Final Report

Project 14-029

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

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The University of Texas - Austin

Air Quality Research Program

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Spatial and temporal resolution of primary and secondary particulate matter in Houston during Deriving Information on Surface conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality (DISCOVER-AQ)

Executive Summary

This project builds on a previously-funded Air Quality Research Program (AQRP) project which characterized initial elemental carbon (EC) and organic carbon (OC) particulate matter (PM) during DISCOVER-AQ (Deriving Information on Surface conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality) Houston Texas 2013 (AQRP 12-032). The overall goals of the current project were to quantify the strength of PM formation and PM emission sources across the Houston metropolitan area. This was accomplished using samples collected over the DISCOVER-AQ sampling period at two primary sites in Houston: Moody Tower (downtown; urban) and Manvel Croix (southern; suburb); and two auxiliary sites: Conroe (far north; suburb) and La Porte (east; urban industrial). The detailed chemical characterization included elemental carbon (EC) and organic carbon (OC), radiocarbon, water soluable OC (WSOC), organic and elemental tracers and inorganic ions. A majority of the analysis focused on samples collected during 9/21/13-9/28/13 at the two primary and two auxiliary sites, which included a period of high ozone concentrations (9/25/13).

For the OC and EC, there were several trends for the September 2013 campaign. The maximum OC concentration for all four sites occurred between 9/24-9/26, which coincided with the peak ozone concentration on 9/25 in Houston. The maximum EC concentration at Conroe and La Porte was also 9/25-9/26. However, the maximum EC concentration at Moody Tower and Manvel Croix was 9/12-9/13. OC had higher correlation among sites than EC when comparing within the Baylor sites and between Baylor and TCEQ monitoring sites. For the remaining bulk species (WSOC and inorganic ions) there were the following trends during the September 2013 campaign. WSOC concentrations were strongly correlated with OC for all four sites with r^2 near 0.9. Conroe had the highest fraction of WSOC ranging from 40-80%. Manvel Croix and Moody Tower were lower with a range of 30-70%, while La Porte had the lowest fraction at 30-55%. Of Moody Tower, Manvel Croix, and Conroe, the highest consistent concentrations of sulfate were measured at Conroe for September 2013. Trace metals were measured at Moody Tower with 24 h samples. A few metals had consistent detectability, including Fe, which had a monthly average of 0.11 +/- 0.09 µg/m³, Zn, which had a monthly average of 0.11 +/- 0.14 µg/m³, and Na, which had a monthly average of 1.6 +/- 1.25 µg/m³. A number of non-combustion based organic tracers were detected in PM samples from all four sites including current-use pesticides, flame retardants, and plasticizers. For example, Permethrin, a commonly used mosquitocide, was detected in 100% of PM samples analyzed at all four sites (week of September 21-

28) with concentrations ranging from 0.025 to 60 ng/m^3. In addition four current-use pesticides, malathion, bifenthrin, λ-cyhalothrin, and chlorothalonil were frequently detected at all four sites. Organophosphate ester (OPEs), an emerging contaminant, were detected at all four sites. ΣOPEs atmospheric concentrations ranged from 160 pg/m^3 to 3400 pg/m^3.

Source apportionment of PM during the week of 9/21-9/28 was accomplished used radiocarbon combined with organic tracer-based chemical mass balance modeling (CMB). The radiocarbon apportionment effectively constrained the CMB results to provide estimation of both primary and secondary contributions to total organic carbon (TOC). The end results indicated that Moody Tower (a site indicative of urban Houston) had a consistent primary motor vehicle exhaust contribution (18-27%) and a fossil secondary organic aerosol (SOA) contribution that varied from 5-33% depending on atmospheric condition. Conroe (a site indicative of aged urban aerosol combined with biogenic contributions) had a lower contribution of motor vehicle exhaust (5-10%) and a similarly variable fraction of fossil SOA (4-25%). Manvel Croix (a site indicative of residential Houston area) had an interim motor vehicle contribution (9-15%) with a variable fossil SOA (5-30%). For contemporary OC, there was minimal wood smoke contribution during the examined week (0-9% at all sites) except one La Porte total suspended particulate matter (TSP) sample which had 16% wood smoke contribution. This indicates that wood smoke is an event-based contribution for summer in Houston at the urban sites. However, the biogenic SOA was a large contributor at all sites; this ranged from 40-75% at Moody Tower, 56-81% at Manvel Croix and 60-79% at Conroe. In summary, the motor vehicle contribution was consistent at each site during the analysis week, the biogenic SOA was consistently high, while the fossil SOA showed the most variability and dependence on atmospheric conditions.

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List of Abbreviations

AQRP	Air Quality Research Program
BC	Black carbon
CMB	Chemical mass balance
CPI	Carbon preference index
DISCOVER-AQ	Deriving Information on Surface conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality
DRI	Desert Research Institute
EC	Elemental carbon
EPA	Environmental Protection Agency
HV	High Volume
HV $PM_{2.5}$	High Volume $PM_{2.5}$
HV TSP	High Volume TSP
MV	Medium Volume
MV $PM_{2.5}$	Medium Volume $PM_{2.5}$ sampler
NASA	National Aeronautics and Space Administration
NOSAMS	National Ocean Sciences Accelerator Mass Spectrometry Facility
OC	Organic carbon
OPEs	Organophosphate ester
PAHs	Polycyclic aromatic hydrocarbons
$PM_{2.5}$	Fine particulate matter
PILS	Particle-into-liquid sampler
PIs	Primary investigators
POA	Primary organic aerosols
POPs	Persistent organic pollutants
QAQC	Quality assurance quality control
QFF	Quartz fiber filter
SEAC4RS	Studies of Emissions, Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys
SOA	Secondary organic aerosol
SRM	Standard Reference Material
TCEQ	Texas Commission of Environmental Quality
TOC	Total Organic Carbon
TOR	Thermal-optical reflectance
TOT	Thermal-optical transmission
TC	Total carbon (does not include inorganic carbon)
TSP	Total suspended particulate
WSOC	Water soluble OC

Introduction

Particulate matter (PM) concentrations can display large spatial and temporal heterogeneity across urban areas and have been linked to a number of air quality and atmospheric chemistry issues including human health. With dense industrial zones like the Houston Ship Channel and heavy traffic during peak rush hour periods, distinct regimes in urban PM are expected. Variable time resolution sampling at the four Houston sites was designed to capture these regimes. 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 strengths of DISCOVER-AQ (Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality), specifically the spatial and temporal sampling strategies (i.e. multiple ground-based sites sampled for approximately 25 days). These strategies allow for the examination of both regional and long-range transport as well as anthropogenic and biogenic influences on air quality. The primary investigators applied 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. These unique results are discussed in Deliverable 8. The primary outcome of the project was a spatially and temporally-resolved "map" of PM source contributions for the Houston metropolitan area with four anchor points upon which detailed DISCOVER-AQ flight, mobile unit, and ground studies can be overlaid. Maps of OC and EC are included in Deliverable 10, while source apportionment across Houston is discussed in Deliverables 7-9.

The DISCOVER-AQ Houston Texas 2013 sampling campaign served to examine near-surface air pollution and to help fill current knowledge gaps that exist between surface-based atmospheric measurements and satellite observations. This project provided a unique opportunity to combine an aircraft intensive sampling campaign over specific focus areas with concurrent surface-based measurements. Elemental carbon (EC) and organic carbon (OC) aerosols are strong contributors to particulate pollution and identification of their sources strengths are crucial for understanding PM in Houston. Primary and secondary sources of total organic carbon (TOC) are discussed in Deliverable 8. Expanding surface-based measurements to include carbonaceous aerosols strengthened the DISCOVER-AQ ground measurements and will continue to help improve our understanding of regional aerosol air pollution in Texas by improving our ability to interpret satellite observations through detailed particulate characterization. In addition, the archived filter samples from this intensive air quality study will continue to act as an invaluable source of research opportunities and collaborations.

