

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	6/8/2015
REPORTING PERIOD	From: May 1, 2015 To: May 31, 2015	REPORT #	10

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 May 2015 was to continue to characterize and apportion primary organic aerosols through organic tracers and radiocarbon. In May, Baylor PIs received radiocarbon data from NOSAMS (National Ocean Sciences Accelerator Mass Spectrometry). Radiocarbon data was received for all four sites (Moody Tower, Manvel Croix, Conroe, and La Porte). In this study, ¹⁴C abundance and organic tracer measurements are applied to apportion and characterize carbonaceous aerosols for the week of Sept 21-28, 2013 in Houston, TX. The large difference in end members between fossil and contemporary carbon allows precise quantification of fossil fuel combustion and biomass burning contribution using radiocarbon. Contemporary carbon is used to define all carbon (elemental and organic) that is derived from biomass combustion (wildfires, biofuels, agricultural fuel and residential firewood combustion) and biogenic emission (primary biogenic emissions and secondary organic aerosols produced from biogenic volatile organic carbon). The precision in the radiocarbon apportionment can be used to validate the accuracy of the fossil:contemporary split in chemical mass balance (CMB) modeling utilizing organic tracers, while the organic tracers can more specifically target contributions of biomass burning and motor vehicle exhaust.

For collaboration and data sharing, we have been working with ENVIRON and Hildebrandt Ruiz (14-024) to get them the finalized organic, elemental and water soluble carbon at all four Baylor sites for air quality modeling.

During May 2015, the PIs submitted a draft final report and a quarterly report in addition to the monthly technical and financial reports. Graduate student Stephanie Ortiz presented two posters at the regional meeting of the Society for Toxicology and Environmental Chemistry in Lafayette, LA.

Analysis of quartz fiber filters for organic tracers. The analysis of PM_{2.5} samples is progressing for the ground-based sampling sites: Moody Tower, Manvel Croix and Conroe. The organic tracer analysis for La Porte has been completed. Both fine particulate matter (PM_{2.5}) and total suspended particulate matter (TSP) have been analyzed for Jun 20-24, 2013. The samples for Jun 25-28 will be completed in the next two weeks. 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, levoglucosan, 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 June 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 (Figures 1-6). Preliminary organic tracer data has been included for Manvel Croix (PM_{2.5}) and La Porte (TSP). The Manvel Croix site represents the suburban 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. TSP samples (24 hr) were collected at La Porte, while both TSP and fine particulate matter (PM_{2.5}) were collected at Manvel Croix. Organic tracers measured at Manvel Croix and La Porte included 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). The abbreviations for the OPEs are as follows: *tris* (2-chloroethyl)phosphate (TCEP), tri-*n*-butyl phosphate (TBP), *tris*(3,5-dimethylphenyl)phosphate (T35DMPP), triphenyl phosphate (TPP), *tris* (1-chloro-2-propyl) phosphate (TCPP), *tris* (1,3-dichloro-2-propyl) phosphate (TDCPP), tri (butoxyethyl) phosphate (TBEP), *tris* (2-ethylhexyl) phosphate (TEHP), *tris* (2-isopropylphenyl) phosphate (T21PPP), tri-*o*-tolyl-phosphate (TOTP), and tri-*p*-tolyl-phosphate (TPTP), 2-ethylhexyl-di-phenylphosphate (EHDPP). The distribution of these OPEs will be used to understand spatial and temporal differences in atmospheric processing within Houston and to understand the transport mechanisms of OPEs on particulate matter.

Radiocarbon (^{14}C) measurements (Figure 7. National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS), the contract laboratory responsible for all radiocarbon measurements associated with this project, has returned all the radiocarbon data for the project in the last few days of May. The PIs are in the process of analyzing the data, including blank subtraction and choice of end member for radiocarbon source apportionment. The radiocarbon source apportionment will be presented as percent contribution of fossil and contemporary sources; it will also be presented as ambient concentrations for fossil carbon and contemporary carbon. However, the preliminary $\Delta^{14}\text{C}$ is included for all sites here for select samples (24h and daytime for each site).

