 2005; Chan et al. 2009; Presto et al. 2010). Since a majority of IVOC emissions are difficult to identify, current attempts to include IVOC in modeling atmospheric OA formation estimate their emissions by scaling from POA emissions (Robinson et al. 2007; Shrivastava et al. 2008). However, the ratio of IVOC to POA emissions is expected to vary by source and data are becoming available for major source categories such as vehicles. Scaling IVOC to VOC emissions may be a more effective strategy for point sources and gasoline vehicles (Gordon et al., 2013). TCEQ's point source emissions inventory data collected in the State of Texas Air Reporting System (STARS) includes detailed chemical species emissions from chemical industry sources in Texas. We will conduct a literature review to identify the most recent IVOC emission estimates and analyze the 2012 STARS point source emission inventory to better estimate IVOC emissions in the Houston region. We will also conduct a literature review of all of the existing albeit limited data on SOA formation from IVOC. Both literature analyses will be used to construct a list of IVOC species to study in Task 2. Other studies that will be considered to identify IVOC species to be studied in Task 2 will include mobile source emission studies (e.g., Gordon et al., 2013) and prior studies of SOA formation potential (Pye and Pouliot, 2012).

Task 1 deliverables (to be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project):

- a list of IVOC species for study in Task 2
- an experiment plan showing how many experiments will be conducted with each species and under which conditions,
- methods for implementing IVOC emissions in CAMx modeling under Task 4

Task 1 dependencies: none

Task 2. Environmental Chamber Experiments and Box Modeling - UT Austin and UC Riverside

Approximately fifteen environmental chamber experiments will be conducted to quantify the formation of SOA from the oxidation of IVOC under different conditions. The exact list of species will be determined after Task 1 is completed, but the list will contain larger alkanes (C_{12} and greater) and PAHs. Experiments will be conducted using different ratios of VOC to oxides of nitrogen (NOx) since the level of NOx has been shown to affect SOA mass yields and volatility. Most experiments will be conducted under dry conditions, but a few exploratory experiments will be conducted at higher relative humidity (RH) to examine the effect of relative humidity on SOA formation.

Experiments will be conducted in UT-Austin's environmental chamber, which is a ~ 12 m^3 Teflon® reactor suspended inside of a temperature-controlled room. The walls of the room are lined with UV lights which enable the simulation of photo-oxidation reactions; for example, the UV lights can photolyze H_2O_2 producing 2 HO· or HONO producing HO· and NOx. A typical experiment starts by filling the Teflon® bag with clean air, produced using an Aadco zero air generator (Model 737-14A). Inorganic seed particles (usually ammonium sulfate, $(NH_4)_2SO_4$) are then injected which serve as surface area onto which oxidized organic vapors can condense, and which aid in the correction for wall losses (Hildebrandt et al. 2009). The IVOC of choice will then be injected using a heated injector. An oxidant precursor is also injected - H_2O_2 will be used for low NOx experiments; HONO or a combination of H_2O_2 and NOx will be injected for high NOx experiments. When everything is injected into the chamber and well mixed, the UV lights are turned on photolyzing the H_2O_2 or HONO and commencing the oxidation reactions to form SOA.

The concentration and composition of gas- and particle-phase species will be monitored throughout the experiment. Some gas-phase species will be monitored using UT Austin's High Resolution Time of Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS). However, the HR-ToF-CIMS cannot quantify most IVOC due to their low vapor pressure. Therefore, total airborne IVOC concentrations will be monitored by first collecting them on Tenax® TA sorbent tubes. The collection system consists of a calibrated air pump, PTFE tubing, a primary sampling tube and a backup tube. The backup tubes will be used to check for breakthrough. The sampling flow rate and time will be optimized before formal tests to ensure quantification and avoid breakthrough. Duplicate air samples and a field blanks will also be collected at each sampling time. Following collection, the IVOCs will be thermally desorbed by a thermal desorber (TD) (Turbomatrix 650 ATD) from the tubes and then analyzed via gas chromatograph - mass spectrometry (GC-MS) (Agilent 7890A GC- 5975MS). The sorbent tubes will be desorbed for 30 min at 300°C, with a helium flow of 50 ml/min, and a cold trap temperature of minus 30°C. The cold trap has a narrow bore (Low Flow Trap Tube) packed with Tenax TA sorbent and a small piece of silylated glass wool. Flash heating of the cold trap to 350°C transfers the analyte through the valves at 250°C and the transfer line at 250°C to the GC. The GC-MS has a constant pressure resulting in a flow rate of 1.6 ml/min at 80°C, and will be equipped with a 30 m × 0.25 mm DB-5MS column and operated at a 5:1 split injection. All tubes will be analyzed in two successive desorptions to ensure complete desorption of both the tube and the TD-GC-MS system.

The amount of SOA formed will be monitored using an aerosol chemical speciation monitor (ACSM, Ng et al., 2011), which measures non-refractory PM_1 species (organics, nitrate, sulfate

and ammonium). The volume of SOA formed will also be measured using a scanning electrical mobility system (SEMS, Brechtel Manufacturing, Inc.), which measures particle size distributions from which total particle volume can be calculated. Data from the SEMS will primarily be used to correct the ACSM data for collection efficiency. The ACSM also measures the total organic aerosol mass spectrum, from which the SOA oxygen-to-carbon ratio (O:C) can be estimated (Aiken et al. 2007). The O:C ratio of the SOA will be used in the parameterizations for the 1.5D VBS used in CAMx (tasks 3 and 5).

The production of SOA from the oxidation of the IVOCs will be quantified using a fractional aerosol mass yield, Y, which is defined as the ratio of the concentration of SOA formed (C_{OA}), divided by the mass of IVOC reacted (ΔC_{IVOC}):

$$Y = \frac{C_{OA}}{\Delta C_{IVOC}} \qquad (1)$$

The SOA is assumed to be in equilibrium, and the partitioning of organic compounds between the gas and particle phase can be characterized by an effective saturation mass concentration C_i^*. The fraction of a given compound i in the condensed (particle) phase is given by (Donahue et al., 2006):

$$\xi_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \quad \text{with } C_{OA} = \sum_i C_i \xi_i \quad \text{and} \qquad (2)$$

$$Y = \frac{C_{OA}}{\Delta C_{IVOC}} = \frac{\sum_i C_i \xi_i}{\Delta C_{IVOC}} = \sum_i \frac{C_i}{\Delta C_{IVOC}} \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \qquad (3)$$

where C_i is the total concentration of compound i. In the VBS the C_i^* are used as independent variable. Thus, to develop parameterizations for the VBS, the C_{OA} and Y will be measured during the experiments, and the C_i will be fit to the data to obtain VBS distributions for SOA formed from different IVOC under different conditions.