Previous AQRP Funded Project (12-032)

Filter-Based Samplers Field Campaign. (PIs Sheesley and Usenko)

Fine particulate matter ($PM_{2.5}$) and total suspended particulate (TSP) matter were sampled concurrently with National Aeronautics and Space Administration's (NASA) P-3B and B200 aircraft at the Moody Tower and Manvel Croix surface sampling sites. In addition, filter-based samples were collected at two collaborative sites (La Porte; TSP and Conroe; $PM_{2.5}$). Characterization of $PM_{2.5}$ is relevant for understanding potential impacts of inhalable PM and improves understanding of source contributions to the regulated fraction of PM. High-volume (HV) TSP collection is relevant for characterization of coarse PM and for understanding fate and transport of organic contaminants. PM samples were collected on quartz fiber filters (QFF) and Teflon filters. These filter substrates were selected specifically to meet the needs of the project as well as a wide range of future research projects.
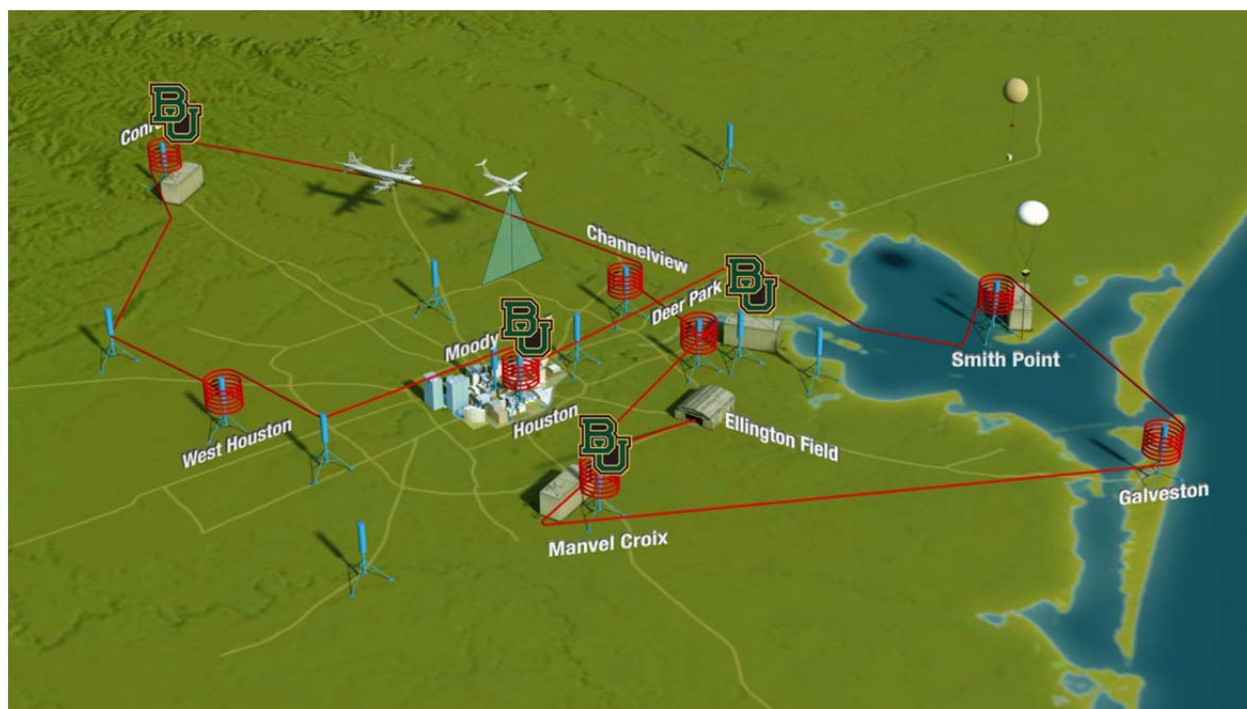
Figure 1. Graphic depiction of DISCOVER-AQ Houston 2013 observation strategy with Baylor University's four ground-based sites operated in conjunction with TCEQ and DISCOVER-AQ.

Samplers. Atmospheric $PM_{2.5}$ was collected on a 90 mm QFF using an URG Corporation medium-volume air samplers (MV $PM_{2.5}$; URG Corporation, Chapel Hill, NC) with a 2.5 µm cyclone inlet. At Moody Tower, sampling rates were 4.9 m³/hr for the QFF sampling train and 0.6 m³/hr for the Teflon membrane filter sampling train. At Manvel Croix, the sampling rate was 5.5 m³/hr for the single sampling train (QFF). The

airflow of the URG air sampler was controlled by a critical orifice and as a result only periodic calibration was needed (no change was recorded between the start and mid-point of the campaign). Atmospheric $PM_{2.5}$ was also collected on a 102 mm QFF using a Tisch high-volume air sampler (HV $PM_{2.5}$; Tisch Environmental Inc. Cleves, OH). Sampling rates were set at 12 m³/hr for Moody Tower and 13.5 m³/hr for Manvel Croix and Conroe. Filters used to capture atmospheric $PM_{2.5}$ were analyzed for OC and EC and the remainder (~97.5%) was archived for further characterization. TSP air samples were collected on a 20 X 25 cm QFF using a Tisch HV TSP. Sampling rates were 102 m³/hr for Manvel Croix, 68 and 70 m³/hr for Moody Tower and 60 m³/hr for La Porte; each sampler had been calibrated at these listed flow rates at the start of the campaign. The HV TSPs were calibrated using a standard orifice manometer calibration kit from Tisch once during the campaign. TSP filters were analyzed for OC and EC (see Analytical Method section) while the remainder (99.7%) were archived for further characterization. All filters are being stored at -10 °C in freezers that are routinely monitored.

Bulk carbon analysis. Filter samples from Moody Tower and Manvel Croix were analyzed for OC and EC by thermal-optical transmission (TOT) using a Sunset Labs carbon analyzer. An aliquot of each filter was removed using a filter punch (1.5 cm²).

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Research Objectives and Approach

DISCOVER-AQ represented a significant opportunity to examine the spatial and temporal heterogeneity in the Houston metropolitan area. The PIs of this proposal previously collected filter-based PM samples from four ground-based field sites during DISCOVER-AQ at Moody Tower, Manvel Croix, Conroe, and La Porte. The proposed project characterized PM through the quantification of EC, OC, water soluble OC (WSOC), inorganic ions, elemental tracers, organic tracers, and ^{14}C from select PM filters collected from four anchor sites. The number of samples to be analyzed for this project included approximately 60 EC/OC samples, 130 WSOC samples, 30 elemental tracers and inorganic samples and 50 ^{14}C and organic tracer samples. It is important to note that multiple analyses were performed on the same particulate filter whenever possible. The quantitative source apportionment efforts included radiocarbon source apportionment and chemical mass balance (CMB) modeling using organic and inorganic molecular markers (hopanes, steranes, polycyclic aromatic hydrocarbons (PAHs), alkanes, levoglucosan and elemental tracers). This current project enhanced our understanding of PM in the Houston metropolitan area and specifically addressed the AQRP 2014-2015 priority research area "Improving the understanding of ozone and PM formation, and quantifying the characteristics of emissions in Texas through analysis of data collected during NASA's DISCOVER-AQ and Studies of Emissions, Atmospheric

Composition, Clouds and Climate Coupling by Regional Surveys (SEAC4RS) campaigns".

Research Goal: *The overall goal was 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 required the in-depth characterization of PM and its sources in the Houston metropolitan area.