Preliminary data:

Preliminary organic tracer data from select samples which will be used to quantify the spatial and temporal contributions from specific emission sources (see example Figures 1 through 6). See abbreviations of OPEs on page 2. Additional figures from Moody Tower, Manvel Croix, and La Porte are available upon request. Preliminary radiocarbon data which will be used in radiocarbon source apportionment is included in Figure 7.

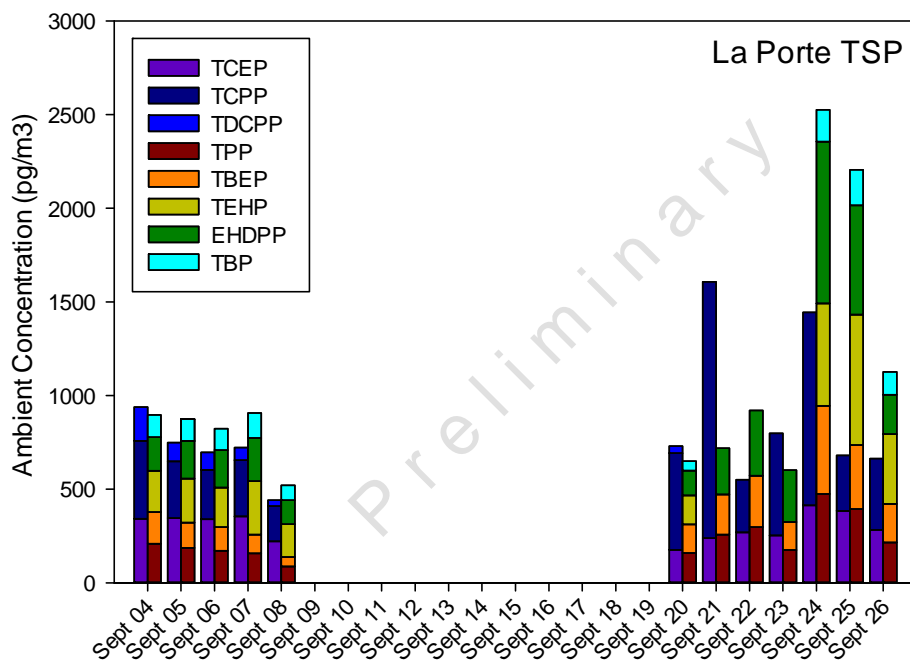


Figure 1. Full set of preliminary organophosphate esters data from La Porte (TSP).

