AQRP Monthly Technical Report

PROJECT TITLE	Spatial and temporal resolution of primary and secondary particulate matter in Houston during DISCOVER-AQ	**PROJECT #**	14-029
PROJECT PARTICIPANTS	Rebecca J. Sheesley Sascha Usenko	**DATE SUBMITTED**	3/8/2015
REPORTING PERIOD	**From:** February 1, 2015 **To:** February 28, 2015	**REPORT #**	7

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Detailed Accomplishments by Task

The major focus of February 2015 was to finalize filter plans of analysis of quartz fiber filters collected during DISCOVER-AQ and ship filters aliquots out for analysis to independent contract laboratories. A filter plan is a systematic strategy that specifies the amount or area of filter to be dedicated for each type of analysis. It is imperative that each set of analyses has a fully vetted filter plan. Filter plans needed to be created for all four ground-based sites (Moody Tower, Manvel Croix, Conroe, and La Porte) as well as for different quartz fiber filters size fractions; specifically total suspended particulates (TSP) and particulate matter 2.5 μm ($PM_{2.5}$). A filter plan for the Conroe $PM_{2.5}$ quartz fiber filters was created in the previously and implemented in December to help support AQRP project (14-024). The focus was to work on the remained of the quartz fiber filter plans including for inorganic ions, metals (elemental Tracers), ^{14}C measurements, and molecular markers.

Baylor students cut and shipped filters to Desert Research Institute (DRI) for inorganic ion analysis (quartz fiber filters from Moody Tower and Conroe) and for metals analysis (Teflon filters from Moody Tower) as part of the project deliverables. Baylor PIs (principal investigators) and students have been in close communication with DRI (specifically, Steven Kohl) in the past month to insure that Moody Tower and Conroe samples are analyzed in a timely manner for inorganic ion and metals (Teflon filters; only Moody Tower). Based on DRI turnaround estimates Baylor PIs should receive inorganic ion and metals data by the end of the February or early March. The invoice for both analyses will be submitted after receiving data. Teflon filters ($PM_{2.5}$) were collected only at Moody Tower and will be used for metal analysis.

No filter plan was needed as the entire Teflon filter is consumed in the analysis. Metal daily concentrations will be measured on $PM_{2.5}$ Teflon filters collected at Moody Tower.

Filter Plans for Inorganic Ion Analysis. Filter plans were created for inorganic ion analysis at Moody Tower. Baylor PIs and student shipped 26 samples and 4 blanks (following project's approved QAQC plan) to DRI for inorganic ion analysis (see Table 1 and 2). Based on DRI turnaround estimates, Baylor should receive inorganic ion data by the end of the February or early March. The percentage dedicated for inorganic ion analysis was approximately 8 to 16% of the quartz fiber filter. The DRI quote cost for inorganic ion analysis was $4750. Conroe filters dedicated for inorganic ion analysis were shipped earlier on in the project to help support AQRP project (14-024). Inorganic ions analysis was not a deliverable for Manvel Croix or La Porte. Inorganic ion analysis for Conroe is a deliverable for 14-024; Baylor graduate students cut and shipped Conroe filters to DRI in December, 2014.

Filter Plans for Metal (Elemental Tracers) Analysis. Metals are only to be measured at Moody Tower and only on Teflon filters. Baylor PIs and student shipped 25 samples and 3 blanks (following project's approved QAQC plan) to DRI for metal analysis in February (see Table 1 and 2). Based on DRI turnaround estimates, Baylor should receive inorganic ion data by the end of the February or early March. The entire Teflon filter was dedicated to the analysis of 51 metals using DRI and XRF. The DRI quote cost for metal analysis was $2342.

