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	5/8/2015
REPORTING PERIOD	**From:** April 1, 2015 **To:** April 30, 2015	REPORT #	9

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 focus of April 2015 was to continue to characterize primary organic aerosols, specifically using a wide range of organic tracers and to begin analyzing the bulk carbon, inorganic ions, and metal datasets. Organic tracer analysis was expanded to La Porte as well as Moody Tower $PM_{2.5}$ quartz fiber filters. In addition to the characterization of primary organic aerosols at a specific site, PIs have also begun the process of site-to-site comparison. This will allow for both the spatial and temporal characterization of primary organic aerosols collected on quartz fiber filters during DISCOVER-AQ. The characterization of primary organic aerosols through direct bulk and specific organic tracer will be used to quantify the strength of aerosol formation and source contributions for emission sources including industrial, motor vehicle exhaust, biomass burning, and biogenic. Organic tracer data will be used to apportion the primary organic aerosol at each site by molecular marker chemical mass balance (CMB) modeling which is a deliverable of the project. Preliminary results were presented at the Texas Air Quality Workshop on April 10.

Analysis of quartz fiber filters for organic tracers. The analysis of $PM_{2.5}$ samples was begun for the ground-based sampling sites: Moody Tower, Manvel Croix, and La Porte. The developed method was applied to atmospheric particulate matter samples collected in the greater Houston, TX metropolitan area (Clark et. al. 2015). The manuscript describing this analytical method was accepted for publication in the journal *Chemosphere* (see citation below). Ambient concentrations of eight classes of organic tracers were determined in pg m^{-3} to ng m^{-3}. Atmospheric PM were characterized for organic tracers including: polycyclic aromatic hydrocarbons (PAHs), alkanes, hopanes, steranes, current and historic-use pesticides (CUPs and

HUPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and organophosphate esters (OPEs). CMB analysis will be conducted in May using spatial and temporal organic tracers datasets as specified in the work plan. Ambient concentrations of PAHs, levoglucosan, hopanes, steranes and alkanes will be used to characterize combustion sources, while CUPs, HUPs, PCBs, PBDEs and OPEs will be used to characterize non-combustion sources of anthropogenic organics.

Preliminary organic tracer data. Preliminary organic tracer data has been included for La Porte and Moody Tower in the figures below. The Moody Tower site (University of Houston; urban site) represents the urban Houston signal. La Porte represents a one of the more heavily industrial sectors on Houston and is roughly located south by southeast of the Houston Ship Channel. The La Porte ground-based sampling site was ~25 km east of Moody Tower. Total suspended particulate samples (24 hr) were collected at La Porte, while both total suspended particulate matter and fine particulate matter ($PM_{2,5}$) were collected at Moody Tower. Organic tracers measured at La Porte and Moody Tower include PAHs, Hopanes, Alkanes, OPEs, Pesticides, and PCBs. Data collected over the course of the DISCOVER-AQ sampling campaign allows for the temporal characterization of primary organic aerosols for a specific site and spatial comparison across sites (see Preliminary data below).

Radiocarbon (^{14}C) measurements. National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) is the contract laboratory responsible for all radiocarbon measurements associated with this project. 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 NOSAMs in February. In April, Baylor PIs have confirmed with NOSAMs that samples are being processed in a timely manner and that a majority of the samples are in the final stage of sample preparation and are ready for analysis. Radiocarbon measurements should be sent to Baylor in May, which should allow for the submission of the final invoice prior to the end of the project.

Bulk carbon, inorganic ions, and metals. In March, Baylor PIs received inorganic ion (Moody Tower and Conroe) and metal data (Moody Tower). This data combined with bulk carbon measurement are moving from data collection and generation to data analysis. Prior to data analysis, datasets received from DRI (inorganic ions and metal data) were and are currently being vetted for errors, incompletion, and/or invalid data. Afterwards, datasets will be used for aerosol characterization and analysis.