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-CMB 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 (SOA) (i.e., 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 project deliverables

Overview: highlighted in the project work plan were ten different but connected deliverables/tasks. Detailed results and discussion of the deliverables is included in later sections.

1. Organic Carbon and Elemental Carbon: Daily OC and EC measurements reported previously from PM samples collected at Moody Tower and Manvel Croix will be combined with daily measurements from Conroe and La Porte.
2. Water Soluble Organic Carbon: Measure daily WSOC concentrations from PM samples collected from Moody Tower, Manvel Croix, La Porte, and Conroe.
   > Note: In the original proposal, the PIs proposed using the EPA WSOC La Porte dataset. However, daily WSOC concentrations were measured on La Porte HV TSP samples associated with this project. The analysis was performed to allow for improved data turnover (i.e. sampling processing

time) as well as to improve the comparability among La Porte measurements (i.e. utilize the same filter for all bulk carbon, radiocarbon and organic analysis).

3. Inorganic Ions: 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 (PILS) dataset collected from Manvel Croix (14-009) and inorganic ion dataset from Conroe PM filters samples (14-024).

4. Elemental Tracers: Daily concentrations of ~51 elemental tracers will be reported for Teflon PM Filters collected at Moody Tower.

5. Organic Tracers: A detailed characterization of relative high OC (relative to EC) and ozone days (9/21-9/28) will be provided using organic tracers.

6. Radiocarbon Measurements: Radiocarbon measurements were made on samples collected from all four ground-based sites during 9/21-9/28. This included daily (24-hour) and high resolution samples (4-12 time average sampling periods).

7. Chemical Mass Balance Modeling: Organic tracers and select elemental tracers will be used to apportion the primary organic aerosol (POA) at each site by molecular marker chemical CMB using known profiles.

8. Fossil combustion-derived POA constrained by radiocarbon analysis

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 CMB modeling to examine the efficacy of regulatory efforts and fleet modernization.

10. Complement on-going PM characterization efforts at TCEQ monitoring sites by increasing the spatial extent and specificity of carbon apportionment.

Analytical Methods

Details of the analytical methods and procedures including quality control and quality assurance (QAQC) were originally described in the project's Quality Assurance Project Plan. Details of the quality control and quality assurance are included in the method descriptions below. Chain of custody forms were only used when the analysis was completed outside of Baylor facilities. Details of sample collection, including field blanks, was reported for AQRP project number 12-032.

Bulk carbon analysis. The analysis of OC and EC has been described previously in detail [1]. Briefly, all filter samples (TSP and PM$_{2.5}$) were analyzed for OC and EC using a Sunset Labs carbon analyzer. Thermograms were visually monitored for inorganic carbonate carbon peaks, and an acidification study was performed to verify the absence of carbonate in the study samples. The following QAQC deliverables were completed for the OC and EC analysis: duplicate analysis on every tenth sample, collection and

analysis of field and laboratory blank filter, site and sampler-based blank subtraction, calibration check with spikes of glucose solution (detailed below). Preliminary OC and EC for Moody Tower and Manvel Croix were reported in a previously funded AQRP project (12-032), while the finalized OC and EC for all four sites are included in the current report.

All filter samples (TSP, MV $PM_{2.5}$ and HV $PM_{2.5}$) were analyzed for OC and EC concentrations using a Sunset Lab carbon analyzer utilizing the TOT carbon analysis method[2]. Punches of filter (1.5 cm^2) were used for OC and EC analysis, accounting for 2.64% of HV $PM_{2.5}$ filters, 3.14% of MV $PM_{2.5}$ and 0.38% of TSP filters. An instrument blank was run prior to daily analysis and showed no instrument-associated OC. Sucrose standard recoveries and triplicates were run every 10 samples. Sucrose standard recovery efficiency was tested by placing 10 µl of 56.7 µg C/µl sucrose standard on a 1.5 cm^2 punch of a 99 mm QFF filter. An average of 56.39 µg C/µl was obtained through the analysis, with a standard deviation of 8.38 µg C/µl. Recovery efficiency was 97.89%. Triplicate runs ranged in relative standard deviation from 0.84-3.34%. Blank filter concentrations for HV $PM_{2.5}$ filters for OC and EC averaged 0.68 and 5.9 x 10^{-6} µg/cm^2, respectively, contributing to an average of 8.66% for OC and 0.60% for EC of the final ambient concentrations. MV $PM_{2.5}$ blank filter concentrations for OC and EC averaged 1.47 and 0.06 µg/cm^2, respectively, contributing to an average blank fraction 24.93% of for OC and 9.75% for EC. TSP blank filters for OC and EC averaged 0.49 and 0.00 µg/cm^2, respectively, with OC and EC fraction contributions averaging 2.96% and 3.93%, respectively.

The Baylor EC, OC and total carbon (TC) analysis was accomplished using the TOT carbon analysis method [1]. The Harris County Interagency Monitoring of PROtected Visual Environment (IMPROVE) and Speciation Trends Network network results of EC, OC, and TC were analyzed by thermal-optical reflectance (TOR) by Desert Research Institute (DRI). There are known differences between these methods [1,3], and studies have recommended harmonization algorithms [4].

To facilitate inter-comparison between Baylor carbon measurements and TCEQ/EPA measurements, the PIs utilized existing TOT and TOR datasets commissioned by TCEQ. Galveston and Clinton Ave (Houston) monitoring sites have QFF samples upon which TCEQ has commissioned both TOT and TOR carbon analysis (performed by DRI). TCEQ has shared the Clinton Ave 2013 datasets for these sites with the PIs (n=134). The EC TOT vs. EC TOR regression for 2013 was [TOR]=1.34*[TOT]-0.0079 with an R^2 =0.94; this was sustained through Sept. 2013 with [TOR]=1.35*[TOT]-0.016 and R^2 =0.996 (Figure 8 and 10). The OC TOT vs OC TOR regression for 2013 was [TOR]=0.91[TOT]+0.0067 with an R^2=0.997. The 2013 linear regressions were used to transform all OC and EC at Moody Tower, Manvel Croix, Conroe and La Porte to enable a report of TOT and TOR method values for each site.

Water Soluble Organic Carbon. Filter area required for WSOC analysis was based on mass of OC from each filter. WSOC analysis required aliquots of 60 μg of OC, or 4.75 cm^2 from the HV $PM_{2.5}$ filters (Moody Tower, Manvel Croix and Conroe) and 2.65 cm^2 from the TSP filters (La Porte). Samples from Moody Tower, Manvel Croix and Conroe had field blanks for analysis. La Porte utilized a TSP QFF lab blank for analysis. Sample aliquots were 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, were pre-cleaned by triple rinsing with deionized water. The extracts were centrifuged for 10 minutes and decanted. The extracts were then 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 was added to remove inorganic carbon from the solution. Samples were processed as batches of 20 with 15 samples and 5 QAQC filters (including filter blank, lab blank, spike and recovery). Sample batches were analyzed using a Shimadzu Total Organic Carbon Analyzer to measure dissolved organic carbon (dynamic linear range: 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 was 0.5 mg L^{-1} [5] (i.e. the lowest point in the calibration curve). Samples were analyzed three times at 100 μl each. The average concentrations of the three injections were reported. Sucrose spike and recovery experiments provided an average recovery rate of 101.9%. The calibration curve ranged from 0.5 to 5.00 mg/L, with average recovery percentage of 102.5%. Water blanks averaged 0.06 +/- 0.05 mg/L. Average instrument blank values were calculated as 0.07 mg/L. $HV_{2.5}$ QFF filters used field blanks from the campaign and TSP QFF samples used a lab blank, both prepared and stored in the lab. There was not a significant difference between field and laboratory blanks. Filter Blank fraction contributions to filter concentrations of the filter sample concentration was 20.38% for $HV_{2.5}$ and 13.40% for TSP. Each sample includes a blank correction, calculated batch-wise, as an average of field and lab blank concentrations subtracted from the instrument concentration.