VBS distributions can also be obtained from a combination of thermodenuder data and an evaporation model (Riipinen et al. 2010). In a thermodenuder, the aerosol is heated to a predefined and controlled temperature. The SOA is measured after being subjected to this heating and compared to the SOA that bypassed the thermodenuder, obtaining a mass fraction remaining after heating (Lee et al. 2010). These data can then be used in an evaporation model to estimate VBS distributions of the organic aerosol (Riipinen et al. 2010). A thermodenuder will be built as part of this project, and VBS distributions will be obtained from both methods – fitting to the yield data and the thermodenuder data.

The SAPRC chamber simulation software (http://www.cert.ucr.edu/~carter/SAPRC/SAPRCfiles.htm) will be used to simulate environmental chamber experiments and thereby evaluate chemical mechanisms. The software has been used extensively to evaluate oxidant mechanisms such as SAPRC and Carbon Bond. In this study, UCR and ENVIRON will add the ability to model SOA formation in the chamber model using the VBS scheme developed by ENVIRON. Simulations are specific to each

chamber due to the effects of chamber walls and illumination. The chamber model will be calibrated using experiments to characterize the UV intensity and to measure the rates of NOx off-gasing and HONO generation from the Teflon® walls as suggested by Carter et al. (2005). Losses of particles and IVOCs to the walls will also be measured and included in the model.

At the conclusion of Task 2 we will summarize results from the chamber characterization experiments (UV intensity, rates of NOx off-gasing and HONO generation from the walls, loss of particles and IVOCs to the walls), as well as results from the SOA generation experiments (amount of organic PM_1 formed, aerosol mass yields), thermodenuder measurements (organic mass fraction remaining as a function of temperature), results from the thermodenuder model (volatility basis set distributions) and results from the chamber simulation software. These products will be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project.

Task 2 deliverables (to be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project):

- Results from the chamber characterization experiments (UV intensity, rates of NOx off-gasing and HONO generation from the walls, loss of particles and IVOCs to the walls)
- Results from the SOA generation experiments (amount of organic PM_1 formed, aerosol mass yields), thermodenuder measurements (organic mass fraction remaining as a function of temperature)
- Results from thermodenuder measurements (organic mass fraction remaining as a function of temperature)
- Results from the thermodenuder model (volatility basis set distributions)
- Results from the chamber simulation software

Task 2 dependencies:

- Identities of IVOC species to study in chamber experiments from Task1

Task 3. Chemical Mechanism - ENVIRON

This task will improve the chemical mechanisms in CAMx to better represent SOA formation from IVOCs. Mechanism improvements will be implemented for CB6r2 gas-phase chemistry and the 1.5D VBS. Based on Tasks 1 and 2 we will add several classes of IVOC to represent ranges of precursor classes and properties (OA yields and volatility distributions). One possibility for alkanes is to differentiate normal, branched, and cyclic compounds (Pye & Pouliot 2012).

Task 3 deliverables (to be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project):

- Tables of updated mechanism listing and VBS parameters.

Task 3 dependencies:

- Identities of IVOC species to use in chemical mechanism development from Task 1
- Data on aerosol formed when IVOCs react from Task 2

Task 4. Photochemical Modeling - ENVIRON

We will use the Comprehensive Air-quality Model with Extensions (CAMx, ENVIRON, 2013) to model OA during DISCOVER-AQ (August-October, 2013). The modeling platform is adapted from a 2013 Texas ozone forecast modeling application developed by ENVIRON for the TCEQ (Johnson et al. 2013). The modeling domain consists of a 36-km continental-scale grid and a nested 12-km grid that covers entire Texas and a 4-km nested grid covering the Houston area. The Weather Research and Forecasting (WRF) (Skamarock et al., 2008) meteorological model will be used in hindcast mode to develop the August-October 2013 meteorological fields required for input to CAMx.

Emission inventory data for anthropogenic sources will be obtained from the TCEQ in CAMx-ready format. Biogenic emissions will be estimated using MEGAN version 2.1 (Guenther et al., 2012). The anthropogenic emission inventory will be updated with the IVOC emissions estimated using methodologies developed in Task 1.

Figure 2. CAMx modeling domain with outer 36 km grid and nest 12 km (blue) and 4 km (green) grids.

CAMx will be run with Revision 2 of the CB6 chemical mechanism (CB6r2) (Hildebrandt Ruiz, and Yarwood, 2013). Primary and secondary organic PM will be modeled using the 1.5D VBS. The VBS scheme uses 4 separate basis sets to differentiate fossil (anthropogenic) from modern (biogenic) carbon as well as SOA or aged POA from fresh emissions. Source-specific volatility distribution factors are applied for POA emissions from gasoline and diesel vehicles, other anthropogenic sources, and biomass burning. We will use the improved chemical mechanism for SOA formation from IVOCs developed in Task 3. We will evaluate model performance using TCEQ monitoring data and the combined set of OA data collected during DISCOVER-AQ (Task 0).

Task 4 deliverables (to be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project):

- Updated emissions summary table.

Task 4 dependencies:

- Identities of IVOC species to use in chemical mechanism development from Task 1
- Methods to add IVOC emissions to inventories from Task 1
- Chemical mechanism for SOA formation from IVOC developed in Task 3

Task 5. Discover-AQ Data Analysis – UT Austin

During September 2013, UT-Austin took measurements of gas and particle-phase composition and concentrations in Conroe, TX, as part of the DISCOVER-AQ program. Preliminary data on PM_1 concentration and composition from the ACSM shows that on average about 70% of PM_1 measured and Conroe was organic. Other measurements included the organic aerosol mass spectrum from the ACSM, particle size distributions using the SEMS, gas-phase composition and concentrations using the HR-ToF-CIMS, and ozone, NOx and NO_2 concentrations using gas-phase monitors for each species. Preliminary data analysis has been performed (Hildebrandt Ruiz & Yarwood 2013), but additional quality assurance, calibrations, comparison to other data and further analysis of the data collected by UT-Austin is necessary and will provide additional and important insights into the sources of organic particulate matter in the Houston region. Quality assurance of the data will be done on the combined data set, including data from AQRP projects 14-009 and 14-029 (Task 0).