CMB. Preliminary CMB runs for Manvel Croix and Moody Tower data were done using the published 9/11-9/14 results (hopanes, PAHs and alkanes) plus levoglucosan. These preliminary results indicate low impact from biomass burning and 10-20% of ambient organic carbon contributed by primary motor vehicle emissions. Additional optimization is planned.

Preliminary data:

Preliminary organic tracer data which will be used to quantify the spatial and temporal contributions from specific emission sources (see example Figure 1 and 2). Additional figures from Moody Tower, Manvel Croix, and La Porte are available upon request.

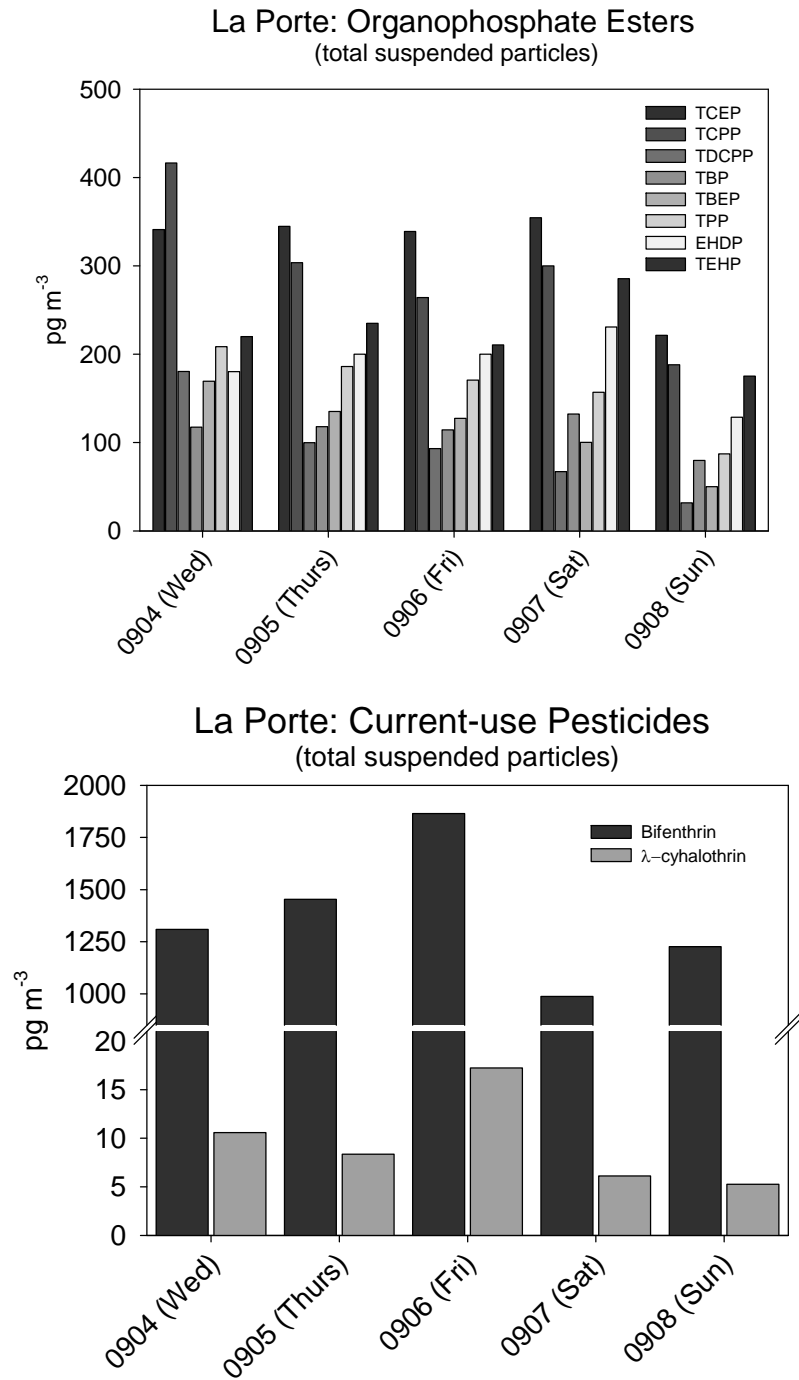Figure 1. Preliminary organic tracer data from La Porte TSP.

