

Quality Assurance Project Plan

Project 14-029

Spatial and temporal resolution of primary and secondary particulate matter in Houston during DISCOVER-AQ

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Summary of Project

QAPP Category Number: III

Type of Project: Measurement

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

May 29, 2014

GENERAL REQUIREMENTS

The project will characterize PM through the quantification of water soluble organic carbon (WSOC), organic tracers, elemental carbon (EC), organic carbon (OC), carbon-14 (^{14}C), select inorganic ions, and elemental tracers from particulate matter (PM) filters collected from four DISCOVER-AQ anchor sites including Moody Tower, Manvel Croix, Conroe, and La Porte. Principal 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.

This project is a research measurement project to collect data to support nonregulatory environmental research and decision making. This document is based loosely on the Environmental Protection Agency EPA's National Risk Management Research Laboratory (NRMRL) QAPP requirements for a measurement project. See <http://www.epa.gov/nrmrl/qa/qappreq.html> (accessed December 2010). This QAPP is in effect for the duration of this project: July 2014 through June 2015.

0.1 TITLE

This document is a Level III Quality Assurance Project Plan for the *Spatial and temporal resolution of primary and secondary particulate matter in Houston during DISCOVER-AQ* project. This project is managed by the staff at Baylor University.

0.2 DISTRIBUTION LIST

Below is a list of individuals and their organizations that need copies of the approved QA Project Plan and any subsequent revisions, including all persons responsible for implementation (e.g., project managers), the QA managers, and representatives of all groups involved. Paper copies need not be provided to individuals if equivalent electronic information systems can be used.

Air Quality Research Program (AQRP), University of Texas

David Allen, AQRP Director

Elena McDonald-Buller, AQRP Project Manager

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1.0 PROJECT DESCRIPTION AND OBJECTIVES

1.1 Project description

This project builds on a previously-funded AQRP project tasked at the initial elemental carbon (EC), organic carbon (OC), and optical black carbon (BC) characterization of particulate matter (PM) at Moody Tower and Manvel Croix during DISCOVER-AQ Houston Texas 2013 (AQRP 12-032). Under the original framework of PIs Sheesley and Usenko's AQRP ECOC Project, samples were to be collected over the entire DISCOVER-AQ sampling period at two primary sites: Moody Tower and Manvel Croix. Collaborations developed during the early stages of this project increased the sampling intensity at the two primary sites and expanded PM sampling efforts to Conroe and La Porte.

The overall goal is to quantify the strength of PM formation and PM emission sources, including shipping emissions, motor vehicle exhaust, biomass burning and biogenic emissions, across the Houston metropolitan area. This work builds on the spatial and temporal sampling strategies (i.e. multiple ground-based sites sampled for approximately 28 days) of DISCOVER-AQ. These strategies allow for the examination of both regional and long-range transport as well as anthropogenic and biogenic influences on air quality. The project will characterize PM through the quantification of water soluble organic carbon (WSOC), organic tracers, EC, OC, ^{14}C , select inorganic ions, and elemental tracers from PM filters collected from four DISCOVER-AQ anchor sites including Moody Tower, Manvel Croix, Conroe, and La Porte. 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.

1.2 Objectives

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 filters collected during Task 1.

Project Objectives:

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 (persistent organic pollutants; POPs) and rural impacts (pesticides).
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 chemical mass balance study to examine the efficacy of regulatory efforts and fleet modernization.
 - a. Complement on-going PM characterization efforts at Texas Commission of Environmental Quality (TCEQ) monitoring sites by increasing the spatial extent and specificity of carbon apportionment.

List of Deliverables:

Project deliverables are derived from project objectives (see above).