Filter Plans for Radicarbon Analysis. Filter plans were created for radiocarbon analysis at Moody Tower, Manvel Croix, Conroe, and La Porte. Baylor PIs and student shipped samples and blanks (following project's approved QAQC plan) to National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) for radiocarbon analysis in February (see Table 1 and 2). Based on NOSAMS turnaround estimates, Baylor should receive inorganic ion data by the end of the April or early May. Samples and blanks were shipped in batches to help improve turnaround time for the submission of invoices. A total of 48 filters (including samples and blanks) were shipped to NOSAMS. The number of filters submitted for each site is listed in table 2. The NOSAMS cost for radiocarbon analysis is approximately $26,000. Exact final costs are dependent upon factors in the analysis process and will not be determined until final invoicing.

Filter Plans for Organic Tracer Analysis. Filter plans were created for organic tracer analysis at Moody Tower, Manvel Croix, Conroe, and La Porte (see Table 1 and 2). Baylor PIs and student will cut and analyze aliquots of quartz fiber filter for organic tracers for each site using the method previously described. Organic tracer analysis will follow QAQC criteria described in the project's QAPP. Approximately 50 plus samples and blanks will be analyzed for organic tracers. Filter plans were finalized using relationship between bulk organic carbon and organic tracer concentrations. Note: Organic carbon, elemental carbon, and water soluble organic carbon

concentrations were measured earlier on in the project and was discussed and compared with other DISCOVER-AQ PIs at the December 2014 American Geophysical Union conference in San Francisco. Organic tracer concentrations were measured on a subset of representative samples. These two datasets were used to explore the relationship between bulk organic carbon and organic tracer concentrations. These tracer to organic carbon relationships were correlated with an R squared of greater than 0.97 (see Results, Figure 1). Baylor PIs used these relationships to help determine the mass of organic carbon needed to measure organic tracers, while consuming the least amount of filter. The mass of organic carbon needed was converted into a percentage of the filter that would be dedicated for organic tracer analysis. The mass of organic carbon was measured on every filter, which allowed Baylor PIs to calculate the percentage dedicated for organic tracer analysis for each filter. This is extremely important because the overall loading varied by the duration of the sampling effort as well as from day to day and from site to site. Typically, the percentage dedicated for organic tracer analysis was approximately 10 to 60% of the quartz fiber filter. This preliminary effort is designed to reduce the number of non-detects for organic tracer analysis while potentially allowing preservation of more filter for future analysis.

Table 1: Filter plan including ground site, analyte lists, filter type, duration, and percentage dedication.

Analysis	Moody Towervz	Manvel Croix	Conroe	La Porte
Radiocarbon	Quartz fiber filter $PM_{2.5}$ 14-24h 5-16% of filter	Quartz fiber filter $PM_{2.5}$ 10-14h 5-16% of filter	Quartz fiber filter $PM_{2.5}$ 24h 3-8% of filter	Quartz fiber filter TSP 24h 1% of filter
Organic Tracers	Quartz fiber filter $PM_{2.5}$ 14-24h 40-60% of filter	Quartz fiber filter $PM_{2.5}$ 10-14h 40-60% of filter	Quartz fiber filter $PM_{2.5}$ 24h 30-50% of filter	Quartz fiber filter TSP 24h 10-20% of filter
Inorganic ions	Quartz fiber filter $PM_{2.5}$ 4-14h 8-16% of filter		Quartz fiber filter $PM_{2.5}$ 24h 8% of filter	
Trace elements	Teflon filters $PM_{2.5}$ 24h Whole filter			

Organic and elemental carbon and water-soluble organic carbon were completed on quartz fiber filters at all sites as reported previously.

Table 2: Filter plan including ground site, analyte lists, number of samples, status, laboratory, and estimated cost for contract analysis.