Inorganic Ions. Filter-based measurements were conducted to obtain inorganic ion (SO4, Cl, NO3, NH4 and K) mass concentrations for Moody Tower $PM_{2.5}$. Samples were processed by the certified contract laboratory Desert Research Institute (DRI) using ion chromatography and included a chain of custody. Filter plans describe the plan for specific filters and analysis. Filter plans were designed for HV $PM_{2.5}$ utilizing sulfate concentrations from TCEQ monitoring in Houston during September 2013. Sample aliquots sent to DRI were calculated based on HV $PM_{2.5}$ air volume combined with Houston ambient concentrations to obtain a minimum concentration of 1.5 MDL of the instrument at DRI. Percentage of filter sent for analysis was 3.44 cm^2, averaging 6.06% of the total filter area. Blank HV $PM_{2.5}$ QFF filters were also analyzed for inorganic

analysis with measured concentration of 0.00 µg /sample, contributing negligible amounts of inorganics to the concentrations on the filters.

Elemental Tracers. Teflon filters (MV PM2.5) from Moody Tower were analyzed for 51 elemental tracers. Filter-based elemental tracer measurements were conducted by the certified contract laboratory DRI and included submission of a chain of custody. X-Ray Fluorescence analysis utilized the entire filter[6]. Field blanks and laboratory blanks were submitted for blank subtraction and calibration of X-Ray Fluorescence system. Elemental tracers were measured using X-Ray Fluorescence and included Sodium, Magnesium, Aluminum, Silicon, Phosphorous, Sulfur, Chlorine, Potassium, Calcium, Scandium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Gallium, Arsenic, Selenium, Bromine, Rubidium, Strontium, Yttrium, Zirconium, Niobium, Molybdenum, Palladium, Silver, Cadmium, Indium, Tin, Antimony, Cesium, Barium, Lanthanum, Cerium, Samarium, Europium, Terbium, Hafnium, Tantalum, Wolfram, Iridium, Gold, Mercury, Thallium, Lead, and Uranium. It is performed on a PANalytical Epsilon 5, EDXRF analyzer using a side‑window, liquid‑cooled, 100 KeV, 24 milliamp dual anode (Sc/W) x‑ray tube and secondary targets.

Organic Tracers. Organic tracer analysis follows QAQC criteria described in the project's Quality Assurance Project Plan. Filter plans were created for organic tracer analysis at Moody Tower, Manvel Croix, Conroe, and La Porte. Filter plans were finalized using the relationship between bulk OC and organic tracer concentrations. Organic tracer concentrations were first measured on a subset of representative samples (9/4-6/13 and 9/11-14/13). These two datasets were used to explore the relationship between bulk OC and organic tracer concentrations. These tracer-to-OC relationships were correlated with an R squared of greater than 0.97 by particle size ($PM_{2.5}$ and TSP). Baylor PIs used these relationships to help determine the mass of OC needed to measure organic tracers, while consuming the least amount of filter. For TSP samples, an area of the filter corresponding to approximately 1300 µg of OC was utilized per extraction while for $PM_{2.5}$ samples, filter areas corresponding to approximately 400 µg of OC was utilized. The mass of OC 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. The percentage dedicated for organic tracer analysis was 10 to 60% of the QFF. This initial organic tracer effort enabled reduction of the number of non-detectable results for organic tracer analysis while allowing preservation of filter for future analysis for the 9/21-28/13 samples.

Baylor PIs and students cut and analyzed aliquots of ~50 plus QFF samples and blanks for organic tracers including TSP, MV $PM_{2.5}$ and HV $PM_{2.5}$ filter samples from the week of 9/21-9/28-13 (24h and high time resolution). The analysis of organic tracers has been previously described by Clark et al [7]. Briefly, aliquots of each QFF were spiked

with isotopically labeled surrogate standards, including surrogate standards for polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), pesticides, Organophosphate ester (OPEs), and PAHs, and allowed to rest for one hour prior to extraction. Surrogate standards were used to account for losses during sample preparation steps. Organic tracers were extracted using pressurized liquid extraction with methylene chloride:acetone (2:1 v/v) at 100 °C with three (5 min) static cycles, flush volume of 80%, and a 100 s N_2 purge. The extraction was performed using a Dionex/Thermo Accelerated Solvent Extractor (ASE) 350 system. Extracts were concentrated via a gentle stream of N_2 and spiked with isotopically labeled internal standards with a final volume of ~250 μl. Extracts were analyzed via gas chromatography-mass spectrometry (Agilent 7890 GC coupled to an Agilent 5975 quadrupole MS, utilizing both electron impact and negative chemical ionization). Organic tracers used a 6 to 9 point calibration curve depending on the specific chemical. Calibration solutions were analyzed separately, prior to sample analysis and or after instrument maintenance. The dynamic linear range was determined for each target analyte using r^2 values of 0.99 or greater.

Detailed organic tracer characterization included measurement of organic tracers for fossil fuel combustion (hopanes and PAHs), biomass burning (levoglucosan and PAHs), vegetative detritus/primary biogenic (alkanes) and non-combustion urban development (PBDEs) [8-10]. The organic tracers were used to apportion the POA at each site by molecular marker chemical mass balance modeling using known profiles [8, 11] with the fossil combustion-derived POA constrained by radiocarbon analysis [12]. Aliquots (10 to 25 μl) of the final extract were derivatized and analyzed for levoglucosan. Levoglucosan was analyzed using gas chromatography-mass spectrometry with electron impact ionization.

Samples were analyzed in batches of 4 to 8 samples, and at least 1 lab blank, 1 field blank or Standard Reference Material (SRM). A laboratory or field blank was also extracted and analyzed every third sample. Lab blanks were used to verify limited contamination in the laboratory sample preparation and analysis protocols, while field blanks gave the total contamination for filters for both field and laboratory preparations. Field blanks comprised 35% of all blanks extracted and were used for blank corrections. For both lab and field blanks, approximately 25% of the total filter area was used for TSP filters and approximately 50% of the filters were used for $PM_{2.5}$. For PCBs, PBDEs, OPEs, hopanes, steranes, and pesticides, blank values were negligible. For PAHs and alkanes, blank corrections were achieved using a field blank of the same sample site, size fraction and sampler type, when available (Moody Tower TSP were corrected with a Moody Tower TSP field blank, Moody Tower HV2.5 were corrected with a HV2.5 field blank, etc.), except where field blanks were not available, in which case lab blanks from the associated sample batch were utilized. Approximately every fifth sample, a SRM was also extracted and analyzed. Two SRMs, prepared by the National Institute of Standards

and Technology (NIST), were used in this study to validate the method: SRM 1649b (Urban Dust) and SRM 2585 (House Dust). These two SRMs include most of our analytes; PCBs, Pesticides, Alkanes, and PAHs were present in SRM 1649b while PBDEs were measured in SRM 2585. For PBDEs, PCBs, Pesticides, PAHs, and alkanes, average percent error was 26%, 19%, 24%, 31%, and 31%, respectively, when compared to reported certified, reference, and informational values given in the certificates of analysis.

The QAQC deliverables for the organic tracer analysis included: analysis of standard reference materials for a minimum of every 20th sample, analysis of filter blanks spiked with compounds of interest for a minimum of every 20th sample, determination of method detection limits, development of five point calibration curves, analysis of calibration curve check standards for each batch of organic tracers analyzed, analysis of field, laboratory and instrument blanks, field blank subtraction of all reported organic tracer concentrations.