$PM_{2.5}$ quartz fiber filters were also collected. Dr. Rebecca Sheesley and her research team will analyze these filters for concentrations of total organic carbon (OC), total elemental carbon (EC) and water soluble organic carbon (WSOC) as part of AQRP project 14-029. Dr. Sheesley will also have a subset of the filters analyzed for the fraction of the OC due to fossil vs. modern carbon. The results from her analysis will be useful for this study, and she will share data on OC, EC, and fossil vs. modern carbon with us as summarized in Task 0. For example, we will use the concentrations of EC to adjust the ACSM data, since this is a species that cannot be measured by the ACSM but is measured by the SEMS. The radiocarbon analysis will be useful in better understanding the sources of organic aerosol in Houston – SOA formed from oxidation of IVOCs is expected to be from fossil carbon. In addition to using data from Dr. Sheesley in our analysis and quality assurance, we will send collected filter samples to the Desert Research Institute (DRI) Environmental Analysis Facility (EAF), where concentrations of inorganic ions including NH_4^+, K^+, Na^+ SO_4^-, NO_3^- and Cl^-, will be determined. This analysis will be very useful for quality assurance of our data and will also provide some additional insights – for example, particulate Cl cannot be measured by our instrumentation. Finally, we will compare the data from our ACSM to the data from a High Resolution Time of Flight Aerosol Mass Spectrometer by Dr. Griffin and research group (AQRP project 14-009) for additional quality assurance.

Gas-phase data will also be analyzed in more detail as they are expected to yield important insights into OA precursors and the chemistry controlling OA concentrations in Houston. Specifically, the sensitivity of the HR-ToF-CIMS can be different for each species, and as part of this project we will calibrate the instrument for selected observed species including isoprene and

alpha-pinene. Furthermore, meteorological data will be analyzed to gain insights into the source region of the sampled air masses. The use of back trajectories to glean additional insights into aerosol source will also be explored. Back trajectories will be calculated using the National Oceanographic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model.

At the conclusion of Task 5 we will summarize the quality-assured data collected during DISCOVER-AQ. The data summary will include PM_1 concentrations and composition, particle size distributions, concentrations of NO_x, NO_2 and ozone, concentrations of toluene and isoprene, and concentrations of inorganic ions in $PM_{2.5}$. These products will be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project.

Task 5 deliverables (to be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project):

- Summary of quality-assured data collected during DISCOVER-AQ including PM_1 concentrations and composition, particle size distributions, concentrations of NO_x, NO_2 and ozone, concentrations of toluene and isoprene, and concentrations of inorganic ions in $PM_{2.5}$.

Task 5 dependencies:

- Sending $PM_{2.5}$ filter samples to DRI for analysis
- Sharing of data with Drs. Sheesley and Griffin as described in Task 0 for comparison of measurements and quality assurance.

Task 6. Positive Matrix factorization – ENVIRON and UT Austin

Positive matrix factorization (PMF) analysis will be conducted on the organic aerosol mass spectra using the PMF2 algorithm (version 4.2) by P. Paatero to solve the bilinear unmixing problem (Paatero & Tapper 1994). Different PMF solutions (obtained by varying the number of factors and other PMF settings) will be evaluated with respect to ancillary data (not included in the PMF analysis, e.g. PM sulfate, gas-phase concentrations, etc.) and mathematical diagnostics (Ulbrich et al. 2008; Hildebrandt et al. 2010; Hildebrandt et al. 2011). PMF analysis is expected to provide insights into organic aerosol types and sources with different source signatures (organic aerosol mass spectra). This analysis, and other detailed analysis of our ACSM data, will benefit from comparison of our data with the data collected by the research group of Dr. Griffin (Rice University), who operated a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) during the DISCOVER-AQ measurements, which was co-located with our instruments during approximately 70 hours of the campaign. The HR-ToF-AMS collects data at higher time and mass resolution and therefore provides a more detailed OA mass spectrum, which can aid in the interpretation of the ACSM mass spectrum; for example, estimates of OA O:C can be more accurate from the HR-ToF-AMS compared to the ACSM, and it will be useful to compare the HR-ToF-AMS estimates of O:C to ACSM estimates of O:C during the times of instrument co-location. The PMF analysis will be performed on the combined data set including data from AQRP projects 14-009 and 14-029 (Task 0).

Task 6 deliverables (to be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project):

- Summary of PMF results consisting of the time series of factors and the factor profiles
- A list of sensitivity tests to be conducted in Task 7 based on results from tasks 1, 3, 4, and 6

Task 6 dependencies:

- Quality assurance of data done under Task 5
- Sharing of data with Drs. Sheesley and Griffin as described in Task 0

Task 7. Model Evaluation – ENVIRON and UT Austin

The base case model performance will be evaluated for oxidants as well as OA TCEQ monitoring data and OA data collected at during DISCOVER-AQ, using the combined data set including data from AQRP project 14-029 and from AQRP project 14-009 (Task 0). Several sensitivity simulations with alternate IVOC emission estimates and chemical mechanisms will also be performed and evaluated. Sensitivity tests will be defined in Task 7 by considering results from Tasks 1, 3, 4 and 6.The model performance evaluation results from Task 4 will be analyzed and used to refine IVOC emission estimates from Task 1 and chemistry from Task 3. Source contributions from the CAMx deterministic modeling will be compared to ambient source apportionment results developed in Task 6. In particular, contributions of fossil and modern carbon to total OA will be compared to provide insight on relative importance of anthropogenic and natural sources which is relevant to developing control strategies for OA and $PM_{2.5}$ in Houston.