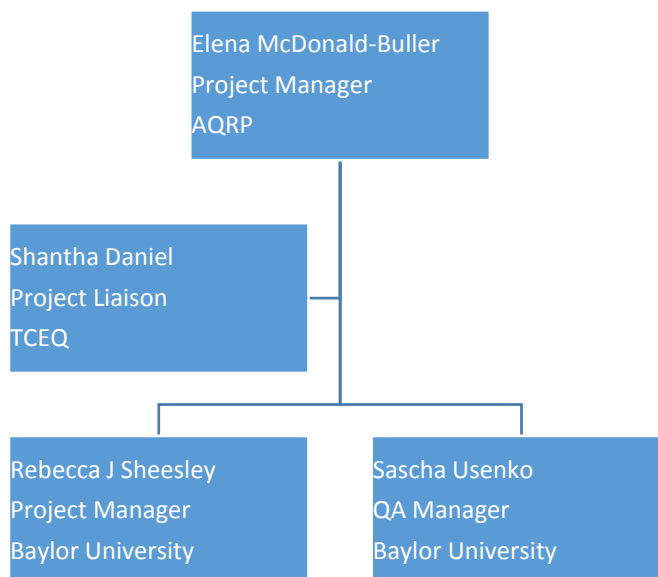
1. Characterize and quantify daily PM measurements from Moody Tower, Manvel Croix, Conroe, and La Porte during DISCOVER-AQ.
 - a. Combine daily OC and EC measurements determined previously from PM samples collected at Moody Tower and Manvel Croix with new daily measurements from Conroe and La Porte.
 - b. Measure daily WSOC from PM samples collected from Moody Tower, Manvel Croix, and Conroe and combine with the EPA WSOC La Porte dataset.
 - c. Measure inorganic ions (sulfate (SO₄), chloride (Cl), Nitrate (NO₃), Ammonium (NH₄) and Potassium (K)) at Moody Tower and combined datasets with particle into liquid sampler data collected from Manvel Croix and Dr. Hildebrandt Ruiz (14-024; Sources of Organic Particulate Matter in Houston: Evidence from DISCOVER-AQ data, Modeling and Experiments) data collected from Conroe PM filter samples.
 - d. Measure daily concentrations of ~53 elemental tracers from Teflon PM Filters collected at Moody Tower. This work will be contracted to an approved contract laboratory.
2. Provide a detailed characterization of relative high OC (relative to EC) and ozone over the period of (9/21-9/28) using organic tracers and ¹⁴C measurements combined with daily (24 hour) and high-resolution samples (4-12 hour time average sampling periods). This period also corresponds to four of the National Aeronautics and Space Administration (NASA) flights (September 24, 25, 26, and 27) and has been identified as a period of interest by multiple AQRP PIs.
 - a. Organic tracers, such as polycyclic aromatic hydrocarbons (PAHs), will be measured in both daily samples (24 hour) and short term (i.e. higher time resolution) periods of 4-12 hour time average sampling periods at Moody Tower and Manvel Croix.

- b. Fossil and modern fractions of carbon will be analyzed using ¹⁴C measurements. ¹⁴C measurements will focus mainly on daily samples, but will also be performed on a few short term (i.e. higher time resolution) PM samples.

2.0 ORGANIZATION AND RESPONSIBILITIES

2.1 Key personnel

The following flow chart identifies the key personnel at each organization that are responsible for the QA and deliverables listed in this document.