Site	Filter Type	Analysis	# of Samples	Status	Contract laboratory quote
Moody Tower	Quartz fiber filters	Inorganic ions	26 + 4 blanks	Submitted to DRI	$4750
Moody Tower	Teflon	Trace metals	25 + 3 blanks	Submitted to DRI	$2342
Moody Tower	Quartz fiber filters	Organic Tracers	18 + 2 blank	Processing	
Moody Tower	Quartz fiber filters	Radiocarbon	18 + 2 blank	Submitted to NOSAMS	$10,720
Conroe	Quartz fiber filters	Inorganic ions	25 + 2 blanks	Submitted to DRI	NA, 14-024
Conroe	Quartz fiber filters	Organic Tracers	8 + 1 blank	Processing	
Conroe	Quartz fiber filters	Radiocarbon	8 + 1 blank	Submitted to NOSAMS	$4824
Manvel Croix	Quartz fiber filters	Organic Tracers	11 + 1 blank	Processing	
Manvel Croix	Quartz fiber filters	Radiocarbon	11 + 1 blank	Submitted to NOSAMS	$6432
La Porte	Quartz fiber filters	Organic Tracers	7	Processing	
La Porte	Quartz fiber filters	Radiocarbon	7	Submitted to NOSAMS	$3752

Preliminary data:

Results for the project's organic carbon, elemental carbon, and water soluble organic carbon concentrations as well as the method for organic tracers were presented at the December 2014 American Geophysical Union conference in San Francisco.

Organic carbon and organic tracer concentrations were used to understand the relationship between organic carbon loading and organic tracer contractions at Houston during DISCOVER-AQ. The organic tracer concentrations were measured from a small subset of exploratory filters. Figures 1 and 2 are representative data sets for polycyclic aromatic hydrocarbon (Moody Tower) and hopanes and steranes (Moody Tower). These relationships, in conjunction with AGU discussions with DISCOVER-AQ PIs (including Jim Crawford; NASA's DISCOVER-AQ PI), allowed Baylor PIs to determine the percentage of each quartz fiber filter to be dedicated for organic tracer analysis.