Task 7 deliverables (to be delivered in monthly progress reports and as part of the final data set submitted to the TCEQ at the conclusion of this project):

- Graphs and tables of the model performance metrics for the base and sensitivity cases
- Modeled source contribution results for the final case
- Updates to the IVOC emission estimates and chemistry mechanism as identified from the sensitivity modeling analysis.

Task 7 dependencies:

- Identities of IVOC species to use in chemical mechanism development from Task 1
- Methods to add IVOC emissions to inventories from Task 1
- Chemical mechanism for SOA formation from IVOC from Task 3
- Results of base CAMx simulation from Task 4
- Ambient source apportionment results from Task 6

2. ORGANIZATION AND RESPONSIBILITIES

2.1 Project Personnel

This project is being conducted by UT-Austin, ENVIRON and the University of California, Riverside (UCR) under a grant from the Texas Air Quality Research Program. The project Co-Principal Investigators (PIs) are Prof. Lea Hildebrandt Ruiz of UT-Austin and Dr. Greg Yarwood of ENVIRON. Dr. Lea Hildebrandt Ruiz is responsible for the laboratory chamber experiments and chamber modeling. Dr. Ying Xu is responsible for off-line analysis and quantification of IVOCs. Dr. Greg Yarwood of ENVIRON is responsible for the modeling efforts. Dr. Gookyoung Heo of UC Riverside will advise PI Hildebrandt Ruiz and her research group on the use and calibration of the chamber simulation software. The Co-PIs will assume overall responsibility for the research and associated quality assurance. All Principal Investigators will contribute to the final report. The project will be overseen by AQRP Project Manager Dr. Elena McDonald-Buller and a TCEQ Project Liaison Shantha Daniel.

The scientists working on this project and their specific responsibilities are listed in Table 2-1.

Table 2-1. Project participants and their responsibilities.

Participant	Project Responsibility
Dr. Lea Hildebrandt Ruiz (UT-Austin)	Principal Investigator, with overall responsibility for laboratory chamber experiments, data analysis and interpretation, quality assurance review and reporting.
Dr. Ying Xu (UT-Austin)	Co-Principal Investigator, with responsibility for off-line analysis and quantification of IVOCs
Surya Venkatesh Dhulipala (UT-Austin)	Graduate Student Researcher, with responsibility of conducting the laboratory chamber experiments and analyzing the data.
Dongyu Wang (UT-Austin)	Graduate Student Researcher, with responsibility of building and evaluating the thermodenuder before its use in laboratory chamber experiments.
Jeffrey Bean (UT-Austin)	Graduate Student Researcher, with responsibility of conducting chamber characterization experiments and calibration of the HR-ToF-CIMS for measurements taken during DISCOVER-AQ.
Yirui Liang (UT-Austin)	Graduate Student Researcher, with responsibility for air sampling and off-line analysis and quantification of IVOCs
Dr. Greg Yarwood (ENVIRON)	Co-Principal Investigator with project oversight; Developing gas-phase chemical mechanisms

Participant	Project Responsibility
Dr. Bonyoung Koo (ENVIRON)	Developing particle-phase chemical mechanisms; Implementing chemical mechanisms in CAMx
Dr. Tanarit Sakulyanontvittaya (ENVIRON)	Conducting CAMx modeling
Mr. Justin Zagunis (ENVIRON)	Assist Dr. Sakulyanontvittaya with CAMx modeling
Dr. Gookyoung Heo (UC Riverside)	Advise on chamber characterization and modeling

2.2 Project Schedule including main milestones

The project schedule by task is presented below. Technical work will not begin until authorization is received from TCEQ and AQRP. The entire project will be completed by June 30, 2015.

	2014							2015					
	J	J	A	S	O	N	D	J	F	M	A	M	J
Task 1 - Inventory Analysis													
Task 2 - Chamber Experiments													
Task 3 - Chemical Mechanism													
Task 4 - QA of DISCOVER-AQ Data													
Task 5 - Photochemical Modeling													
Task 6 - PMF Analysis													
Task 7 - Model Evaluation													
Task 8 - Reporting													

UT-Austin will prepare and submit monthly technical progress reports at the 8th of the month (or following business day) as well as quarterly reports due on August 30 and December 1, 2014, and February 27 and May 29, 2015. Deliverables for this project also include a draft final report due May 18, 2015 and final project report due June 30, 2015, documenting all work from Tasks 1 through 7, and a project summary presentation to AQRP anticipated to occur in June 2015. AQRP will receive an electronic copy of all data generated for this project. All reports will be in the format requested by AQRP.

3. SCIENTIFIC APPROACH

The objectives of this project are to quantify the contributions of intermediate volatility organic compounds (IVOC) to secondary organic aerosol (SOA). Our work will include analysis of recently collected ambient data during DISCOVER-AQ, new environmental chamber experiments, and photochemical modeling of the Houston region.

Note: this project consists of two main parts – Measurements (lead by Dr. Hildebrandt Ruiz) and Secondary Data Evaluation (lead by Dr. Greg Yarwood). The heading of each sub-section within parts 3, 4, 5, 6 and 7 below indicates whether the discussion applies to the Measurement (MEAS) or Data Evaluation (DATA) portion of the project.

3.1 Experimental Design (MEAS)

We will conduct environmental chamber experiments to quantify the formation of SOA from IVOC. The UT chamber is a ~ 12 m^3 Teflon bag suspended inside of a temperature-controlled room. The walls of the room are lined with UV lights which enable the production of photochemical radicals, e.g. they hydroxyl radical ·OH.

The Statewide Air Pollution Research Center (SAPRC) chamber simulation software (http://www.cert.ucr.edu/~carter/SAPRC/SAPRCfiles.htm) will be used to simulate environmental chamber experiments and thereby evaluate chemical mechanisms. The software has been used extensively to evaluate oxidant mechanisms such as SAPRC and Carbon Bond. In this study, UCR and ENVIRON will add the ability to model SOA formation in the chamber model using the VBS scheme developed by ENVIRON. Simulations are specific to each chamber due to the effects of chamber walls and illumination. The chamber model will be calibrated using experiments to characterize the ultraviolet (UV) intensity and to measure the rates of NOx off-gasing and nitrous acid (HONO) generation from the Teflon® walls as suggested by Carter et al. (2005). Losses of particles and IVOCs to the walls will also be measured and included in the model.