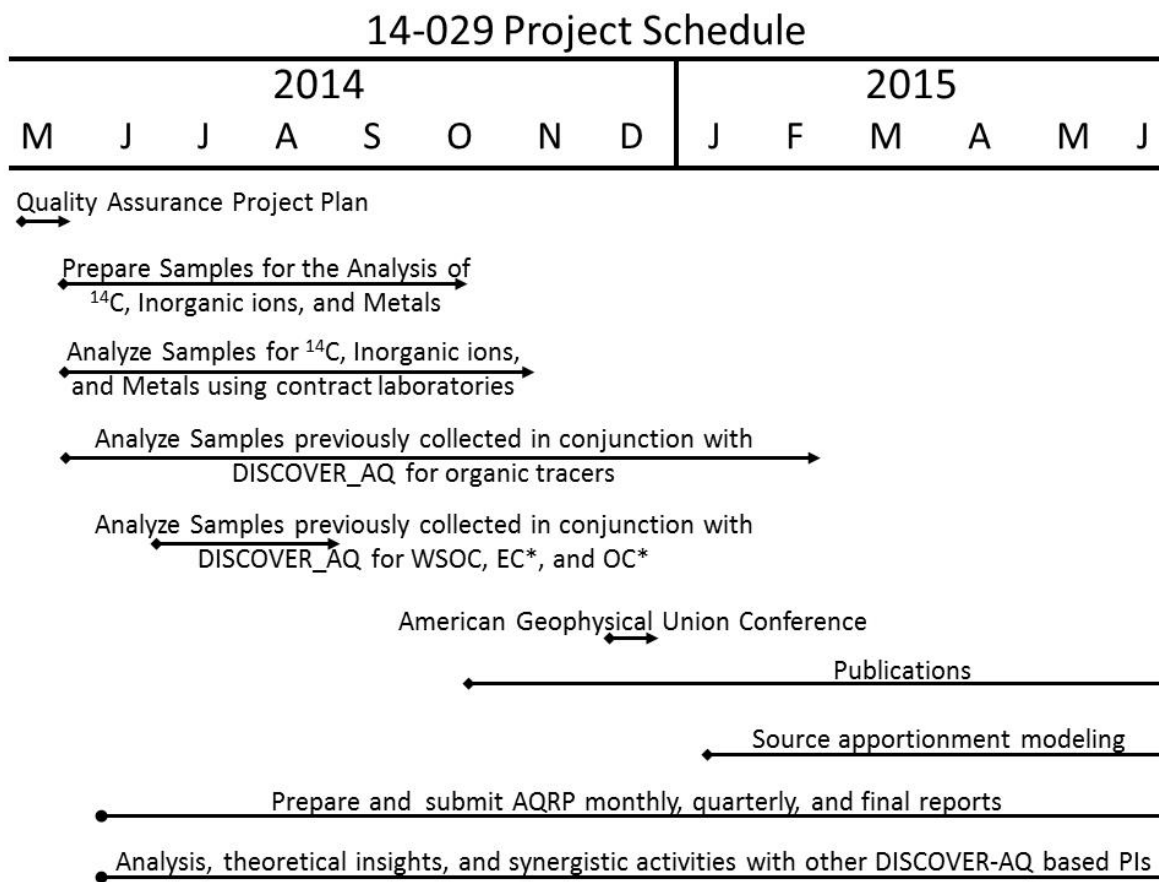
2.2 Project schedule

Table 1. The schedule and key milestones for this project.

AQRP FY14-15 Report Schedule

REPORT	PERIOD COVERED	DATE DUE	DUE TO
Exec Summary	Program Start	Friday, May 30, 2014	PM
Quarterly Report #1	July, August 2014	Friday, August 30, 2014	PM
Quarterly Report #2	September, October, November 2014	Monday, December 1, 2014	PM
Quarterly Report #3	December 2014, January & February 2015	Friday, February 27, 2015	PM
Quarterly Report #4	March, April, May 2015	Friday, May 29, 2015	PM
Quarterly Report #5	June, July, August 2015	Monday, August 31, 2015	PM
Quarterly Report #6	September, October, November 2015	Monday, November 30, 2015	PM

