

Scope of Work For
Project 14-029
**Spatial and temporal resolution of primary and secondary
particulate matter in Houston during DISCOVER-AQ**

Prepared for

Air Quality Research Program (AQRP)
The University of Texas at Austin

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1. Statement of Work

1.1 Introduction

This document is the work plan for the Texas Air Quality Research Program (TX AQRP) project 14-029 “Spatial and temporal resolution of primary and secondary particulate matter in Houston during DISCOVER-AQ.” DISCOVER-AQ stands for Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality. Work on the project will be completed by June 30, 2015. There are two Co-Investigators for the project: Drs. Rebecca J. Sheesley and Sascha Usenko, both of Baylor University.

Particulate matter (PM) concentrations can display large spatial and temporal heterogeneity across urban areas and have been linked to a number of air quality and atmospheric chemistry issues including human health. Distinct temporal and spatial regimes in urban PM are expected for Houston with its dense industrial zones like the Houston Ship Channel and heavy traffic during peak rush hour periods. Variable time resolution sampling at four Houston sites during DISCOVER-AQ was designed to capture these regimes. The overall goal is to quantify the strength of PM formation and PM emission sources across the Houston metropolitan area, including shipping emissions, motor vehicle exhaust, biomass burning and biogenic emissions. This work builds on the strengths of DISCOVER-AQ, specifically the spatial and temporal sampling strategies (i.e. multiple ground-based sites sampled for approximately 28 days). These strategies allows for the examination of both regional and long-range transport as well as anthropogenic and biogenic influences on air quality. Principle Investigators (PIs) will apply a combination of radiocarbon source apportionment of organic and elemental carbon with source-specific organic and inorganic molecular tracers to tightly constrain urban and regional fossil and biomass burning/biogenic sources. The primary outcome of the project will be a spatially and temporally-resolved map of PM source contributions for the Houston metropolitan area with four anchor points upon which detailed DISCOVER-AQ flight, mobile unit, and ground studies can be overlaid.

1.1.1 Research Objective: *The overall goal is to quantify the strength of PM formation and contributions of PM emission sources, including industrial sources, motor vehicle exhaust, biomass burning and biogenic emissions, across the Houston metropolitan area.* This research goal requires two major research tasks. Task 1 is the initial collection and characterization of PM filter samples during DISCOVER-AQ. Task 1 was accomplished through AQRP grant (12-032) and surpassed initial expectations. Task 2 is the in-depth characterization of PM and its sources in the Houston metropolitan area. This proposed project will specifically address Task 2 utilizing particulate filter collected during Task 1.

1.2 Scope of Work for Task 2 (14-029)

1.2.1 Synopsis. DISCOVER-AQ represents a significant opportunity to examine the spatial and temporal heterogeneity in the Houston metropolitan area. The PIs of this proposal previously collected filter-based PM samples from four ground-based field sites during DISCOVER-AQ at Moody Tower, Manvel Croix, Conroe, and La Porte. The proposed project will characterize PM through the quantification of water-soluble organic carbon (WSOC), organic tracers, elemental carbon (EC), organic carbon (OC), radiocarbon ($\Delta^{14}\text{C}$), select inorganic ions, and elemental tracers from PM filters collected from four anchor sites. Number of samples to be analyzed for this project included approximately 130 WSOC samples, 60 EC/OC samples, 50 $\Delta^{14}\text{C}$ and organic tracer samples, 30 elemental tracers and inorganic samples. It is important to note that multiple analyses will be performed on the same particulate filter whenever possible. This work will build on the PIs' previous EC, OC, and black carbon (BC) measurements made at Moody Tower and Manvel Croix. The quantitative source apportionment efforts will include radiocarbon source apportionment and chemical mass balance (CMB) modeling using organic and inorganic molecular markers (hopanes, steranes, polycyclic aromatic hydrocarbons (PAHs), alkanes, levoglucosan and elemental tracers). The semi-quantitative efforts will utilize multi-linear regression to investigate relationships among apportioned radiocarbon-apportioned OC, organic tracers and WSOC. This proposal will further enhance our understanding of PM in the Houston metropolitan area and specifically addressing AQRP 2014-2015 priority research area "Improving the understanding of ozone and PM formation, and quantifying the characteristics of emissions in Texas through analysis of data collected during the DISCOVER-AQ and SEAC4RS campaigns". SEAC4RS stands for Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys.