The instruments listed in Table 5.1 will all be used in environmental chamber experiments. The sampling lines for the standard monitors (ozone, nitric oxide, nitrogen dioxide) and the HR-ToF-CIMS are ¼ inch (inner diameter) Teflon ® tubing. The sampling lines of the SEMS and the ACSM are ¼ inch stainless steel tubing.

3.2 Process Measurements (MEAS)

Total particle volume will be measured with a Scanning Electric Mobility System (SEMS) from Brechtel Manufacturing, Inc. PM_1 bulk composition will be measured with an aerosol chemical speciation monitor (ACSM) (Ng et al. 2011). Concentrations of IVOCs will be measured by first collecting them on Tenax® TA sorbent tubes. Following collection, the IVOCs will be thermally desorbed from the tubes and then analyzed via gas chromatograph - mass spectrometry (GC-MS). Organic compounds in the gas phase will be identified and measured with a High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HRToF-CIMS) (Yatavelli et al. 2012). The volatility of the SOA will be evaluated using a thermodenuder, which will be built as part of this project. Other instruments which will be used include gas monitors for NO_x, NO_2 and O_3. The complete list of instruments used is included in Table 5.1. The exact list of species

will be determined after Task 1 is completed, but the list will contain larger alkanes (C_{12} and greater) and PAHs.

3.3 General Experimental Approach (MEAS)

For the environmental chamber experiments the general experimental design is as follows: First, the Teflon® bag is filled with clean air, produced using an Aadco zero air generator (Model 737-14A). Inorganic seed particles (usually ammonium sulfate, $(NH_4)_2SO_4$) are then injected which serve as surface area onto which oxidized organic vapors can condense, and which aid in the correction for wall losses (Hildebrandt et al. 2009). The IVOC of choice will then be injected using a heated injector. An oxidant precursor is also injected - H_2O_2 will be used for low NOx experiments; HONO or a combination of H_2O_2 and NOx will be injected for high NOx experiments. When everything is injected into the chamber and well mixed, the UV lights are turned on photolyzing the H_2O_2 or HONO and commencing the oxidation reactions to form SOA. A thermodenuder will be set up in front of the ACSM and SEMS, and the air mass will alternatively be passed through the thermodenuder (causing partial evaporation of the SOA) or through a bypass line (avoiding evaporation) to evaluate the vapor pressure of the SOA. The data from the thermodenuder will be used in conjunction with an evaporation model (Riipinen et al. 2010) to estimate the volatility basis set (VBS) distributions of the SOA. The VBS distributions, combined with estimated SOA oxidation state from the ACSM data, will provide important inputs for the chamber model as well as the regional CAMx modeling.

3.4 Air Quality Modeling (DATA)

CAMx will be used for all air quality modeling simulations in this project. CAMx is an Eulerian grid model that has been approved by the EPA for regulatory applications (http://www.epa.gov/ttn/scram/photochemicalindex.htm) and is the model used by the State of Texas for ozone attainment demonstrations and air quality planning. The model has been applied extensively for both regulatory and research applications in the United States and internationally. The model and supporting documentation have been developed by ENVIRON International Corporation (http://www.camx.com/). The latest version of CAMx (Version 6.10) will be used.

CAMx modeling will use a database based on a 2013 Texas ozone forecast modeling application (Johnson et al., 2013). The modeling domain covers the continental US with 36-km horizontal grid resolution and the entire Texas with 12-km resolution. A 4-km grid focusing on the Houston region will be added. The modeling period will cover the DISCOVER-AQ field campaign (August-October 2013). The meteorological conditions will be provided by a Weather Research and Forecasting (WRF) model (in hindcast mode) and the emissions inputs will be updated with the IVOC emissions developed under this study.

4. SAMPLING PROCEDURES

4.1 Sampling Methods (MEAS)

Concentrations of IVOC will be evaluated by first collecting IVOC on Tenax® TA sorbent tubes. The collection system consists of a calibrated air pump, polytetrafluoroethylene (PTFE) tubing, a primary sampling tube and a backup tube. The backup tubes will be used to check for breakthrough. The sampling flow rate and time will be optimized before formal tests to ensure quantification and avoid breakthrough. Duplicate air sample and a field blank will also be collected at each sampling time. Following collection, the IVOCs will be thermally desorbed by a thermal desorber (TD) (Turbomatrix 650 ATD) from the tubes and then analyzed via gas chromatograph - mass spectrometry (GC-MS) (Agilent 7890A GC- 5975MS). The sorbent tubes will be desorbed for 30 min at 300°C, with a helium flow of 50 ml/min, and a cold trap temperature of minus 30°C. The cold trap has a narrow bore (Low Flow Trap Tube) packed with Tenax TA sorbent and a small piece of silylated glass wool. Flash heating of the cold trap to 350°C transfers the analyte through the valves at 250°C and the transfer line at 250°C to the GC. The GC-MS has a constant pressure resulting in a flow rate of 1.6 ml/min at 80°C, and will be equipped with a 30 m × 0.25 mm DB-5MS column and operated at a 5:1 split injection. All tubes will be analyzed in two successive desorptions to ensure complete desorption of both the tube and the TD-GC-MS system.

All other measurements conducted as part of this work utilize instruments which take measurements in real time – air is sampled into the instruments and concentrations of different compounds are measured and stored electronically. As such, no physical samples are collected for those measurements and this section does not apply to them.

5. MEASUREMENT PROCEDURES

5.1 Methods Used (MEAS)

Table 5.1 summarizes the instruments used for gas- and particle phase measurements. Brief descriptions of the measurement methods are presented thereafter.

Table 5.1 Summary of measured species and instrumentation used

Species	Instrumentation		
	Make and Model	Principle	Comments
O_3	Teledyne Instruments Model T265	Chemiluminescence	Standard chemiluminescence combined with NO to reduce interference.
NO, NO_2 NO_x	Teledyne Instruments Model TML41	Chemiluminescence	Standard ambient monitoring instrument for NO/NO_2/NO_x measurements.