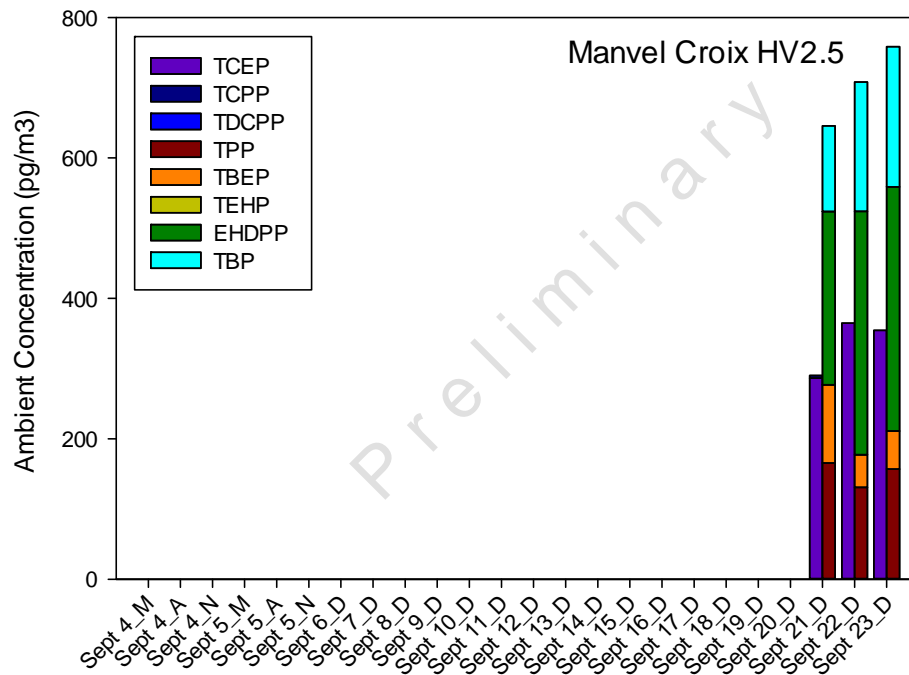


Figure 2. Preliminary organophosphate ester data from Manvel Croix (PM_{2.5}). “M” denotes morning sample collected from 6:30 to 10:00. “A” denotes afternoon sample collected from 10:00 to 20:00. “D” denotes day sample collected from 6:30 to 20:00. “N” denotes night samples collected from 20:00 to 6:30.

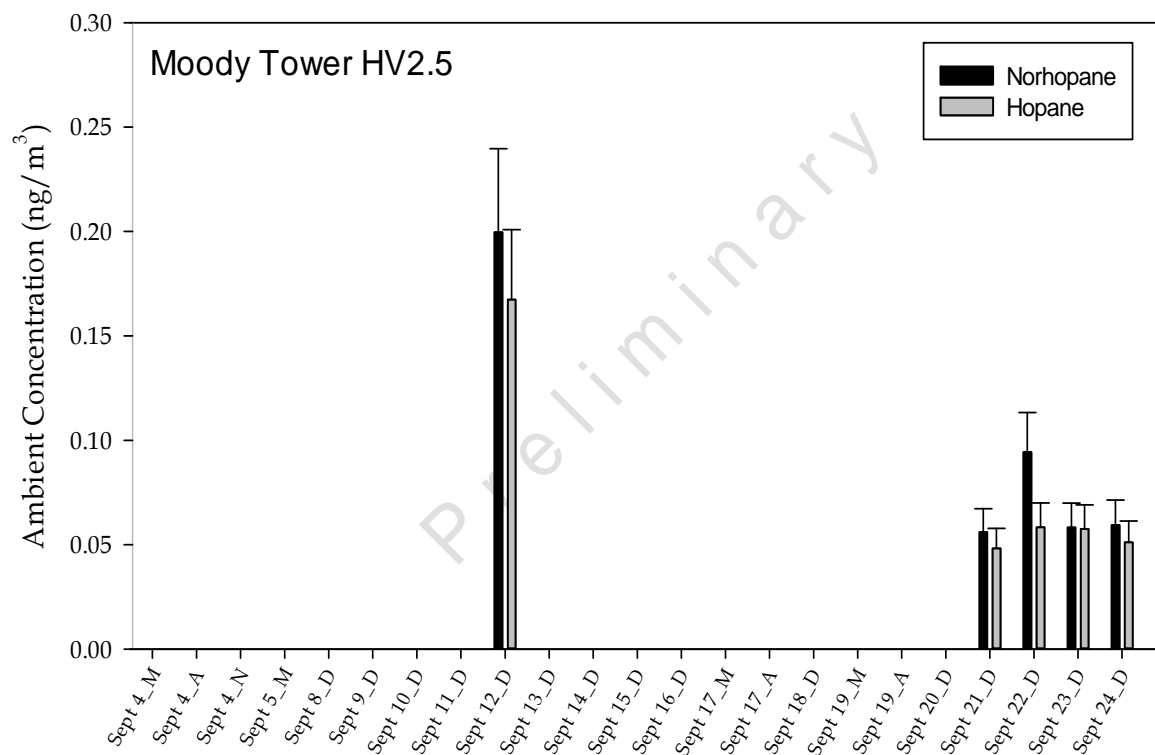


Figure 3. Preliminary hopane data from Moody Tower (PM_{2.5}) for quartz fiber filters. “M” denotes morning sample collected from 6:30 to 10:00. “A” denotes afternoon sample collected from 10:00 to 20:00. “D” denotes day sample collected from 6:30 to 20:00. “N” denotes night samples collected from 20:00 to 6:30. Error bars denote the uncertainty in (ng/m³).