The work is focused on addressing the following objectives:

1.2.2 Project Objectives under Task 2:

- 1) Characterize and quantify PM formation and emission contributions at four synoptic sites across Houston to assess daily and diel source apportionment during DISCOVER-AQ.
 - a) Utilize molecular marker chemical mass balance modeling enhanced with radiocarbon source apportionment to tightly constrain fossil and contemporary sources including motor vehicle exhaust, biomass burning, ship emissions and total biogenic contribution.

- b) Utilize semi-quantitative tracers to characterize secondary organic aerosol (WSOC), local urban emissions (organic tracers) and rural impacts (pesticides).

Deliverables: Daily OC and EC measurements reported previously from PM samples collected at Moody Tower and Manvel Croix will be combined with daily measurements from Conroe and La Porte. Daily WSOC concentrations from PM samples collected from Moody Tower, Manvel Croix, and Conroe will be combined with the United States Environmental Protection Agency (EPA) WSOC La Porte dataset. Inorganic ions (sulfate, chloride, nitrate, ammonium and potassium) at Moody Tower will be combined datasets with particle-into-liquid sampler (PILS) data collected from Manvel Croix by Griffin and inorganic ion data from Conroe PM filter samples measured by Hildebrandt. Daily concentrations of ~53 elemental tracers will be reported for Teflon PM Filters collected at Moody Tower (this work will be contracted to an approved contract laboratory).

A detailed characterization of relative high OC (relative to EC) and ozone days (9/21-9/28) will be provided using organic tracers and $\Delta^{14}\text{C}$ measurements for 4-24 hour samples. This period also corresponds to four of the NASA flights (9/24-9/27) and has been identified as a period of interest by multiple AQRP PIs. The organic tracers will be used to apportion the primary organic aerosol (POA) at each site by molecular marker chemical mass balance modeling (MM-CMB) using known profiles [Sheesley *et al.*, 2010a; Sheesley *et al.*, 2010b] with the fossil combustion-derived POA constrained by radiocarbon analysis [Sheesley *et al.*, 2011].

- 2) Quantify changes in emission contributions for diesel- and gasoline-powered motor vehicles and biomass burning in the Houston metropolitan area since the 1997-98 CMB study to examine the efficacy of regulatory efforts and fleet modernization.
 - a) Complement on-going PM characterization efforts at Texas Committee on Environmental Quality (TCEQ) monitoring sites by increasing the spatial extent and specificity of carbon apportionment.

Deliverables

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). The lead PI will submit the reports, unless that responsibility is otherwise delegated with the approval of the Project Manager. 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 2015, January & February 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

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	Project Start – July 31, 2014	Friday, August 8, 2014
Technical Report #2	August 1 - 31, 2014	Monday, September 8, 2014
Technical Report #3	September 1 - 30, 2014	Wednesday, October 8, 2014
Technical Report #4	October 1 - 31, 2014	Monday, November 10, 2014

Technical Report #5	November 1 - 30 2014	Monday, December 8, 2014
Technical Report #6	December 1 - 31, 2014	Thursday, January 8, 2015
Technical Report #7	January 1 - 31, 2015	Monday, February 9, 2015
Technical Report #8	February 1 - 28, 2015	Monday, March 9, 2015
Technical Report #9	March 1 - 31, 2015	Wednesday, April 8, 2015
Technical Report #10	April 1 - 28, 2015	Friday, May 8, 2015
Technical Report #11	May 1 - 31, 2015	Monday, June 8, 2015

Financial Status Reports

Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzone) 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	Project Start – July 31, 2014	Friday, August 15, 2014
FSR #2	August 1 - 31, 2014	Monday, September 15, 2014
FSR #3	September 1 - 30, 2014	Wednesday, October 15, 2014
FSR #4	October 1 - 31, 2014	Monday, November 17, 2014
FSR #5	November 1 - 30 2014	Monday, December 15, 2014
FSR #6	December 1 - 31, 2014	Thursday, January 15, 2015
FSR #7	January 1 - 31, 2015	Monday, February 16, 2015
FSR #8	February 1 - 28, 2015	Monday, March 16, 2015
FSR #9	March 1 - 31, 2015	Wednesday, April 15, 2015
FSR #10	April 1 - 28, 2015	Friday, May 15, 2015
FSR #11	May 1 - 31, 2015	Monday, June 15, 2015
FSR #12	June 1 - 30, 2015	Wednesday, July 15, 2015
FSR #13	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