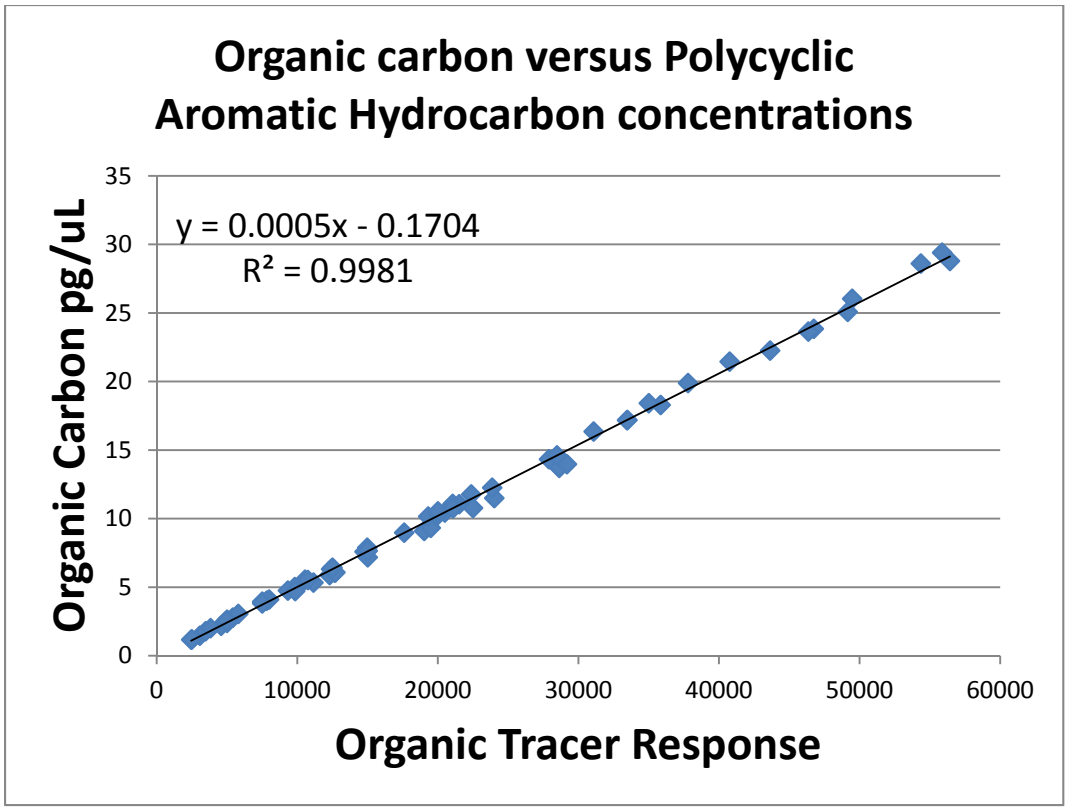

Figure 1. Organic carbon versus polycyclic aromatic hydrocarbon concentrations measured on quartz fiber filters collected at Moody Tower.

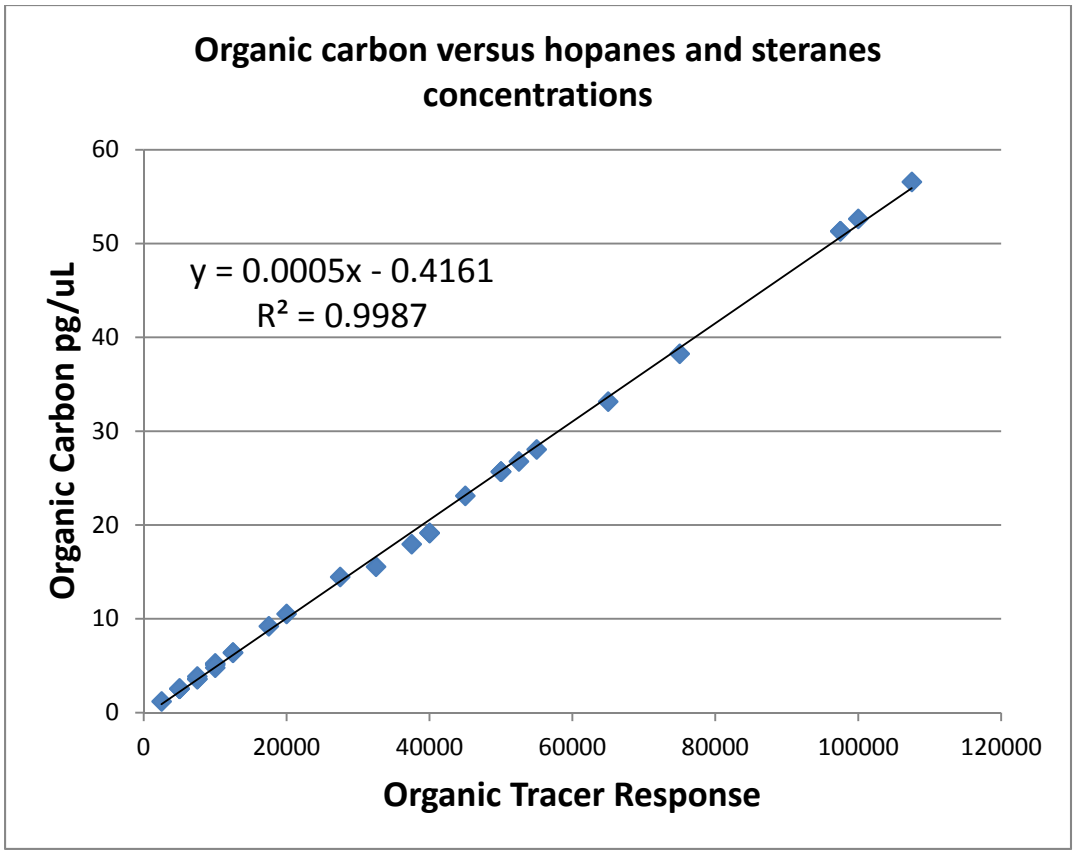

Figure 2. Organic carbon versus hopanes and steranes concentrations measured on quartz fiber filters collected at Moody Tower.