Tech Report #1	Project Start – July 31, 2014	Friday, August 8, 2014	PM & PL
Tech Report #2	August 1 - 31, 2014	Monday, September 8, 2014	PM & PL
Tech Report #3	September 1 - 30, 2014	Wednesday, October 8, 2014	PM & PL
Tech Report #4	October 1 - 31, 2014	Monday, November 10, 2014	PM & PL
Tech Report #5	November 1 - 30 2014	Monday, December 8, 2014	PM & PL
Tech Report #6	December 1 - 31, 2014	Thursday, January 8, 2015	PM & PL
Tech Report #7	January 1 - 31, 2015	Monday, February 9, 2015	PM & PL
Tech Report #8	February 1 - 28, 2015	Monday, March 9, 2015	PM & PL
Tech Report #9	March 1 - 31, 2015	Wednesday, April 8, 2015	PM & PL
Tech Report #10	April 1 - 28, 2015	Friday, May 8, 2015	PM & PL
Tech Report #11	May 1 - 31, 2015	Monday, June 8, 2015	PM & PL
FSR #1	Project Start – July 31, 2014	Friday, August 15, 2014	Maria Stanzione
FSR #2	August 1 - 31, 2014	Monday, September 15, 2014	Maria Stanzione
FSR #3	September 1 - 30, 2014	Wednesday, October 15, 2014	Maria Stanzione
FSR #4	October 1 - 31, 2014	Monday, November 17, 2014	Maria Stanzione
FSR #5	November 1 - 30 2014	Monday, December 15, 2014	Maria Stanzione
FSR #6	December 1 - 31, 2014	Thursday, January 15, 2015	Maria Stanzione
FSR #7	January 1 - 31, 2015	Monday, February 16, 2015	Maria Stanzione
FSR #8	February 1 - 28, 2015	Monday, March 16, 2015	Maria Stanzione
FSR #9	March 1 - 31, 2015	Wednesday, April 15, 2015	Maria Stanzione
FSR #10	April 1 - 28, 2015	Friday, May 15, 2015	Maria Stanzione
FSR #11	May 1 - 31, 2015	Monday, June 15, 2015	Maria Stanzione
FSR #12	June 1 - 30, 2015	Wednesday, July 15, 2015	Maria Stanzione
FSR #13	Final FSR	Wednesday, August 15, 2015	Maria Stanzione
Draft Final Report	-	Monday, May 18, 2015	PM & PL
Ultimate Final Report	-	Tuesday, June 30, 2015	PM & PL
Data Files	All Project Related Data	Friday, July 30, 2015	PM
AQRP Workshop	WILL BE IN FIRST HALF OF JUNE 2015 - PLEASE HOLD		



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

3.0 SCIENTIFIC APPROACH

The project will characterize PM from PM filters collected at Moody Tower, Manvel Croix, Conroe, and La Porte during DISCOVER-AQ. Select filters will be characterized using a wide variety of tracers including WSOC, organic tracers, EC, OC, ¹⁴C, select inorganic ions, and elemental tracers. Our scientific approach leverages the spatial and temporal sampling strategies of DISCOVER-AQ, specifically the multiple ground-based sites sampled for approximately 28 days. This work also builds on a previous AQRP grant (12-032), which was tasked with the initial collection and characterization of PM filter samples during DISCOVER-AQ. A detailed description of the sampling design, sites, and procedures as well as the sample description, handling, and preservations is described in AQRP grant (12-032) QAPP.

4.0 MEASUREMENTS PROCEDURES

4.1 Method Description

Bulk carbon analysis. The analysis of organic carbon and elemental carbon has been described previously in detail (Schauer et al. 2003). Briefly, all filter samples (total suspended particulate

matter; TSP and fine particulate matter or particles less than 2.5 micrometers in diameter; PM_{2.5}) will be analyzed for OC and EC by thermal optical methods using a Sunset Labs carbon analyzer. Thermograms will be visually monitored for inorganic carbonate carbon peaks, and flagged filters will be analyzed with duplicate acidified filter sections to quantify inorganic carbon contributions.

The Baylor EC, OC and total carbon (TC) analysis was accomplished using the thermal-optical transmission (TOT) carbon analysis method (Schauer et al. 2003). The Harris County Interagency Monitoring of PROtected Visual Environment (IMPROVE) and Speciation Trends Network (STN) network results of EC, OC and TC will be analyzed by thermal-optical reflectance (TOR) by Desert Research Institute (DRI). There are known differences between these methods (Schauer et al. 2003; Cheng et al. 2011), and studies have recommended harmonization algorithms (Zhi et al. 2011). The PIs will provide transformed OC and EC results (TOT to TOR) to TCEQ for their on-going PM_{2.5} studies in Harris County.

To facilitate inter-comparison between Baylor carbon measurements and TCEQ/EPA measurements, the PIs will upgrade Baylor's Sunset Labs TOT carbon analyzer with dual optics for concurrent transmittance and reflectance measurement. This will enable Baylor to analyze filter samples with the IMPROVE method as needed for validation of the harmonization algorithm (rerun DISCOVER-AQ filters) and for future Texas projects.