Species	Instrumentation		
	Make and Model	Principle	Comments
NO_2	Environnement, Inc.	Cavity Attenuated Phase Shift Spectroscopy	Measures NO_2 without conversion to NO, thereby avoiding interference from HONO, organic nitrates and other nitrogen-containing species.
Aerosol size distribution	SEMS, Brechtel, Inc.	Scanning Electric Mobility Spectrometer	Particle size based on electric mobility.
Aerosol (PM_1) chemical composition	ACSM, Aerodyne Research, Inc.	Aerosol Chemical Speciation Monitor	PM_1 bulk composition: particles are flash vaporized and resulting vapors are ionized via electron impact and analyzed via quadrupole mass spectrometry
VOC chemical composition	HR-ToF-CIMS, Aerodyne Research, Inc.	High Resolution Time of Flight Chemical Ionization Mass Spectrometer	Determines molecular formula of gas-phase species by time of flight; chemical ionization precludes fragmentation.

More detailed instrument descriptions

Teledyne Instruments Model T265 O_3 Analyzer. This is a commercially available instrument which has been approved by the EPA for ambient monitoring of O_3. It combines standard chemiluminescence with nitric oxide to significantly reduce interferences.

Environnement NO_2 Monitor. This is a commercially available instrument which utilizes cavity attenuated phase shift spectroscopy (CAPS) to provide a direct absorption measurement of nitrogen dioxide at 450 nm in the blue region of the electromagnetic spectrum [7]. Unlike standard chemiluminescence-based monitors, this instrument does not require conversion of NO_2 to another species and thus is not sensitive to interference from other nitrogen-containing species, thus avoiding interference from HONO and organic nitrogen species.

Teledyne Instruments Model TML41 $NO/NO_2/NO_x$ Analyzer. This is a commercially available instrument that is routinely used for the ambient monitoring of NO and NO_2. The analyzer utilizes the same chemiluminescence method as is used in virtually all the national monitoring network.

Brechtel Instruments Scanning Electric Mobility Spectrometer (SEMS). This commercially available instrument measures in the range of 0.01 μm to 2.0 μm electrical mobility diameter and consists of two main parts: a Differential Mobility Analyzer (DMA), which size-selects airborne particles based on their electric mobility, and a condensation particle counter (CPC), which counts the particles. As the DMA scans through different voltages, particles of different sizes pass through the DMA and are counted in the CPC. By scanning through different voltages, the instrument is able to provide measurements of the particle size distribution.

Aerodyne Research High Resolution Chemical Ionization Time of Flight Mass Spectrometer (HR-ToF-CIMS). This commercially available instrument measures the chemical composition of gas-phase species (Yatavelli et al. 2012) using a high resolution Time-of-Flight Mass Spectrometer (ToFMS) from Tofwerk AG (Thun, Switzerland). In contrast to the scanning procedures used by quadrupole mass spectrometers (QMS), ToFMS is a technique which simultaneously measures the concentrations of all mass-to-charge (*m/z)* values of interest. Pulses of ions are accelerated to a high kinetic energy and their subsequent travel times are measured and used to determine *m/z* values. Chemical ionization used in the HR-ToF-CIMS is a soft ionization technique which avoids fragmentation of the molecular components.

Aerosol Chemical Speciation Monitor (ACSM).
This instrument measures the mass concentrations of non-refractory aerosol species including sulfate, nitrate, chloride, ammonium and organics, using thermal particle vaporization, electron-impact ionization and mass spectrometric techniques. The ACSM has an aerodynamic particle lens for efficient gas-particle separation, and it includes and internal calibration reference at automated zeroing using a filter (Ng et al. 2011).

5.2 Calibration Procedures (MEAS)

Standard gas monitors (O_3, NO_x, NO_2)
Calibration methods and time resolution are similar for these instruments and are therefore described together here. In standard operation, these standard gas monitors will be operated with 1-minute time resolution.
The instruments will be calibrated using a 4-point calibration curve before and after this set of experiments. The concentration levels at the 4 points will 0, 50, 100 and 150 ppbv for O_3 and NO_x and 0, 20, 40 and 60 ppbv for NO and NO_2. In addition, a zero calibration will be performed every day that the monitor is operated, and 1-point calibrations will be performed weekly. Full 4-point calibrations will be repeated when the 1-point calibration shows a drift exceeding 10%.For these calibrations, zero air will be used from the AADCO air purification system (see below).

SEMS
The SEMS will be operated with a 2-min time resolution. Particle sizing will be confirmed using polystyrene latex spheres, using the procedures recommended by the manufacturer. The plumbing delay between the DMA and the CPC will be measured before this set of experiments is started, as recommended by the manufacturer.

ACSM
Sample flow into the ACSM will be calibrated using a needle valve and flow measurement (gilibrator). The instrument response to nitrate will be measured using standard calibration

procedures suggested by the manufacturer before and after this set of experiments. The response factor of other species including sulfate and organics relative to nitrate has been measured previously and will be used to quantify sulfate and organics in this work. The collection efficiency of particles in the ACSM will be estimated by comparing total concentrations measured by the ACSM to concentrations measured by the SEMS.

HR-ToF-CIMS
The HR-ToF-CIMS will be operated at a 1 second time resolution, but the data will be averaged to 1 minute time resolution before archiving. The instrument response to specific VOCs including isoprene and toluene will be calibrated using permeation tubes. Procedures for operation and calibration of this instrument will be submitted with the final report.

6. QUALITY METRICS

6.1 QC Checks for Measurements (MEAS)

Standard gas monitors (O_3, NO_x, NO_2)
As mentioned above, a zero and 1-point calibration will be performed every day that the monitor is operated. If the calibration has shifted significantly from the previous day, a full (4-point) calibration will be performed.

SEMS
Particle sizing will be confirmed using polystyrene latex spheres, using the procedures recommended by the manufacturer. The sizing will be checked before and after this set of experiments is performed.

ACSM
The instrument response to nitrate will be measured every two weeks to test and account for changes. Variation in the collection efficiency will be observed and accounted for using total concentration data from the SEMS.

HR-ToF-CIMS
The HR-ToF-CIMS is a new, state-of-the art instrument, and standard QC procedures have not, yet, been established. We will continue to communicate with the manufacturer (Aerodyne Research), as well as other researchers who have participated in the development and the first deployments of this instrument to confirm that the instrument is performing optimally.