Baylor PIs, AQRP Project Manager, and TCEQ Project Liaison participated in a bimonthly conference call in later February. These conference calls are part of a series of interactions designed to help ensure the overall projects success. Baylor PIs provided an updated status report on all filters samples being analyzed by independent contract laboratories, specifically DRI and NOSAMS.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

In February, siloxanes were identified in routine laboratory blanks (frequency of blanks are described in the project's QAPP). In the laboratory, siloxanes are often associated with rubber analytical septum. Siloxanes can potential interfere with the analysis of organic tracers including hopanes. Quartz fiber filter extraction and analysis stopped as soon as the potential problem was identified. PIs and students associated with the project began a systematic investigation to help identify and eliminate the source of siloxanes. The source of siloxanes was identified and the problem was corrected. Specifically, the source of siloxanes was an analytical septum associated with one of the gas chromatographic mass spectrometer system solvent waste vials. The septum was discarded and the analytical systems have been cleaned. Contaminated areas were solvent

rinsed or replaced. New solvent waste vials were purchased and will be placed on a routine replacement schedule (regardless of the presents of siloxane contamination). Additional laboratory blanks are currently being extracted and analyzed to ensure the laboratory is clean. Samples analysis is anticipated to resume in the first weeks of March. Note: the level of siloxane contaminantion would have only potential impacted filter samples with low loadings. No low loaded samples were impacted by the siloxane contaminants. QAPPs are spectifically designed to help identify this type of laboratory issues. The routine analysis of laboratory blanks, as described in the project's approved QAPP, identified the issue and allowed the project's PIs and student to identify and correct it.

Reporting of inorganic ion and metal data has taken longer than the assured 10 days by DRI. Graduate students have been in contact with DRI and are awaiting response. PIs will check in with DRI in early March to verify the reporting and invoicing date for these contract analyses.

In late January and early February, Drs. Sheesley and Usenko participated in a number of AQRP discussions (conference calls and emails). Discussions focused on the identification of TCEQ accepted laboratories that could potentially be used for the analysis of metals (elemental tracers). DRI was previously identified for inorganic ion analysis for both samples from Conroe (shipped to DRI in December) and Moody Tower. As a result of these discussions, the project PIs went back and reviewed the Scope of Work and determined that DRI (utilizing X-ray fluorescence) was the best choice for metals analysis. This was based reviewing: (1) the contracted Scope of Work, (2) timeline for completing deliverables and (3) a consideration of intercomparison with previous TCEQ datasets. This decision was formally submitted to AQRP and TCEQ on 2/4/15.

Goals and Anticipated Issues for the Succeeding Reporting Period

Baylor PI, Dr. Sheesley is on a research sabbatical for Jan-May, 2015. In addition, Baylor PI, Dr. Usenko, has a reduction in teaching for the same period. This facilitates accomplishment of February goals and a successful completion of the project by June 30, 2015.

The major goals for March include:

1. Work with DRI to secure inorganic ion data from Moody Tower.
    a. Submit invoices to AQRP upon receiving inorganic ion datasets.
    b. Datasets will be made available to other AQRP DISCOVER-AQ project PIs

2. Work with DRI to secure metal data from Moody Tower.
    a. Submit invoices to AQRP upon receiving metals datasets.
    b. Datasets will be made available to other AQRP DISCOVER-AQ project PIs

3. Continue to analysis aliquots of quartz fiber filters designated for organic tracers analysis.
    a. We anticipate no issues and should make significant progress in completing this task.

4. Receive positive matrix factorization results from 14-024.
    a. We anticipate no issues and should complete this task in March. PIs have a good working relationship with PIs from (14-024).