Radiocarbon Analysis. Filter preparation and carbon isolation will be accomplished by PI Sheesley and her research group prior to radiocarbon analysis by accelerator mass spectrometry at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS). Radiocarbon analysis is accomplished by measuring the ratio of ¹⁴C to ¹²C for the sample, a blank and a modern reference standard. The reference is 0.95 times the specific activity of National Bureau of Standards Oxalic Acid I (Standard Reference Material 4990B), which is a ¹⁴C/¹²C ratio of $1.176 \pm 0.010 \times 10^{-12}$ (Karlen et al. 1964; Olsson 1970). These three ratios are combined in the following expression to calculate the raw F_{modern} which is reported by NOSAMS: $F_{\text{modern}} = ({}^{14}\text{C}_{\text{sample}}/{}^{12}\text{C}_{\text{sample}} - {}^{14}\text{C}_{\text{blank}}/{}^{12}\text{C}_{\text{blank}}) / ({}^{14}\text{C}_{\text{modern reference standard}}/{}^{12}\text{C}_{\text{modern reference standard}} - {}^{14}\text{C}_{\text{blank}}/{}^{12}\text{C}_{\text{blank}})$. The post processing of raw F_{modern} data for particulate radiocarbon ($\Delta^{14}\text{C}$) analysis will proceed as follows: Filter-based analysis of PM_{2.5} OC and EC for particulate radiocarbon ($\Delta^{14}\text{C}$) via accelerator mass spectrometry will be used for apportionment between fossil and modern carbon sources to further elucidate influence from oil and gas extraction emissions. The basis for ¹⁴C-based source apportionment is that modern biomass fuel is in radioactive equilibrium with the atmosphere ($\Delta^{14}\text{C}$ of about + 90‰) while a geologically-aged fossil fuel would be depleted in ¹⁴C and assigned a $\Delta^{14}\text{C}$ value of -1000‰. Hence, the obtained $\Delta^{14}\text{C}$ EC value reflects the following assumption: $\Delta^{14}\text{C}_{\text{EC}} = (\Delta^{14}\text{C}_{\text{biomass}})(f_{\text{biomass}}) + (\Delta^{14}\text{C}_{\text{fossil}})(1-f_{\text{biomass}})$. Solving this equation for f_{biomass} , the fraction of EC coming from biomass burning is obtained. The contribution from fossil fuel combustion (f_{fossil}) is $(1 - f_{\text{biomass}})$ (Gustafsson et al. 2009). The EC harvesting from the filter samples will be conducted in the Sheesley lab at Baylor University using the Sunset Labs carbon analyzer. ¹⁴C measurements will be contracted to the National Ocean Sciences Accelerator Mass Spectrometry Facility

(NOSAMS) at the Woods Hole Oceanographic Institution. Dr. Sheesley has worked extensively with NOSAMS for multiple projects and has a good working relationship with them. NOSAMS is one of the foremost laboratories in the world capable of making these measurements.

Water Soluble Organic Carbon. Sample aliquots will be placed in 50 ml centrifuge tubes (Bio-Link Scientific, Wimberly, TX) and sonicated in 30 mL of de-ionized water for 15 minutes. All preparatory glassware and consumables, including centrifuge tubes and syringe filters, will be pre-cleaned by triple rinsing with deionized water. The extracts will be centrifuged for 10 minutes and decanted. The extracts will then be filtered using disposable Iso-Disc PTFE-25-2 Filters with a pore size of 0.2 μm (Supelco Analytical, Bellefonte, PA). Sixty microliters of 6N hydrochloric acid will be added to remove inorganic carbon from the solution. Samples will be run in batches of 20 with calibration standards (concentrations of: 0, 0.5, 1, 2, 3, 4, and 5 mg L^{-1}) measured prior to and periodically throughout each batch. The reporting limit for the method at Baylor University is 0.5 mg L^{-1} (Barrett and Sheesley 2014). Each sample will be analyzed three times at 100 μl each. The reported values will be the average concentrations of the three injections. All samples will be blank subtracted using an average filter blank value for the DISCOVER-AQ campaign.