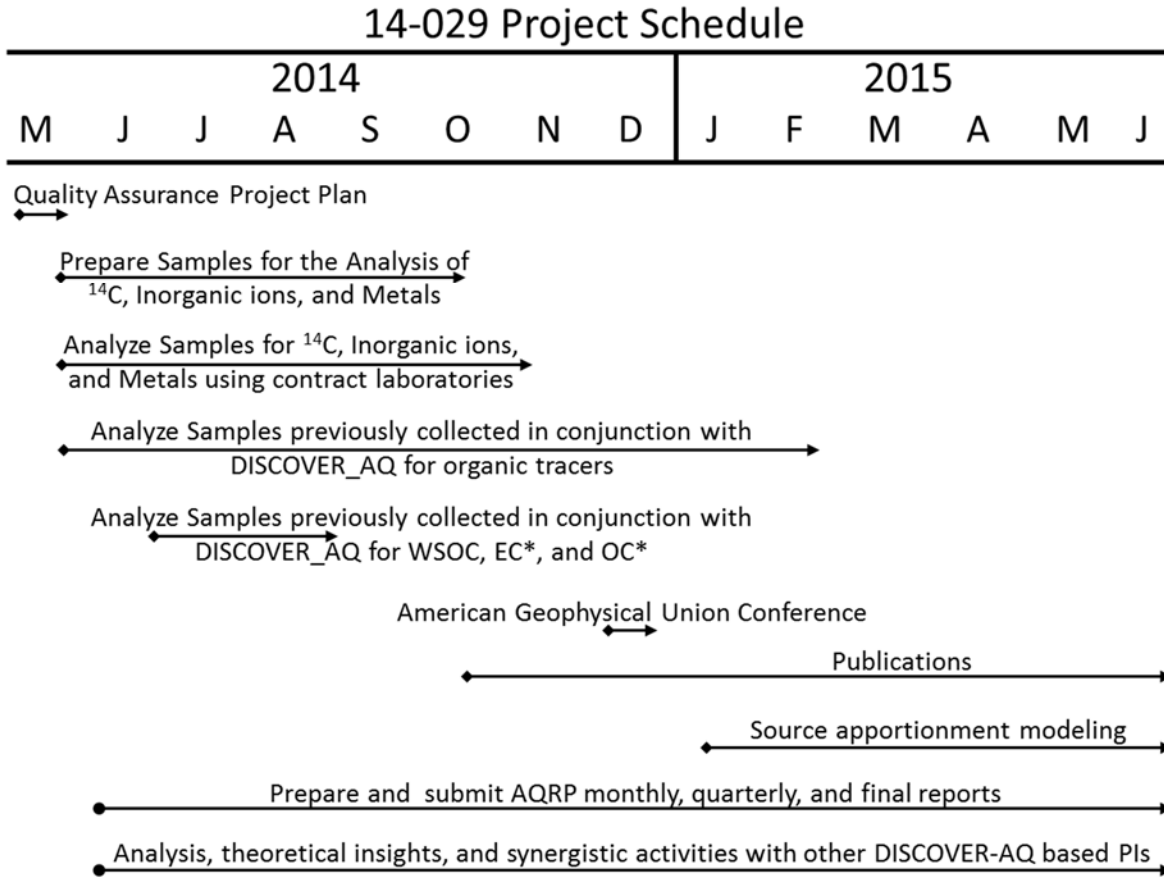
Project Data

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.

AQRP Workshop

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

1.3 General Timeline and Schedule.



* denotes focus on Conroe and La Porte PM Filter samples.

1.4 Data Sharing

Data collected during DISCOVER-AQ will be shared among the PIs of projects 14-009, 14-0024 and 14-029 (Drs. Griffin, Hildebrandt Ruiz and Sheesley, respectively). Deliverable 1c (14-029) will be performed on the combined dataset including all shared data. The remaining deliverables 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 PM₁ sulfate, ammonium, nitrate and organics, the fraction of organic PM₁ due to molecular fragments at a mass to charge ratio

(m/z) 44 (f_{44}), used as a proxy for organic PM_{10} 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_{10} 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 (14-024, 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, toluene and isoprene measured throughout the DISCOVER-AQ measurements.

- 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_{10} sulfate, ammonium, nitrate and organics, the oxidation state of organic PM_{10} 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 (14-024, Task 5). Data collected at other stationary measurement sites will be used for comparison to modeled concentrations (14-024, 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 (Deliverable for Objective 1).

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 (14-024, Task 5), i.e. concentrations of inorganic ions in $PM_{2.5}$.

- 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 (Deliverable for Objective 1).

February 2015:

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

March 2015

- Dr. Sheesley (14-029) will share results from radiocarbon analysis of filter samples, focusing on the final week of the September campaign (Deliverable for Objective 1).