5. Requested organic carbon and elemental carbon datasets for Houston during September 2013 from TCEQ.
    a. Clinton Drive: (waiting on DRI for organic carbon and elemental carbon) daily measurements for the duration of the project.
    b. Galveston: (waiting on DRI for organic carbon and elemental carbon) daily measurements for the duration of the project.
    c. Deer Park: black carbon and continuous organic carbon and elemental carbon for the duration of the project
    d. Aldine: organic carbon and elemental carbon every 6th day for the duration of the project

Detailed Analysis of the Progress of the Task Order to Date

List of project deliverables highlighted in the project work plan were subdivided into ten different but connected deliverables/tasks.

1. Daily organic carbon and elemental carbon measurements reported previously from PM samples collected at Moody Tower and Manvel Croix will be combined with daily measurements from Conroe and La Porte. ***Completed***
    a. Preliminary data has been shared with AQRP DISCOVER-AQ investigators.
    b. QAQC deliverables
        i. Duplicate analysis on 1 and 10
        ii. Field, Lab, Instrument, Filter blanks
        iii. Sugar spikes
        iv. Method detection limits determined
        v. Matrix spikes
        vi. Field samples completed

c. Comparison of the trends for 9/21-9/28 with the DISCOVER-AQ NASA's Jim Crawford (December 2014: at the American Geophysical Union conference).
    i. Poster titled "Spatial trends in surface-based carbonaceous aerosol, including organic, water-soluble and elemental carbon, during DISCOVER-AQ in Houston, TX"

2. Measure daily WSOC from PM samples collected from Moody Tower, Manvel Croix, and Conroe will be combined with the EPA WSOC La Porte dataset. ***Completed***
    a. Preliminary data has been shared with AQRP DISCOVER-AQ investigators
    b. QAQC deliverables
        i. Triplicate sample injections
        ii. Duplicate analysis on 1 and 10
        iii. Field, Lab, Instrument, Filter blanks
        iv. Sugar spikes
        v. Method detection limits determined
        vi. Calibration curves developed (10 pt)
        vii. Matrix spikes
        viii. Field samples completed
    c. Comparison of data and trends with the Environmental Protection Agency (December 2014: at the American Geophysical Union conference)
        i. Poster titled "Spatial trends in surface-based carbonaceous aerosol, including organic, water-soluble and elemental carbon, during DISCOVER-AQ in Houston, TX"

3. Measure inorganic ions (SO_4, Cl, NO_3, NH_4 and K) concentrations at Moody Tower. Moody Tower dataset will be combined and compared with the particle-into-liquid sampler dataset collected from Manvel Croix (14-009) and inorganic ion dataset from Conroe PM filters samples (14-024).
    a. Pulled AQS datesets and received particle-into-liquid sampler dataset (14-009)
        i. Used to estimate inorganic concentrations
        ii. Performed by PIs
    b. Developed a filter plan for Conroe
        i. Submitted filters from analysis by DRI (Dec 2014)
        ii. To be charged to (14-024) as part of their deliverables
        iii. Performed by PIs
    c. Developed a filter plan for Moody Tower
        i. Submitted filters from analysis by DRI (Feb 2015)
            1. Quote received: estimated cost $4750 (ten day turn-around)
        ii. Submit invoice by end of February or early March
        iii. Data distribution by end of March

4. Daily concentrations of ~51 elemental tracers will be reported for Teflon PM Filters collected at Moody Tower.
    a. DRI has been selected as an accredited TCEQ approved laboratory
    b. Submitted filters from analysis by DRI for analysis by X-ray fluorescence
        i. No filter plan needed
        ii. Submit second week of February to DRI
            1. Quote received: estimated cost $2342 (ten day turn-around)
        iii. Submit invoice by end of February or early March

5. A detailed characterization of relative high organic carbon (relative to elemental carbon) and ozone days (9/21-9/28) will be provided using organic tracers.
    a. Filter plan to be completed (Feb 20150
        i. Performed by graduate students under the supervision of PIs
        ii. Determined the organic carbon-to-tracer ratio complete (used to calculate the percent/mass of the filter needed for analysis
    b. QAQC deliverables
        i. Standard Reference Materials Analyzed
        ii. Method detection limits determined
        iii. Calibration curves developed
        iv. Matrix spikes
        v. Field Samples in progress
        vi. Performed by graduate students under the supervision of PIs
    c. Ozone data from TCEQ sites has been pulled and will be related to organic tracer results
        i. Performed by PIs