Inorganic Ions. Filter-based measurements will be conducted to obtain inorganic ion (SO_4 , Cl, NO_3 , NH_4 and K) mass concentrations. The certified contract laboratory Desert Research Institute will be utilized for this analysis.

Organic Tracers. Particulate organic molecular tracer concentrations will be analyzed via gas chromatography-mass spectrometry (GC/MS): Filters will be extracted for GC/MS analysis and quantification of organic tracers for motor vehicle exhaust, biomass burning, aromatics-associated secondary organic aerosol, and vegetative detritus/primary biogenic (Yunker et al. 2002; Sheesley et al. 2010b). Fractions of select filters will be designated for pressurized solvent extraction and detailed organic characterization by gas chromatography-mass spectrometry GC/MS utilizing both electron impact and negative chemical ionization. Detailed organic characterization will include measurement of organic tracers for fossil fuel combustion (hopanes and polycyclic aromatic hydrocarbons - PAHs), biomass burning (levoglucosan and PAHs), aromatics-associated secondary organic aerosol (aromatic acids), vegetative detritus/primary biogenic (alkanes) and non-combustion urban development (PBDEs) (Usenko et al. 2007; Sheesley et al. 2010b). An Agilent multi-mode inlet will increase the mass on the column by roughly 30 times and help account for the potential low loadings on the higher time resolution filters. The organic tracers will be used to apportion the primary organic aerosol (POA) at each site by molecular marker chemical mass balance modeling 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).

5.0 QUALITY ASSURANCE/METRICS

Quality Assurance (QA) is an integrated management strategy utilized by organizations that insures the quality of their products. This management strategy includes planning, implementation, documentation, reporting, and evaluation of environmental data produced by the laboratory. QA policies are created to document the organization's activities and to assure that the organization meets its quality expectations. PIs Sheesley and Usenko at Baylor University are committed to meeting all quality expectations to insure that environmental data produced by the center meets the highest quality expectations. The quality system follows EPA policy on quality standards, which is based on American National Standards Institute/American Society of Quality Control E4-1994. Quality Control (QC) is the overall system of technical field and laboratory activities that measures the attributes and performance of a process, item, or service against defined standards to insure quality data. Ultimately, the QC process provides a standard for which environmental data can be judged acceptable or unacceptable.

The purpose of the QA program is to ensure that the operation of each laboratory is technically correct and in compliance with standard operating procedures. Essential to the quality of data collected in these experiments is the use of appropriate methods of sampling and lack of bias in collection and handling of samples, and subsequent laboratory analysis of materials. Samples will be handled in a chain-of-custody process. This includes tracking forms, custody sheets and labels for identification which are computer generated by the laboratory information management system. The Baylor Sciences Building employs a state-of-the-art back-up power generation system. Storage temperatures will be carefully monitored and recorded to assure that any recommended temperatures are not exceeded.

All analytical determinations will be accomplished using state-of-the-science instrumentation and methods that have been extensively tested and subjected to thorough peer review by US EPA and their contractors. Once samples have been collected, they will be transferred to the appropriate laboratory with labels for identification. Control charting will be used as part of preventive maintenance procedures to alert project personnel of problems with equipment instruments, and/or operator performance. Reproducibility will be assessed by intrinsic intra- and inter- experiment controls in each experiment, and accuracy will be assessed by sensitivity and selectivity of response of positive controls in each experiment. Standard quality assurance/quality control procedures (e.g., American Public Health Association, ASTM, EPA) will be followed including the use of known reference chemicals when appropriate. Each data set developed will have both internal and external measures for precision and accuracy.

Analytical determinations using outside or contracts laboratories such as NOSAMS (radiocarbon analysis) will be or were selected based on their well-established instrumentation and methods. Sample characterization utilizing a contract laboratory for the analysis of radiocarbon (NOSAMS) and inorganic ions (to be determined) will follow well-described and accepted QC and QA checks and objectives.

