

## AQRP Monthly Technical Report

<b>PROJECT TITLE</b>	Spatial and temporal resolution of primary and secondary particulate matter in Houston during DISCOVER-AQ	<b>PROJECT #</b>	14-029
<b>PROJECT PARTICIPANTS</b>	Rebecca J. Sheesley Sascha Usenko	<b>DATE SUBMITTED</b>	4/8/2015
<b>REPORTING PERIOD</b>	<b>From:</b> March 1, 2015 <b>To:</b> March 31, 2015	<b>REPORT #</b>	8

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 15<sup>th</sup> of the month following the reporting period shown above.

### Detailed Accomplishments by Task

The focus of March 2015 was the detailed organic analysis of quartz fiber filters collected during DISCOVER-AQ and preliminary data analysis of the inorganic and metals data reported back by the independent laboratory, DRI. This fits with the major goals that were set for March in the February monthly technical report, which included: working with DRI on the inorganic analysis for Moody Tower, working with DRI on the metals analysis from Moody Tower, continue organic tracer analysis, receive positive matrix factorization results from 14-024, requested Houston OCEC and BC data from TCEQ.

In Nov-December 2014 and Jan-Feb. 2015, filter plans were made and filter fractions were cut and submitted for inorganic ion analysis for Conroe and Moody Tower at DRI. All the inorganic ion data from DRI was received by Baylor Principal Investigators (PIs) in Mar. 2015. In the sections below data receipt and processing will be discussed by site.

*Inorganic ion data from Conroe.* DRI progress on analysis was monitored by Baylor grad students to insure timely response. Raw data was sent to Baylor grad students and PIs in Mar; this raw data was forwarded to PI Hildebrandt Ruiz (14-024). DRI was informed to send the invoice for this analysis to PI Hildebrandt Ruiz (14-024) at UT-Austin. Raw inorganic ion mass was converted to ambient concentrations by Baylor grad students and shared with PI Hildebrandt Ruiz (14-024). For this dataset the following anions and cations were reported: chloride, particulate nitrate, sulfate, ammonium, sodium and potassium. The two filter blanks had non-detects for all ions. Of the 25 samples (9/4/2013 – 9/28/2013), there were 25 detects for all except particulate nitrate which only had detects on 14 of the 25. This is in partial fulfillment of

the 14-029 deliverable of combining inorganic ion datasets for Conroe, Manvel Croix (PILS by Griffin at Rice) and Moody Tower (detailed below).

*Inorganic ion data from Moody Tower.* DRI progress on analysis was monitored by Baylor grad students to insure timely response. Raw data was sent to Baylor grad students and PIs in Mar. Raw inorganic ion mass was converted to ambient concentrations by Baylor grad students. An invoice was requested in Mar and a PO was just processed by Baylor University and returned to DRI. The final combined invoice for inorganics plus metals from DRI for Moody Tower was \$320 less than the original DRI quotes. For this dataset the following anions and cations were reported: chloride, particulate nitrate, sulfate, ammonium, sodium and potassium. The four filter blanks had non-detects for all ions. Of the 27 samples (9/4/2013 – 9/28/2013; note that these are 4-14 h samples and the sampler was down for 9/6-9/7), there was the following detects for each reported anion and cation: 16 detects for chloride, 23 detects for particulate nitrate, 27 detects for sulfate, 26 detects for ammonium, 26 detects for soluble sodium and 24 detects for soluble potassium. This is in partial fulfillment of the 14-029 deliverable of combining inorganic ion datasets for Conroe, Manvel Croix (PILS by Griffin at Rice) and Moody Tower.

*Metals data from Moody Tower.* DRI progress on analysis was monitored by Baylor grad students to insure timely response. Raw data was sent to Baylor grad students and PIs in Mar. Raw metal mass was converted to ambient concentrations by Baylor grad students. An invoice was requested in Mar and a PO was just processed by Baylor University and returned to DRI. The final combined invoice for inorganics plus metals from DRI for Moody Tower was \$320 less than the original DRI quotes. For this analysis, 25 samples (9/4/2013 – 9/28/2013), 24h each, were submitted to DRI. For this dataset the following 51 metals were reported, with the number of detects above filter blanks in parentheses: Sodium (15), Magnesium (5), Aluminum (8), Silicon (22), Phosphorous (0), Sulfur (25), Chlorine (25), Potassium (25), Calcium (25), Scandium (0), Titanium (17), Vanadium (18), Chromium (17), Manganese (14), Iron (25), Cobalt (0), Nickel (24), Copper (25), Zinc (25), Gallium (1), Arsenic (0), Selenium (9), Bromine (22), Rubidium (14), Strontium (17), Yttrium (3), Zirconium (21), Niobium (11), Molybdenum (14), Palladium (6), Silver (4), Cadmium (2), Indium (7), Tin (12), Antimony (8), Cesium (2), Barium (Ba), Lanthanum (9), Cerium (12), Samarium (5), Europium (15), Terbium (7), Hafnium (0), Tantalum (0), Wolfram (8), Iridium (0), Gold (2), Mercury (6), Thallium (2), Lead (21) and Uranium (4). The ambient concentrations of the detected metals will be reported as a deliverable of 14-029. In addition, select metals, when detected, will be used as molecular tracers in the chemical mass balance model in partial fulfillment of that deliverable. For example, Aluminum and silicon will be included as molecular tracers for crustal materials and Vanadium will be included as a molecular tracer for ship emissions and crude oil combustion.