Radiocarbon Analysis of Total Organic Carbon. Filter preparation and carbon isolation was accomplished by the PIs prior to radiocarbon analysis by accelerator mass spectrometry at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS). Aliquots of selected filters were cut to obtain at least 60 μg of TOC per sample, based on the OC and EC analysis; this is the minimum mass suggested by NOSAMS. Samples collected the week of 9/21-9/28/13 at Moody Tower, Manvel Croix, Conroe and La Porte were selected for analysis. The aliquots were placed in an ashed glass petri dish (glass was cleaned via heat in a muffle oven to 500 °C), acidified in a dessicator over HCl and sealed in the glass petri dish by wrapping completely in ashed aluminum foil. These prepared samples were then shipped to NOSAMS, frozen, overnight. Radiocarbon analysis was accomplished at NOSAMS by measuring the ratio of ^{14}C to ^{12}C 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 $^{14}C/^{12}C$ ratio of $1.176 \pm 0.010 \times 10^{-12}$ [13, 14].   These three ratios are combined in the following expression to calculate the raw F_{modern} which is reported by NOSAMS: $F_{modern}= (^{14}C_{sample}/^{12}C_{sample} - ^{14}C_{blank}/^{12}C_{blank})/(^{14}C_{modern\ reference\ standard}/^{12}C_{modern\ reference\ standard} - ^{14}C_{blank}/^{12}C_{blank})$.

The post processing of raw F_{modern} data included a transformation to $\Delta^{14}C$, blank subtraction and then apportionment between fossil and contemporary carbon sources. The basis for ^{14}C-based source apportionment is that modern biomass fuel/biogenic material is in radioactive equilibrium with the atmosphere while a geologically-aged fossil fuel is depleted in ^{14}C. The units for $\Delta^{14}C$ are parts per mille using established conventions [15]. Specifically, the $\Delta^{14}C_{fossil}$ component of $\Delta^{14}C_{TC}$ has a value of -1000‰ while $\Delta^{14}C_{biomass}$ can be between +28.1‰ and +107.5‰ [16]. The +28.1‰ corresponds to contemporary biomass sources including primary and secondary biogenic emissions,

meat cooking and combustion of grass, prunings and agricultural waste. The +107.5‰ corresponds to wood smoke. For TOC, both the fossil and contemporary fractions can also include SOA.

The obtained $\Delta^{14}C$ TC value reflects the following assumption: $\Delta^{14}C$ TOC = $(\Delta^{14}C_{biomass})(f_{biomass}) + (\Delta^{14}C_{fossil})(1-f_{biomass})$. Solving this equation for $f_{biomass}$, the fraction of TOC coming from the combined biomass burning/biogenic sources is obtained. The contribution from fossil fuel combustion (f_{fossil}) is $(1- f_{biomass})$ [17].

Results and Discussion

Results will be discussed in terms of the list of the project's ten deliverables. All project related data are available through the AQRP data site. Specific analysis and the samples analyzed are described in the Analytical Methods section. Averaged values are presented with standard deviations. Audits were performed at each step of analysis and for all datasets by PIs as part of their responsibilities to the project and student mentorship.

Deliverable 1: Organic Carbon and Elemental Carbon

Daily organic carbon and elemental carbon measurements reported previously from PM samples collected at Moody Tower and Manvel Croix.

Overview: Complete OC and EC datasets were created for $PM_{2.5}$ and TSP at Moody Tower, Manvel Croix, Conroe and La Porte (Figures 2-7). These datasets were the foundation for further analysis at Baylor's four sites. The OC and EC trends across Houston and the mass loading of OC on the filters enabled decisions about date choice for detailed analysis and creation of filter plans for WSOC, inorganic ion analysis, radiocarbon and detailed organic characterization of organic tracers by gas chromatography mass spectrometry. The week of 9/21-9/28/13 was identified in the proposal based on the high ozone event (9/25), high OC and high potential for contribution of secondary organic aerosol.

Results: The OC and EC analysis was completed using TOT method on a Sunset Laboratory carbon analyzer. Figures 2 through 7 display the OC and EC ambient concentrations for $PM_{2.5}$ and TSP for Moody Tower, Manvel Croix, Conroe and La Porte.

The comparison between TOT carbon analysis and TOR carbon analysis is relevant to the current project. Figures 7-10 include a correlation of TOT and TOR at Clinton Ave (a TCEQ monitoring site) as analyzed by DRI. The correlation is excellent for both EC (r^2= 0.94) and OC (r^2= 0.9997), with a small deviation from 1.0 in the slope for each (1.34 for

EC and 0.91 for OC). This suggests that any general trends seen for EC and OC in the current project could be integrated within the larger monitoring efforts by TCEQ in Houston, assuming that 2013 at Clinton Ave, is representative of Houston aerosol.

Moody Tower HV2.5 September 4-28, 2013
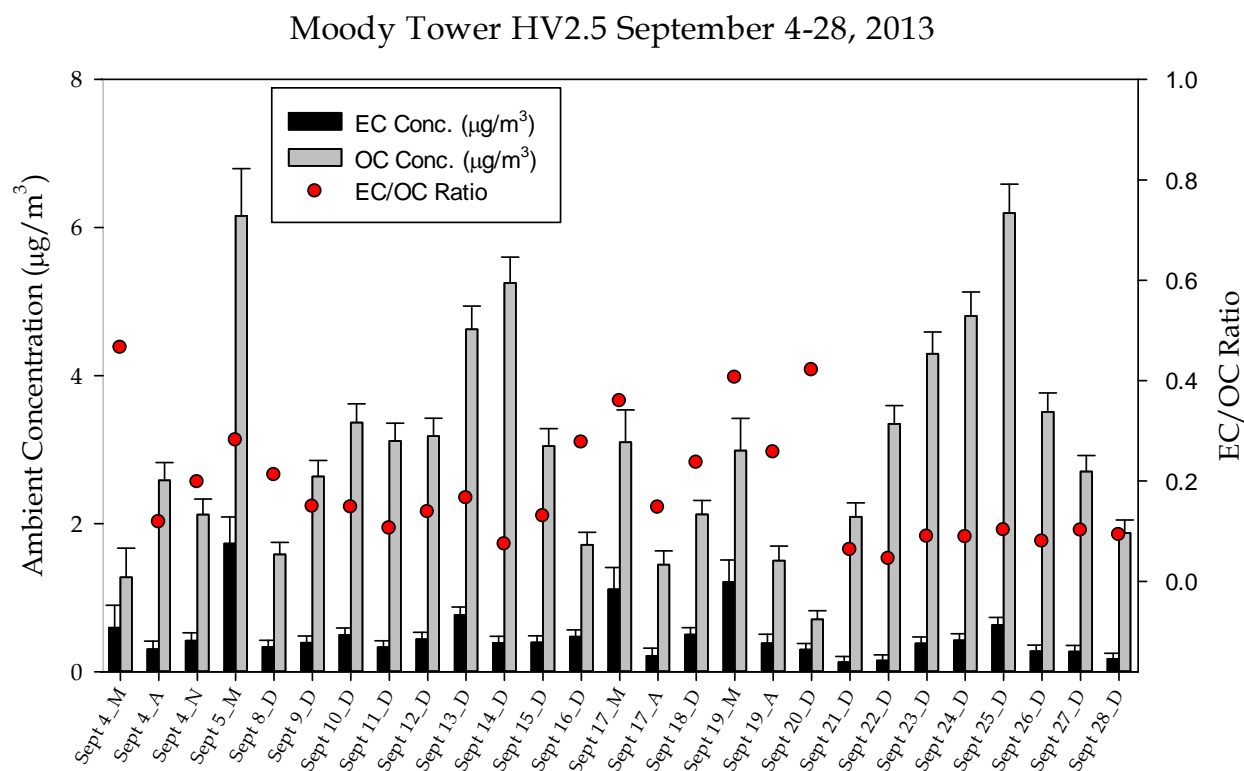
Figure 2. Full set of EC and OC ambient concentrations and EC/OC ratios at Moody Tower (HV PM$_{2.5}$ QFF) by date and time. EC and OC were analyzed using the TOT method. "M" denotes morning sample collected from 6:30 to 10:00. "A" denotes afternoon sample collected from 10:00 to 20:00. "D" denotes day 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 (μg/m³).