5.1 QC Checks and QA Objectives

A total of five data quality attributes will define acceptable data quality criteria: precision, accuracy, representativeness, completeness, and comparability (see Table 2 and 3). These attributes are specific to the following measurements: bulk carbon, organic tracers, and WSOC. NOSAMS will measure radiocarbon on select PM samples. Their overall QC checks and QA objectives for this analysis is widely accepted and included standard protocol for sample preparation and submission as well as data results, handling, and calculations. NOSAMS has previously described and documented precision and accuracy for the required analysis. A similar well established laboratory will be utilized for the analysis of select ion organic ions.

Precision. Precision is a measure of the reproducibility among multiple measurements. Precision will be measured quantitatively utilizing field and laboratory replicate samples as well as replicate instrument injections. A minimum of 10% of the total field samples collected were field duplicate samples. If the relative percent difference (RPD) is greater than specific analysis (see Table 2 and 3) for an individual measurement in the field duplicate samples, the sample will be reanalyzed, if the RPD is still greater than the allowed RPD the analyte will be flagged as failed. In addition, a minimum of 10% of the total number of samples will be replicate instrument injections. If the RPD for replicate instrument injections are greater than specific analysis (see Table 2 and 3), the extract will be reanalyzed and flagged as failed if necessary. Even though sampling and analysis for the specified analyte in PM filter samples are well described by the literature, methods will be validated in triplicate using the target matrix to demonstrate our laboratory's capability. Results from triplicate matrix spike and recovery experiments will be reported in the project's final report. The RPD for triplicate spike and recovery experiments will be less than 30%. These precision criteria and RPDs are consistent with the National Institute for Occupational Safety and Health (NIOSH) 5040 thermal optical transmission method for bulk carbon analysis (NIOSH 1996). These precision criteria and RPDs are also consistent with the organic tracer analysis in the QAPP for the Defining Biota-Sediment Accumulation Factors for the San Jacinto River Waste Pits Project, which was approved by TCEQ (Texas Environmental Health Institute Project Reference #32370108). These precision criteria and RPDs are also consistent with the organic tracer analysis in both QAPPs for the Western Airborne Contaminant Assessment Project and Integrated Atmospheric Deposition Network which were both approved by USEPA.

Accuracy. Accuracy is a measure of the closeness of which an individual measurement or average of measurements reflects the true value. Accuracy of the method will be determined during method validation with actual matrix using triplicate spike and recovery of the target analytes. The recoveries and background concentrations will be reported in the final report and will be fall between 70 to 130%. These acceptance criteria recoveries are consistent with the organic tracer analysis in the QAPP for the Defining Biota-Sediment Accumulation Factors for the San Jacinto River Waste Pits Project, which was approved by TCEQ (Texas Environmental

Health Institute Project Reference #32370108). These acceptance criteria recoveries are also consistent with the recoveries for organic tracer analysis in the QAPP for the Integrated Atmospheric Deposition Network under USEPA Grant #GL 995656-01 approved by USEPA GLNPO in May 2000.

Representativeness. Randomly selected duplicated field sampling will be used to evaluate the data's ability to accurately and precisely represent actual atmospheric concentrations.

Completeness. Completeness, which measures the percentage of QA samples to the number of planned samples. In order to meet the objectives of the project's research plan, the acceptance criteria for field sampling and laboratory completeness is 90%. The completeness of both field and laboratory will be reported. Approximately, 30-200 samples (depending on the analyte and analysis) will be collected and analyzed including; TSP filter samples, PM_{2.5} filter samples, analysis of duplicates, and 10% field blanks.

Comparability. Comparability between one data set and another is crucial. Comparability can be maintained by following QAPPs as well as documenting all analytical procedures and changes to those procedures. Comparability to other laboratories and projects will evaluate using the triplicate spike and recovery data. To ensure data comparability the project will follow and report: use standards techniques for sample collection and analysis, the use of one laboratory for preparation and analysis, specific method detection limits, follow QA criteria, and perform a data quality audit.

Audit of Data Quality. A minimum of 10% of all data will be audited by a member of the team that was not directly associated with the analyses. The findings of the data audits will be included in the final report

Table 2. Quality Assurance Criteria and Data Quality Objectives for Bulk Carbon and WSOC Analysis using TSP and PM_{2.5} filter samples.