*Analysis of quartz fiber filters for organic tracers.* Filter plans were made for all sites for the high volume PM<sub>2.5</sub> filters. The analysis of PM<sub>2.5</sub> samples was begun for Moody Tower, Manvel

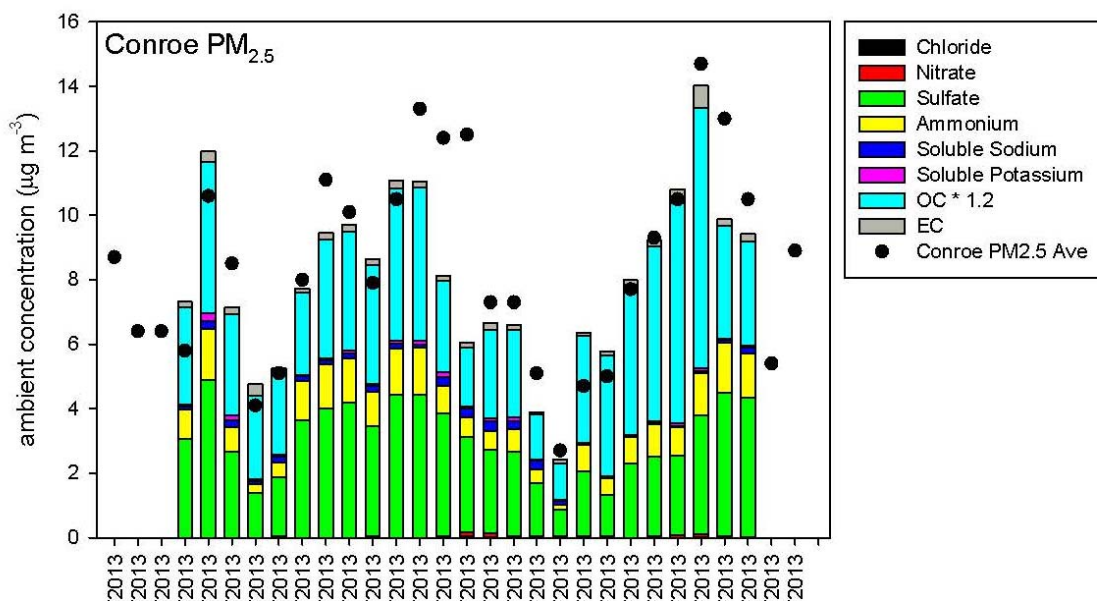
Croix, Conroe and La Porte. Preliminary analysis of three filters from each site revealed contamination in the procedure. Corrective actions were immediately taken. This contamination was confirmed to be bad solvents from the manufacturer which caused a bilayer in the final extract. Replacement solvents have been rush-ordered from a previously confirmed solvent manufacturer (JT Baker). Despite the contamination, preliminary ambient concentrations of organic tracers for PM<sub>2.5</sub> from Moody Tower were calculated for 9/11, 9/12 and 9/14/13. These will be added to previous ambient concentration data to improve filter plans for all sites. These results will be included in deliverable assessing changes in emission contributions of motor vehicles and biomass burning since the 1997-98 study.

*Collaboration and data sharing.* Ambient concentrations of inorganic ions were shared with 14-024 for Conroe. In addition, a request was made for positive matrix factorization results and an updated timeline for sharing of radiocarbon results was given.

**Preliminary data:**

Inorganic data shared with other DISCOVER-AQ AQRP collaborative project PIs (see example Figure 1). Additional figures of preliminary inorganic data and metals data from Moody Tower available upon request.

Figure 1. Preliminary inorganic data from Conroe PM<sub>2.5</sub>.



**Identify Problems or Issues Encountered and Proposed Solutions or Adjustments**

In March, a bilayer was identified in routine laboratory blanks and filter extracts from Manvel Croix, Conroe and La Porte (frequency of blanks are described in the project’s QAPP). In the

laboratory, bilayers are associated with solvents of limited miscibility. Bilayers can potentially interfere with the recovery of organic tracers. 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 the bilayer. The source of the bilayer was identified and the problem was corrected. Specifically, the source of bilayer was a bad batch of solvent. New solvent has been rush ordered. Additional laboratory blanks are currently being extracted and analyzed to ensure the laboratory is clean. Samples analysis is anticipated to resume this week. QAPPs are specifically designed to help identify this type of laboratory issues. The routine analysis of laboratory blanks and immediate analysis of sample extracts, 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 data has been reported. PIs submitted the PO request to Baylor University, a PO was issued on 4/8/15 and was received by DRI on the same day. In addition, the final invoice for inorganics ions and metals analysis from DRI for Moody Tower was \$320 under budget (based on previous DRI quotes). The discrepancy between the DRI quotes and final invoice will be addressed through a proposed budget change. The proposed budget changes would go through the AQRP approval process.

### **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 April include:

1. Work with NOSAMs to secure radiocarbon data from all sites.
  - a. Submit invoices to AQRP upon receiving inorganic ion datasets.
  - b. 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 should make significant progress in completing this task.
  
3. Conduct initial chemical mass balance modeling with 9/11-9/14 organic tracer data from Moody Tower.

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 6<sup>th</sup> 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<sub>4</sub>, Cl, NO<sub>3</sub>, NH<sub>4</sub> 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 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.

- 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.  $^{14}\text{C}$  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 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 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.  $^{14}\text{C}$  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  $^{14}\text{C}$  based off of the nuclear bomb spike. Therefore wood and leaves/grass have different  $^{14}\text{C}$ , with wood having higher  $^{14}\text{C}$  (+108‰) and annual biogenic C having lower  $^{14}\text{C}$  (+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  $^{14}\text{C}$  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 6<sup>th</sup> 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

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Submitted to AQRP by: Rebecca J. Sheesley  
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