PM$_{2.5}$ summary for Moody Tower and Manvel Croix

HV$_{2.5}$ day samples are averages for the period 6:30-20:00. EC ambient concentrations averaged 0.34 +/- 0.14 μg/m³ across Moody Tower and Manvel Croix. EC concentrations ranged from 0.11- 0.77 μg/m³, with the minimum and maximum values occurring on 9/21 at Manvel Croix and 9/13 at Moody Tower of the campaign,

respectively. OC day ambient concentrations averaged 2.88 +/- 1.24, with a range of 0.71-6.20 µg/m³. Minimum and maximum values occurred both at Moody Tower during 9/20 and 9/25 of the campaign, respectively. Maximum OC was the same day as the high ozone event on 9/25 in Houston. EC/OC ratios ranged from 3% - 42%, with the minimum ratio occurring on 9/22 at Manvel Croix and the maximum ratio occurring on 9/20 at Moody Tower. Maximum OC ambient concentrations and EC/OC ratios occurred on 9/20 at Moody Tower. The EC ambient concentrations for daytime for Moody Tower versus Manvel Croix have a correlation of r²= 0.51. The OC concentrations for daytime for Moody Tower versus Manvel Croix have a correlation of r²= 0.80.
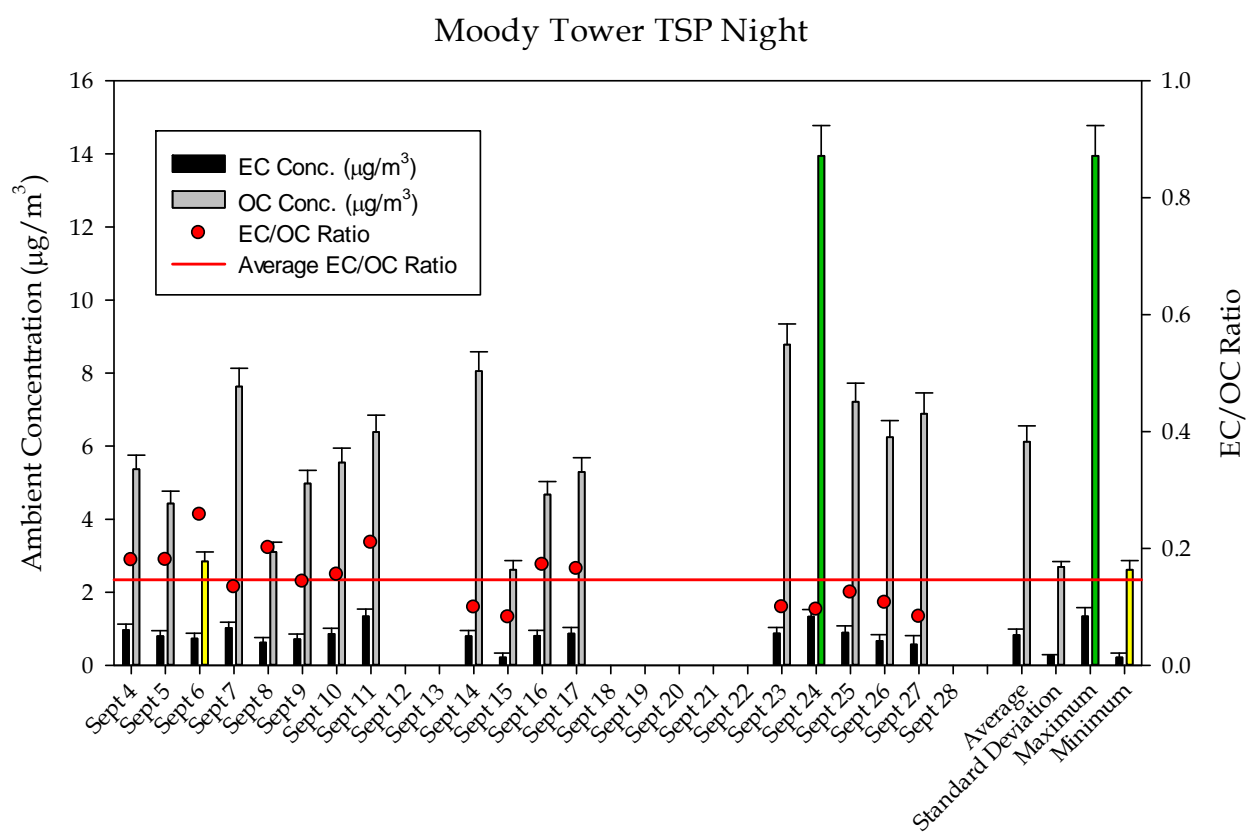
Figure 3. Nighttime EC and OC ambient concentrations and EC/OC ratios at Moody Tower (TSP QFF). EC and OC were analyzed using the TOT method. Night time samples collected from 20:00 to 6:30. Error bars denote the uncertainty in (µg/m³). Green and yellow bars highlight OC maximum and minimum, respectively.