La Porte: Organophosphate Esters
(total suspended particles)

La Porte: Current-use Pesticides
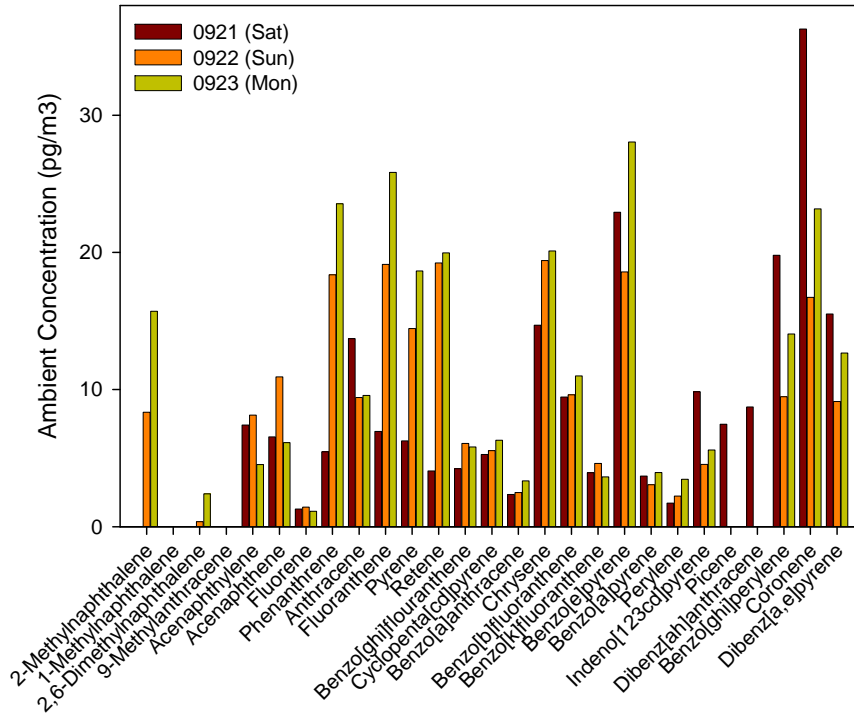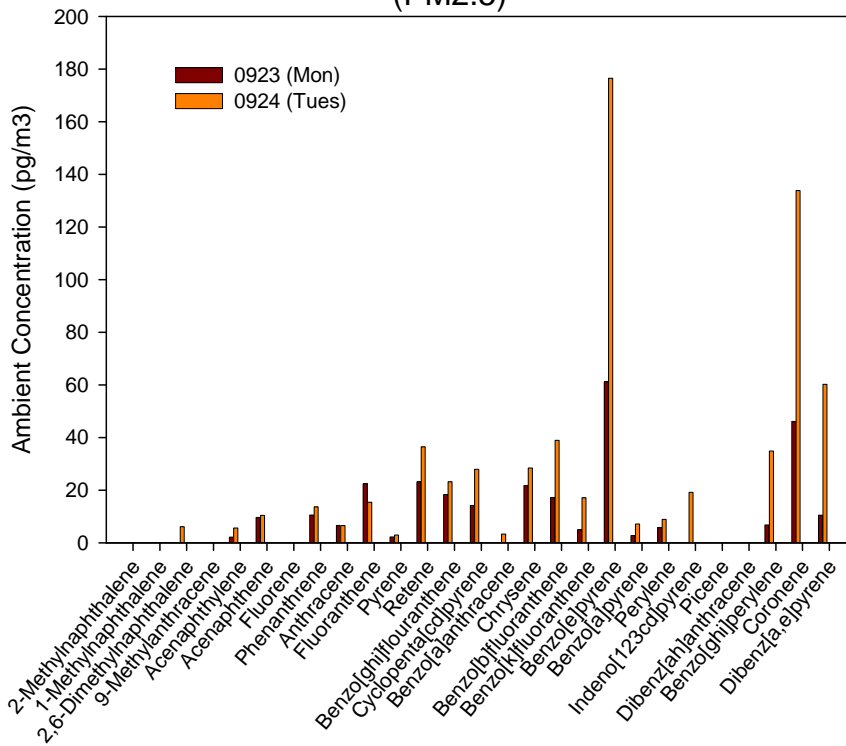(total suspended particles)