6. ^{14}C measurements for 4-24 hour samples.
    a. Filter plan complete in early February
    b. Four batches (9/21-9/28) submitted to National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS: Feb 2015)
        i. Timeline: 6-9 weeks for data and invoicing
        ii. Submit invoice by end of April early May
        iii. Data distribution by May

7. The organic tracers will be used to apportion the primary organic aerosol at each site by molecular marker chemical mass balance modeling (MM-CMB) using known profiles.
    a. Method validated by each student preforming the analysis
        i. Method presented at the December American Geophysical Union conference.

1. Poster titled “A Pressurized Liquid Extraction Technique for the Analysis of Pesticides, PCBs, PBDEs, OPEs, PAHs, Alkanes, Hopanes, and Steranes from Atmospheric Particulate Matter”.
2. Manuscript was subsequently submitted for publication to the *Chemosphere*. The manuscript titled “Pressurized Liquid Extraction Technique for the Analysis of Pesticides, PCBs, PBDEs, OPEs, PAHs, Alkanes, Hopanes, and Steranes in Atmospheric Particulate Matter”.

b. Development and purchase of consumable lists
    i. ongoing
c. First round of model optimization will be based off of preliminary data from deliverable/task 5
    i. ongoing
    ii. Performed by PIs

8. Fossil combustion-derived primary organic aerosol constrained by radiocarbon analysis
a. Get the positive matrix factorization results from 14-024 in March
    i. Performed by PIs
b. Combined positive matrix factorization with preliminary chemical mass balance modeled results to select contemporary end members
    i. Timeline: April
    ii. Performed by PIs
c. ^{14}C source apportionment utilizes end members for contemporary and fossil carbon. The fossil end member is known: -1000‰. The contemporary end member is dependent on contemporary changes in ^{14}C based off of the nuclear bomb spike. Therefore wood and leaves/grass have different ^{14}C, with wood having higher ^{14}C (+108‰) and annual biogenic C having lower ^{14}C (+28‰). Emissions inventories and preliminary source apportionment can help define the local biogenic vs wood smoke split to enable an appropriate contemporary end member choice (see Gustafsson et al, 2009). For Houston, preliminary chemical mass balance and positive matrix factorization results will be used to define biogenic vs wood smoke split in Mar, prior to receipt of the ^{14}C analysis.
    i. Timeline: April-May
    ii. Performed by PIs

9. Quantify changes in emission contributions for diesel- and gasoline-powered motor vehicles and biomass burning in the Houston metropolitan area since the 1997-98. Utilize chemical mass balance modeling to examine the efficacy of regulatory efforts and fleet modernization.
a. Timeline: May through June

b. Performed by PIs

10. Complement on-going PM characterization efforts at TCEQ monitoring sites by increasing the spatial extent and specificity of carbon apportionment.
   a. Completed the Baylor analysis for organic carbon and elemental carbon and black carbon.
      i. Performed by graduate students under the supervision of PIs.
   b. Received organic carbon and elemental carbon data from Jim Price (TCEQ)
      i. Deer Park: black carbon and continuous organic carbon and elemental carbon for the duration of the project
      ii. Clinton Drive: (waiting on DRI for organic carbon and elemental carbon) daily measurements for the duration of the project
      iii. Galveston: (waiting on DRI for organic carbon and elemental carbon) daily measurements for the duration of the project
      iv. Aldine: OCEC every 6th day for the duration of the project
   c. Intercomparison with Baylor's organic carbon and elemental carbon
      i. ongoing
      ii. Performed by graduate students under the supervision of PIs

---

Submitted to AQRP by: Rebecca J. Sheesley
Principal Investigator: Rebecca J. Sheesley