TSP summaries for Moody Tower and Manvel Croix

Day concentrations for TSP samples are averages for the period 6:30-20:00. Elemental carbon ambient concentrations averaged 0.66 +/- 0.36 µg/m³ for Moody Tower and Manvel Croix. EC ambient concentrations ranged from 0.12-1.40 µg/m³, with the minimum value occurring on 9/21 at Manvel Croix, and the maximum value occurring on 9/12 at Moody Tower. OC day ambient concentrations averaged 6.06 +/- 2.20 µg/m³ for Moody Tower and Manvel Croix. OC concentrations ranged from 2.96 – 10.92 µg/m³. The minimum ambient concentrations for OC occurred on the same day as the minimum EC concentrations, 9/21 at Manvel Croix. Heavy precipitation occurred at Manvel Croix and Moody Tower from 9/19-21, which decreased concentrations of OC and EC at Moody Tower and Manvel Croix. Maximum concentrations of OC occurred on 9/24 during the sampling campaign the day preceding the 9/25 high ozone event in Houston. The EC/OC ratios ranged from 3.38%-18.31% across Moody Tower and Manvel Croix. The minimum EC/OC ratio occurred on 9/22 at Manvel Croix, occurring the day after a precipitation event in Houston (9/19-9/21). The highest EC/OC ratio occurred on 9/10 at Moody Tower.
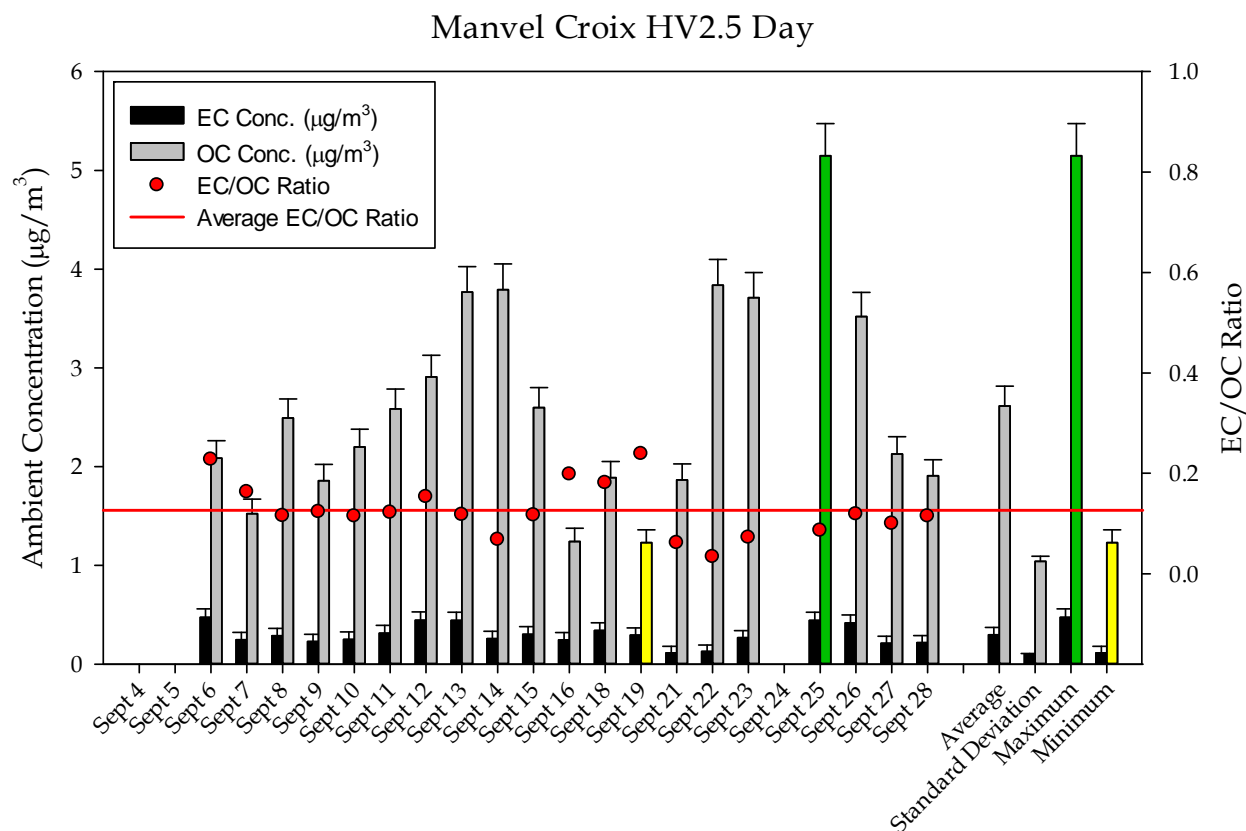
Figure 4. EC and OC ambient concentrations and EC/OC ratios at Manvel Croix (HV PM$_{2.5}$ QFF). EC and OC were analyzed using the TOT method. Day time samples collected from 6:30 to 20:00. Error bars denote the

uncertainty in (µg/m³). Green and yellow bars highlight OC maximum and minimum, respectively.

Conroe PM$_{2.5}$ September 4-28, 2013
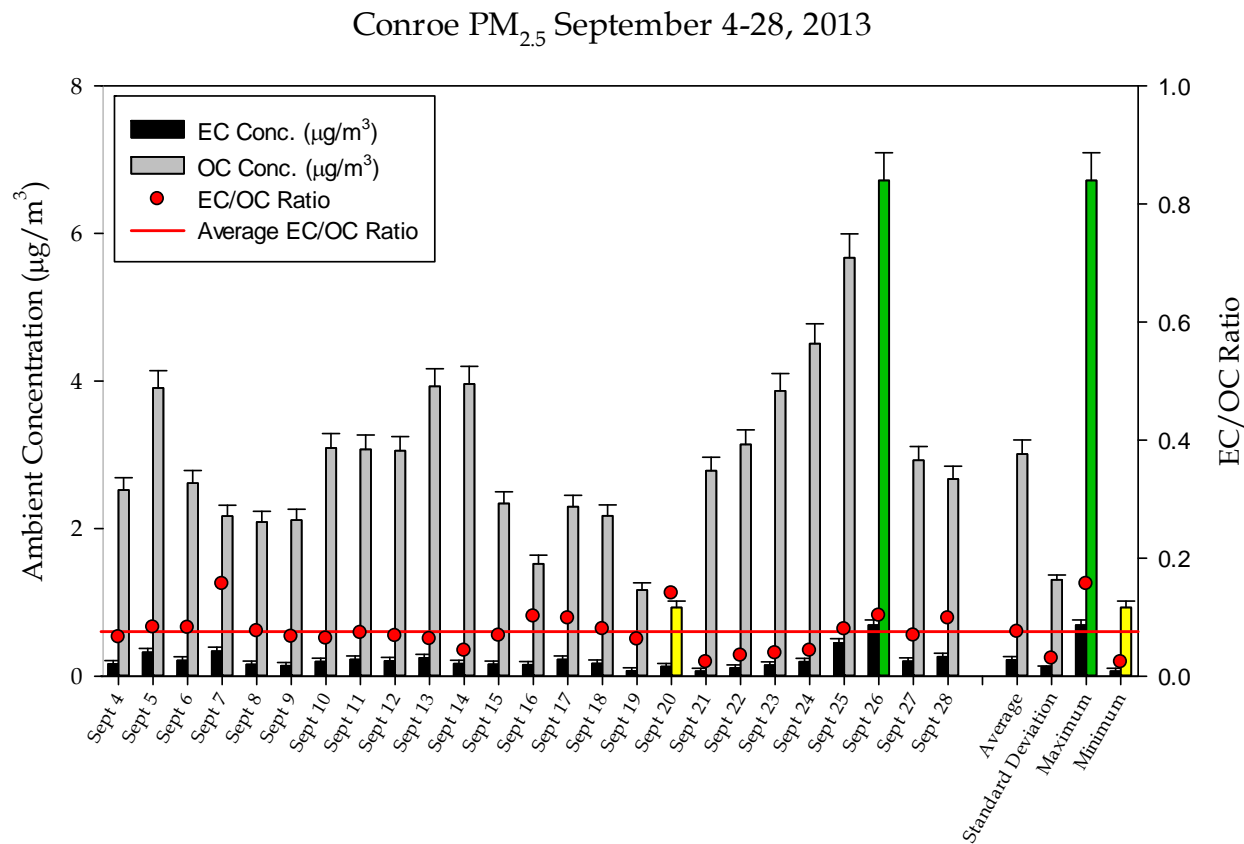
Figure 5. EC and OC ambient concentrations and EC/OC ratios at Conroe (HV PM$_{2.5}$ QFF). EC and OC were analyzed using the TOT method. 24 hour samples collected from 6:00 to 5:30. Error bars denote the uncertainty in (µg/m³). Green and yellow bars highlight OC maximum and minimum, respectively.

PM2.5 summary for Conroe

Twenty four hour concentrations for HV$_{2.5}$ samples are averages for the period 6:00-5:30. Conroe is the site most northern of the four sites chosen for the campaign, and it often displays delays in peak concentrations during the campaign. The EC concentration averaged 0.22 +/- 0.13 µg/m³. EC concentrations ranged from 0.07-0.69 µg/m³, with the minimum concentration occurring on 9/21 (occurring after the precipitation event from 9/19-21) and the maximum occurring on the 9/26 (9/25 was a high ozone event in Houston during the campaign). OC ambient concentrations averaged 3.01 +/- 1.31 µg/m³. OC ambient concentrations ranged from 0.93-6.72 µg/m³, with the minimum concentration occurring on 9/20. The maximum concentration

occurred on the 9/26. The EC/OC ratio ranged from 2.4% - 15.6% at Conroe, with a minimum on 9/21 and a maximum on 9/7.