Sample Type	Frequency	Required Objective	Control Action
<u>Precision</u>			
Filter spikes	10%	Relative percent deviation <25%	Re-analyze if possible or flag samples accordingly
Laboratory replicate analyses (duplicate samples)	10%	Relative percent deviation <25%	Investigate source of imprecision
<u>Accuracy</u>			
Filter spikes	10%	Relative percent deviation <25%	Re-analyze if possible or flag samples accordingly
Matrix spikes	Method validation	70% - 130%	Investigate source of imprecision
<u>Completeness</u>			
Field samples		90%	Report percentage
<u>Detectability</u>			
Method detection limit study	1/project		Reported in yearly QA Report
Routine field samples	All samples	> MDL	Report and flag as below detection limits
<u>Calibration</u>			
Sugar filter spike	1/batch	± 25% of actual mass	Reoptimize instrument and rerun filter spike
Instrument calibration using calibration gas	1/sample run		
<u>Blanks</u>			
Field matrix blank	10%	< 20% of associated sample mass	Flag samples; identify and eliminate source of contamination
Instrument blank	1/batch	0 < 0.25 ug/cm ²	Flag samples; identify and eliminate source of contamination
<u>Project Audit</u>			
Data Quality Audit	1/project	10% of data	if problems are identified, the entire dataset will be audited

MDL indicates method detection limits

Table 3. Quality Assurance Criteria and Data Quality Objectives for Organic Tracers Analysis using TSP and PM_{2.5} filter samples.

Sample Type	Frequency	Required Objective	Control Action
<u>Precision</u>			
Standard Reference Material	10%	Relative percent deviation <100%	Re-analyze if possible or flag samples accordingly
Instrument replicate injections	10%	Relative percent deviation <100%	Re-analyze if possible or flag samples accordingly
Laboratory replicate analyses of matrix spikes	Method validation	Relative percent deviation <50%	Investigate source of imprecision
<u>Accuracy</u>			
Standard Reference Material	10%	Relative percent deviation <100%	Re-analyze if possible or flag samples accordingly
Surrogate spikes	All samples	50% - 130%	Investigate source of imprecision
Matrix spikes	Method validation	50% - 130%	Investigate source of imprecision
<u>Completeness</u>			
Field samples		90%	Report percentage
<u>Detectability</u>			
Method detection limit study	1/project		Reported in yearly QA Report
Routine field samples	All samples	> MDL	Report and flag as below detection limits
<u>Calibration</u>			
Instrument multiple point calibration - 4 point	Monthly	$r^2 > 0.95$	Reoptimize instrument and repeat calibration
Instrument performance calibration check standard	1/batch	$\pm 25\%$ of actual mass	Reoptimize instrument and rerun calibration curve
<u>Blanks</u>			
Field matrix blank	10%	< 20% of associated sample mass	Flag samples; identify and eliminate source of contamination
Lab blank	5%	< 5% of associated sample mass	Flag samples; identify and eliminate source of contamination

MDL indicates method detection limits

6.0 DATA ANALYSIS, INTERPRETATION & MANAGEMENT

The data will be provided to AQRP in time-stamped, delimited text format suitable for use in a database. Data will include the time series of OC, EC, radiocarbon, WSOC, organic and inorganic tracers. The information provided by these data will be useful in understanding PM dynamics in this region and for comparison with flight measurements during DISCOVER-AQ. Data collected/generated during the course of this project will be backed up on servers at Baylor University and will be maintained for a minimum of 3 years after the completion of the project.

7.0 REPORTING

Reporting for this project was presented in Table 1 and includes:

- Monthly (starting July 2014) and interim (as requested) reports including accomplishments, problems encountered and corrective actions, goals for the next reporting period, and a description of the project's progress as described above.
- Draft final and final reports describing all activities and summarizing all findings. The final report will include descriptions of (a) the chemical or elemental analysis (b) instrumental information and (c) preliminary interpretation of collected data. The draft and final report is due May 30th and June 30th, 2015, respectively.

References

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