Figure 2. Preliminary PAH and Alkane data from Moody Tower (PM$_{2.5}$) 09/23-09/24 and La Porte (TSP) for quartz fiber filters collected from 09/21-09/23 2013.

Moody Tower: Alkanes (PM2.5)

La Porte: Alkanes (total suspended particles)
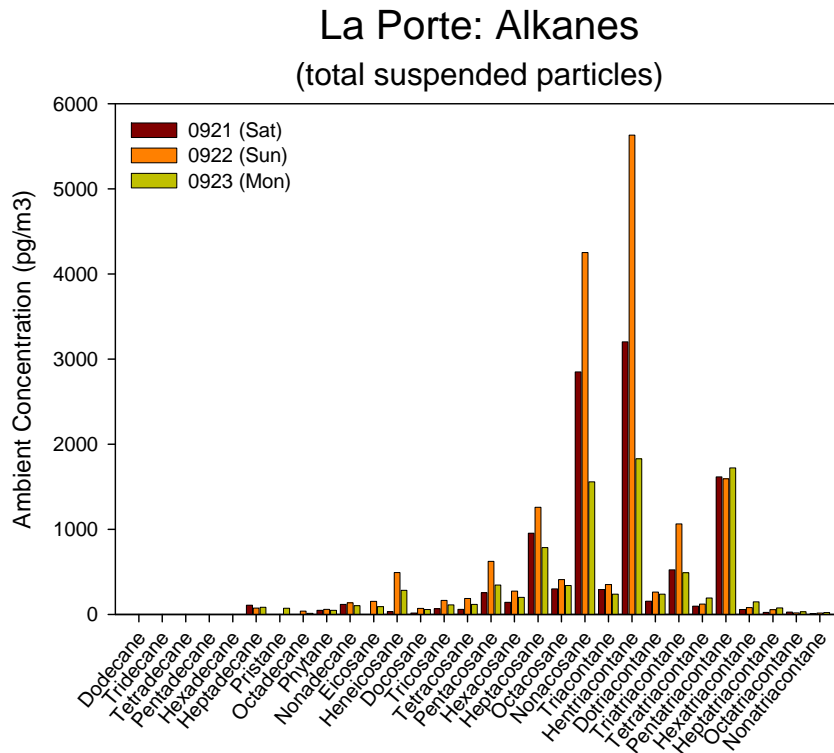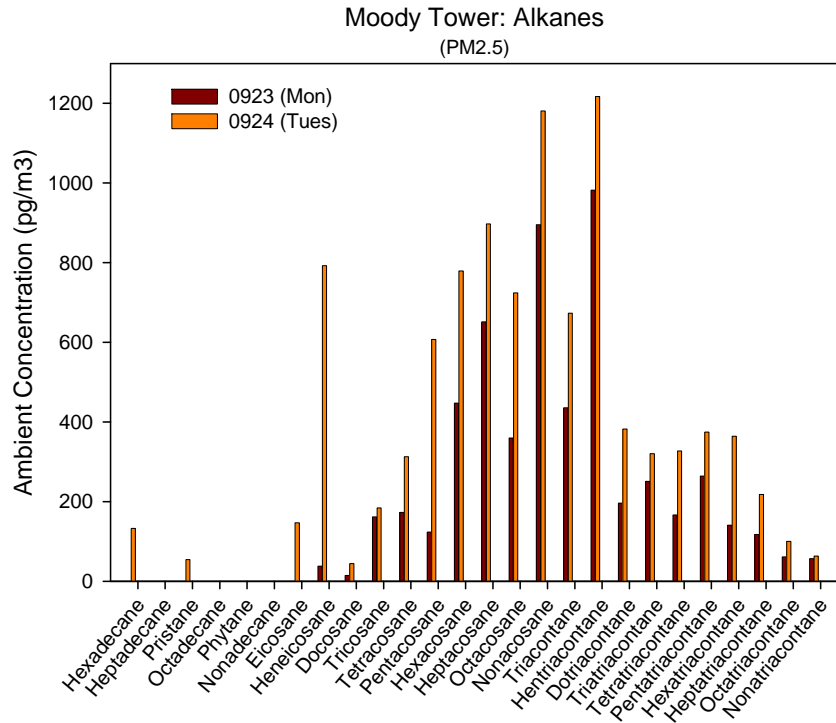
La Porte: PAHs
(total suspended particles)