6.2 (MEAS) Additional QA Objectives (MEAS)

For the HR-ToF-CIMS, the data analysis software provided by the manufacturer provides tools to ensure data quality. For example, the software allows to check and redo the mass calibration of the mass spectrometer and to account for decreasing ion intensity. The mass calibration will be redone / refined at each time step (1 second) for all data collected as part of this project. All data will also be adjusted for decreasing ion intensity.

6.3 Air Quality Model Results (DATA)

Model performance will be evaluated using a combination of quantitative and qualitative comparisons. Quantitative comparisons with observed OA from TCEQ monitoring data and measurements collected at Conroe during DISCOVER-AQ will assess the model OA performance as described in Section 7.4. Qualitative comparisons will be made with average OA level and fraction of oxygenated OA reported in the peer-reviewed literature. Model inputs (data) will be validated by having at least 10% of the data reviewed by two members of the ENVIRON research team.

7. DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT

7.1 Data Reduction (MEAS)

Data from the NO_x, NO_2 and ozone monitors will be saved in time-stamped delimited text formats. These data usually do not need additional processing after they are saved by the instruments.

Data from the Scanning Electric Mobility Spectrometer (SEMS) will be processed by the data analysis software provided by the manufacturer. Raw data are in units of particle count (from the CPC) versus DMA voltage, which corresponds to a certain particle size. The software provided by the manufacturer "inverts" the data from units of number vs. voltage to number vs. particle mobility diameter (D_m), resulting in a particle size distribution. The software also corrects the data for multiply charged particles (assuming a Boltzmann charge distribution) and accounts for diffusion. The resulting time series of particle size distributions will also be saved in time-stamped delimited text format.

Data from the ACSM will be analyzed in Igor Pro using the data analysis software "ACSM Local" provided by the manufacturer. In addition to calculating and displaying the chemically speciated aerosol mass loadings, ACSM Local has tools for examining the ACSM data stream in detail, monitoring instrument performance, calibrating the instrument (in conjunction with ACSM data acquisition software), and preparing data for positive matrix factorization.

Mass spectrometer data from the HR-TOF-CIMS are saved in hierarchical data format (hdf) by the data acquisition software provided by the manufacturer. These data require significant processing before their scientific significance can be interpreted. We will process the data using the data analysis software "Tofware", provided by the manufacturer and written in Igor (Wavemetrics). The functions in Tofware include a correction for the ToF duty cycle, a mass calibration based on selected known ions, interpolation and subtraction of the baseline, and determination of the resolution and shape of the ion peaks. The signal is then integrated - either all signal at a nominal mass to charge ratio (*m/z*) for unit mass resolution (UMR) analysis or each individual ion peak for high resolution (HR) analysis. All final data will be converted to time-stamped delimited text format.

7.2 Data Validation (MEAS)

Data will be validated by having at least 10% of the data analyzed by two researchers, specifically by Dr. Hildebrandt Ruiz (PI) and her Ph.D. student (Surya Dhulipala).

7.3 Data Summary (MEAS)

The data will be summarized in tables and plots. Several statistics will be evaluated, for example the mean and standard deviation of the data. In addition the data may be separated based on meteorological episodes (e.g. air masses from different source regions).

7.4 Air Quality Model Evaluation (DATA)

The spatial and temporal variations of modeled OA will be evaluated through maps, summary statistics, and graphics. For example, spatial maps of 24-hour average and episode average concentrations of OA will be developed. The maps will focus on the 4-km grid covering the Houston region.

Quantitative comparisons of model performance for OA will employ both graphical and statistical methods. Graphical methods will include spatial maps and time-series comparing model predictions to observations (TCEQ monitoring data as well as OA data collected at Conroe during DISCOVER-AQ). Statistical performance metrics to be computed are shown in the table below.

Model outputs will be validated by having at least 10% of the outputs reviewed by two members of the ENVIRON research team.

Metric	**Definition[1]**
Mean Bias (MB)	$\frac{1}{N}\sum_{i=1}^{N}(P_i - O_i)$
Mean Error (ME)	$\frac{1}{N}\sum_{i=1}^{N}\lvert P_i - O_i\rvert$
Mean Normalized Bias (MNB) (-100% to +∞)	$\frac{1}{N}\sum_{i=1}^{N}\left(\frac{P_i - O_i}{O_i}\right)$
Mean Normalized Error (MNE) (0% to +∞)	$\frac{1}{N}\sum_{i=1}^{N}\left\lvert\frac{P_i - O_i}{O_i}\right\rvert$
Normalized Mean Bias (NMB) (-100% to +∞)	$\frac{\sum_{i=1}^{N}(P_i - O_i)}{\sum_{i=1}^{N}O_i}$

Metric	Definition[1]
Normalized Mean Error (NME) (0% to +∞)	$\frac{\sum_{i=1}^{N}\lvert P_i - O_i\rvert}{\sum_{i=1}^{N} O_i}$
Fractional Bias (FB) (-200% to +200%)	$\frac{2}{N}\sum_{i=1}^{N}\left(\frac{P_i - O_i}{P_i + O_i}\right)$
Fractional Error (FE) (0% to +200%)	$\frac{2}{N}\sum_{i=1}^{N}\left\lvert\frac{P_i - O_i}{P_i + O_i}\right\rvert$
Coefficient of Determination (r^2) (0 to 1)	$\left(\frac{\sum_{i=1}^{N}(P_i - \overline{P})(O_i - \overline{O})}{\sqrt{\sum_{i=1}^{N}(P_i - \overline{P})^2 \sum_{i=1}^{N}(O_i - \overline{O})^2}}\right)^2$

[1] P_i and O_i are prediction and observation at the *i*-th site, respectively; $\overline{P}$ and $\overline{O}$ are mean prediction and observation, respectively.

7.5 Data Storage (MEAS and DATA)

Measurement data will be stored on the computer of PI Hildebrandt Ruiz as well as on an external hard-drive. Modeling data at ENVIRON will be stored on hard drive systems with built-in data redundancy (RAID systems). All project data will be delivered to AQRP for archival.