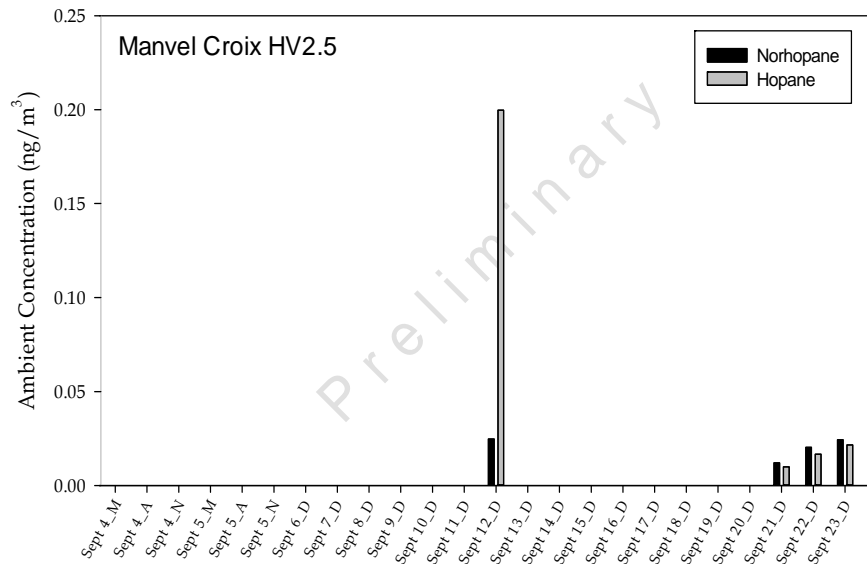


Figure 4. Preliminary hopane data from Manvel Croix (PM_{2.5}) for quartz fiber filters. “M” denotes morning sample collected from 6:30 to 10:00. “A” denotes afternoon sample collected from 10:00 to 20:00. “D” denotes day sample collected from 6:30 to 20:00. “N” denotes night samples collected from 20:00 to 6:30.

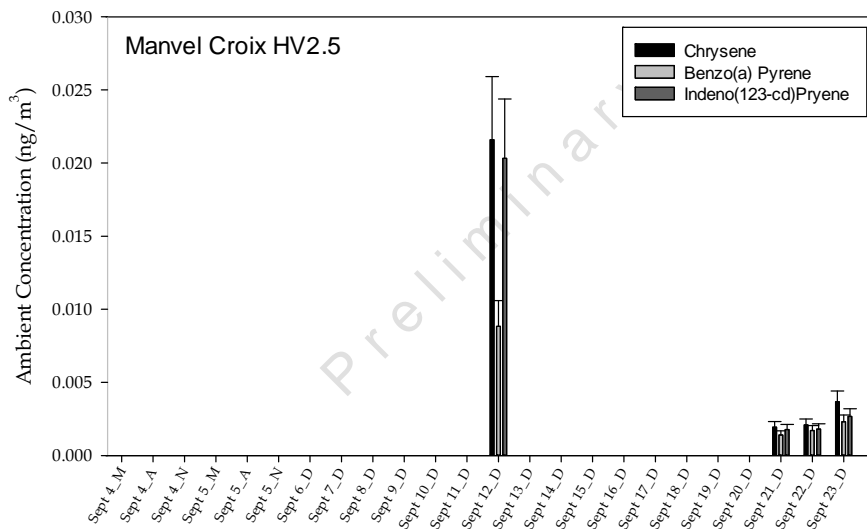


Figure 5. Preliminary data of select PAHs from Manvel Croix (PM_{2.5}) for quartz fiber filters. “M” denotes morning sample collected from 6:30 to 10:00. “A” denotes afternoon sample collected from 10:00 to 20:00. “D” denotes day sample collected from 6:30 to 20:00. “N” denotes night samples collected from 20:00 to 6:30.