Moody Tower: PAHs
(PM2.5)

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

Baylor PIs are working with NOSAMs to ensure that radiocarbon data is received in time to submit invoices prior to the projects end date. Currently, Baylor PIs do not anticipate any issues based on current NOSAMs estimated time of completion (2-3 weeks).   Radiocarbon fees are based, in part, on sample size. The final invoice is now estimated to exceed our budgeted funds for contract services. We will not have the value finalized until it is invoiced, but funds are present in supplies to cover the predicted overage in this final invoice (at most $4500). We have already been in contact with Maria Stanzione, AQRP Grant Manager, about a potential need for a transfer from supplies to contract services.

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 May goals and a successful completion of the project by June 30, 2015.

The major goals for May include:
1. Work with NOSAMs to secure radiocarbon data from all sites.
    a. NOSAMs anticipates completion in 2-3 weeks.
    b. Submit invoices to AQRP upon receiving radiocarbon datasets.
        i. We are working with our accounts to set up POs in advance.
    c. Datasets will be made available to other AQRP DISCOVER-AQ project PIs
        i. We have already communicated with

2. Continue to analyze aliquots of quartz fiber filters designated for organic tracers analysis.
    a. We anticipate no issues and are making progress in completing this task.

3. Begin chemical mass balance modeling with 9/21-9/28 organic tracer data from all sites.

4. Receive positive matrix factorization results from 14-024.
    a. We have been in contact with 14-024 and will exchange data when available.

5. Begin to prepare final report.
    a. Prepare first draft of final report section on OC, EC, WSOC and Inorganic ion dataes.

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). ***Completed***
    a. Pulled AQS datasets 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. Data received, processed and shared
        iii. To be charged to (14-024) as part of their deliverables
        iv. Performed by grad student and 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. Data received and processed
        iii. PO processed by Baylor and sent to DRI
        iv. Submit invoice by end of March or early April
        v. Data distribution by early April

4. Daily concentrations of ~51 elemental tracers will be reported for Teflon PM Filters collected at Moody Tower. ***Completed***
    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. Data received and processed
        iv. PO processed by Baylor and sent to DRI
        v. Submit invoice by end of March or early April

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 completed (Feb 2015)
        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 in May or early June

   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 under revision at *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. Planned for April

   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. 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

Citation:

Clark, A.E; Yoon, S; Sheesley, R.J., Usenko, S. (2015) Pressurized Liquid Extraction Technique for the Analysis of Pesticides, PCBs, PBDEs, OPFRs, 1 PAHs, Alkanes, Hopanes, and Steranes in Airborne Particulate Matter. *In Press Chemosphere*.

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