8. REPORTING

8.1 Deliverables from each Project Participant

AQRP requires certain reports to be submitted on a timely basis and at regular intervals. A description of the specific reports to be submitted and their due dates are outlined below. One report per project will be submitted (collaborators will not submit separate reports), with the exception of the Financial Status Reports (FSRs). PI Dr. Hildebrandt Ruiz will submit the reports but will be assisted by Dr. Greg Yarwood and other project participants in preparing the reports. All reports will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. Report templates and accessibility guidelines found on the AQRP website at http://aqrp.ceer.utexas.edu/ will be followed.

Executive Summary

At the beginning of the project, an Executive Summary will be submitted to the Project Manager for use on the AQRP website. The Executive Summary will provide a brief description of the planned project activities, and will be written for a non-technical audience.

Due Date: Friday, May 30, 2014

Quarterly Reports

The Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Word doc file. It will not exceed 2 pages and will be text only. No cover page is required. This document will be inserted into an AQRP compiled report to the TCEQ.

Due Dates:

Report	Period Covered	Due Date
Quarterly Report #1	June, July, August 2014	Friday, August 30, 2014
Quarterly Report #2	September, October, November 2014	Monday, December 1, 2014
Quarterly Report #3	December 2014, January & Feb. 2015	Friday, February 27, 2015
Quarterly Report #4	March, April, May 2015	Friday, May 29, 2015
Quarterly Report #5	June, July, August 2015	Monday, August 31, 2015
Quarterly Report #6	September, October, November 2015	Monday, November 30, 2015

Technical Reports

Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison as a Word doc using the AQRP FY14-15 MTR Template found on the AQRP website.

Due Dates:

Report	Period Covered	Due Date
Technical Report #1	June 1 - 30, 2014	Tuesday, July 8, 2014
Technical Report #2	July 1 - 31, 2014	Friday, August 8, 2014
Technical Report #3	August 1 - 31, 2014	Monday, September 8, 2014
Technical Report #4	September 1 - 30, 2014	Wednesday, October 8, 2014
Technical Report #5	October 1 - 31, 2014	Monday, November 10, 2014
Technical Report #6	November 1 - 30 2014	Monday, December 8, 2014
Technical Report #7	December 1 - 31, 2014	Thursday, January 8, 2015
Technical Report #8	January 1 - 31, 2015	Monday, February 9, 2015
Technical Report #9	February 1 - 28, 2015	Monday, March 9, 2015

Report	Period Covered	Due Date
Technical Report #10	March 1 - 31, 2015	Wednesday, April 8, 2015
Technical Report #11	April 1 - 28, 2015	Friday, May 8, 2015
Technical Report #12	May 1 - 31, 2015	Monday, June 8, 2015

Financial Status Reports

Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzione) by each institution on the project using the AQRP FY14-15 FSR Template found on the AQRP website.

Due Dates:

Report	Period Covered	Due Date
FSR #1	June 1 - 30, 2014	Tuesday, July 15, 2014
FSR #2	July 1 - 31, 2014	Friday, August 15, 2014
FSR #3	August 1 - 31, 2014	Monday, September 15, 2014
FSR #4	September 1 - 30, 2014	Wednesday, October 15, 2014
FSR #5	October 1 - 31, 2014	Monday, November 17, 2014
FSR #6	November 1 - 30 2014	Monday, December 15, 2014
FSR #7	December 1 - 31, 2014	Thursday, January 15, 2015
FSR #8	January 1 - 31, 2015	Monday, February 16, 2015
FSR #9	February 1 - 28, 2015	Monday, March 16, 2015
FSR #10	March 1 - 31, 2015	Wednesday, April 15, 2015
FSR #11	April 1 - 28, 2015	Friday, May 15, 2015
FSR #12	May 1 - 31, 2015	Monday, June 15, 2015
FSR #13	June 1 - 30, 2015	Wednesday, July 15, 2015
FSR #14	Final FSR	Wednesday, August 15, 2015

Draft Final Report

A Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will include an Executive Summary. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

Due Date: Monday, May 18, 2015

Final Report

A Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

Due Date: Tuesday, June 30, 2015

Project Data

All project data including but not limited to QA/QC measurement data, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion. The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information.

Specifically, the following data will be submitted from the CAMx modeling efforts:

- Updated CAMx source code
- CAMx run control file for the evaluation run
- CAMx model inputs
    - Emissions inputs for the 36/12/4 km grids including the MEGAN inputs/outputs/script
    - Meteorological inputs including the WRF inputs/outputs/script
    - Initial and boundary condition inputs
    - Other auxiliary inputs (ozone column, photolysis rate, land use)
- CAMx model outputs
- Model Evaluation Data
    - Observation data from the TCEQ monitoring sites and the DISCOVER-AQ measurements at Conroe
    - Excel spreadsheet of model performance metrics tables and graphs

The following data will be submitted from the environmental chamber experiments and box modeling

- Excel spreadsheets with concentrations of the following species throughout each experiment:
    - PM_1 organics
    - PM_1 ammonium sulfate (inorganic seeds)
    - PM_1 total volume

    - IVOC
    - O_3, NO, NO_2
- Excel spreadsheet with organic aerosol mass yield for each experiment
- Excel spreadsheet with mass fraction remaining of organic PM_1 as a function of thermodenuder temperature for each experiment.
- Excel spreadsheet with volatility basis set distribution obtained from yield data and thermodenuder data, as well as oxidation state of organics (estimated from mass spectrometer data)
- Updated SAPRC box model source code
- SAPRC model outputs
- Model Evaluation Data (comparison to measurements)

AQRP Workshop

A representative from the project will present at the AQRP Workshop in June 2015.

8.2 Expected Final Product

A Draft Final Report (due May 18, 2015) and a Final Report (due June 30, 2015) will be produced for the Texas AQRP documenting all activities performed for the study, summarizing project findings and recommendations for future research, and emphasizing those findings of interest to modelers and planners at TCEQ. Results from CAMx modeling will be used to develop recommendations for near-term improvements for chemical mechanisms used in current air quality models, taking into account implementation and mechanism size and efficiency issues as well as chemical accuracy, and also to develop recommendations for longer term research. In addition, several journal articles will be prepared summarizing the results of this work.

9. REFERENCES

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