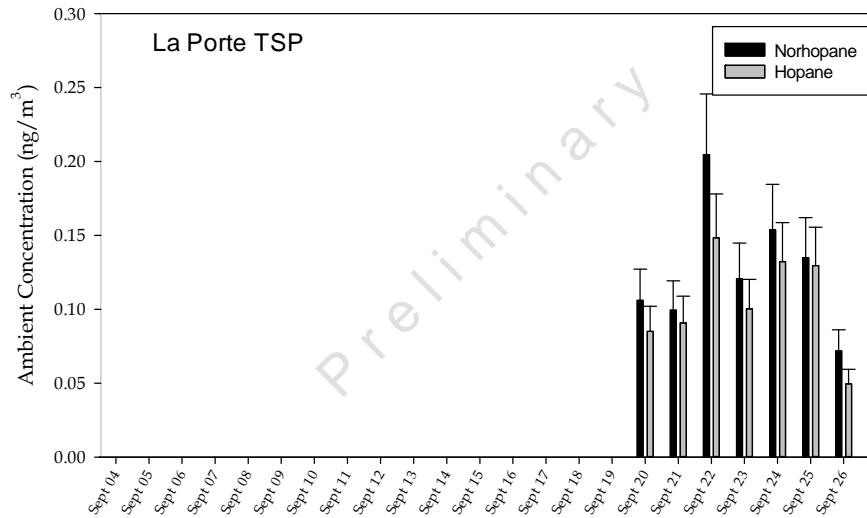


Figure 6. Full set of preliminary hopane data from La Porte (TSP) for quartz fiber filters. Error bars denote the uncertainty in (ng/m³).

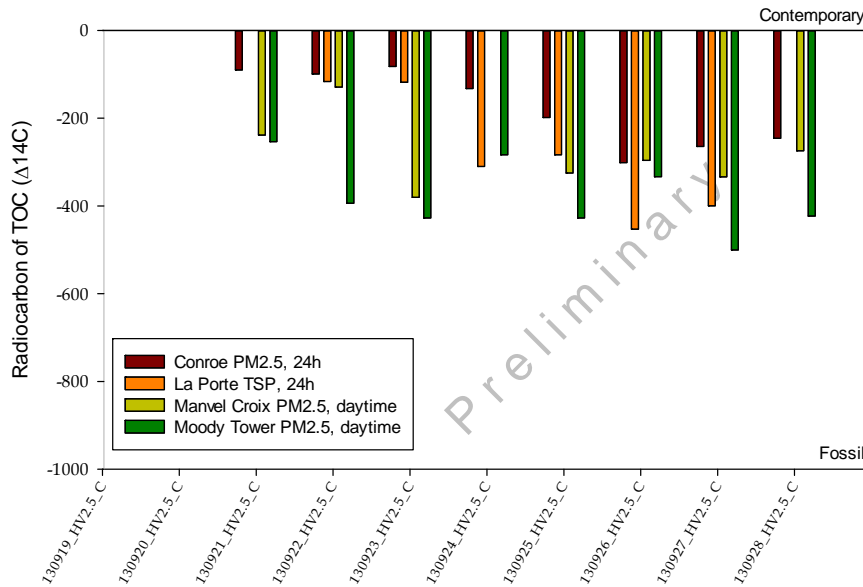


Figure 7. Preliminary radiocarbon of total organic carbon (TOC) at all four sites in Houston. This data has not yet been blank subtracted.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

Currently, Baylor PIs do not anticipate with issues for the next reporting period.

Goals and Anticipated Issues for the Succeeding Reporting Period

Baylor PI, Dr. Sheesley is on 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 June include:

1. Submit remaining invoices for NOSAMS radiocarbon data.
 - a. Baylor PIs have been working with our accounts to set up POs in advance.
 - b. Invoices were and are being submit to AQRP upon receiving radiocarbon datasets.
 - c. Datasets will be made available to other AQRP DISCOVER-AQ project PIs
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 (SO₄, Cl, NO₃, NH₄ 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. **Completed**
 - 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 June

- 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 performing 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 May
 - 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 ($+108\text{‰}$) and annual biogenic C having lower ^{14}C ($+28\text{‰}$). 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: May - June

- 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