La Porte TSP September 4-28, 2013
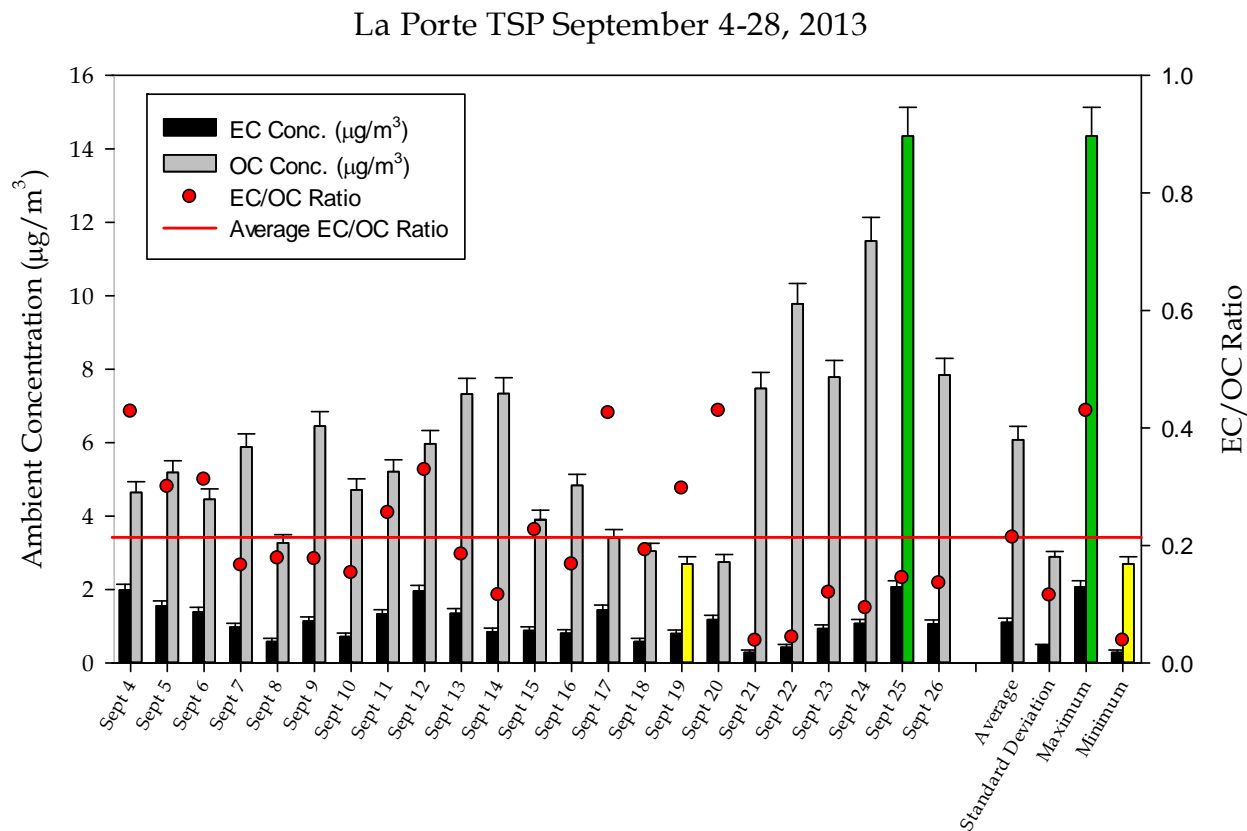
Figure 6. EC and OC ambient concentrations and EC/OC ratios at La Porte (TSP QFF). EC and OC were analyzed using the TOT method. 24 hour samples collected from 6:00 to 5:30. Error bars denote the uncertainty in (μg/m³). Green and yellow bars highlight OC maximum and minimum, respectively.

TSP summary for La Porte

Twenty four hour concentrations for TSP samples are averages for the period 6:30-6:00. Ambient concentration of EC averaged 1.10 +/- 0.48 μg/m³ for the campaign. EC concentrations ranged from 0.29 -2.07 μg/m³, with the minimum concentration occurring on 9/21 (light rain day in La Porte) and the maximum occurring on 9/25 (the high ozone event day in Houston). OC ambient concentrations averaged 6.08 +/- 2.89 μg/m³. OC concentrations ranged from 2.69-14.35 μg/m³, with the minimum concentration occurring on 9/19. The maximum concentration occurred on 9/25, the

same as the EC and the ozone maximum for the campaign. The EC/OC ratio ranged from 3.8% - 42.9% at La Porte, with a minimum on 9/21 and a maximum on 9/4.
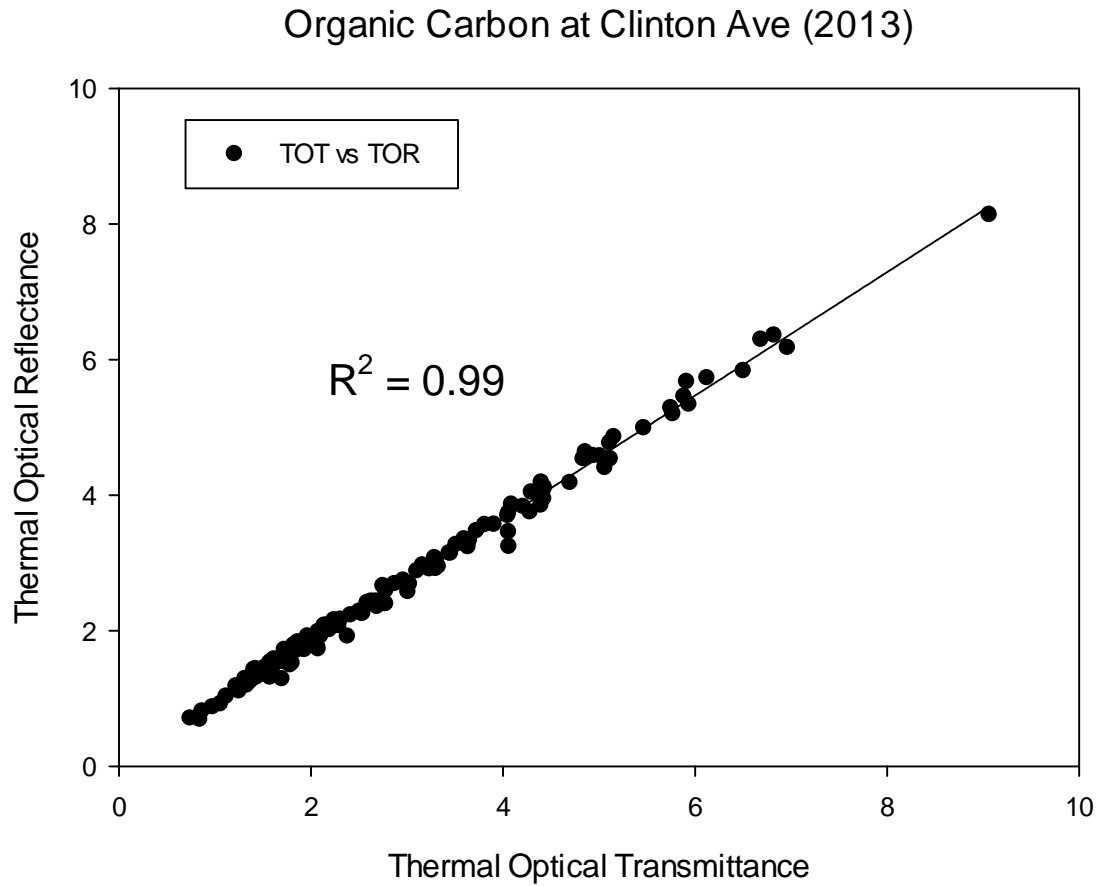
Figure 7. Comparison of organic carbon measurements using thermal optical transmittance versus thermal optical reflectance. Data measuring in 2013 at the TCEQ Clinton Ave air monitoring site.

Elemental Carbon at Clinton Ave (2013)

$R^2 = 0.94$

Thermal Optical Reflectance

Thermal Optical Transmittance

- TOT vs TOR
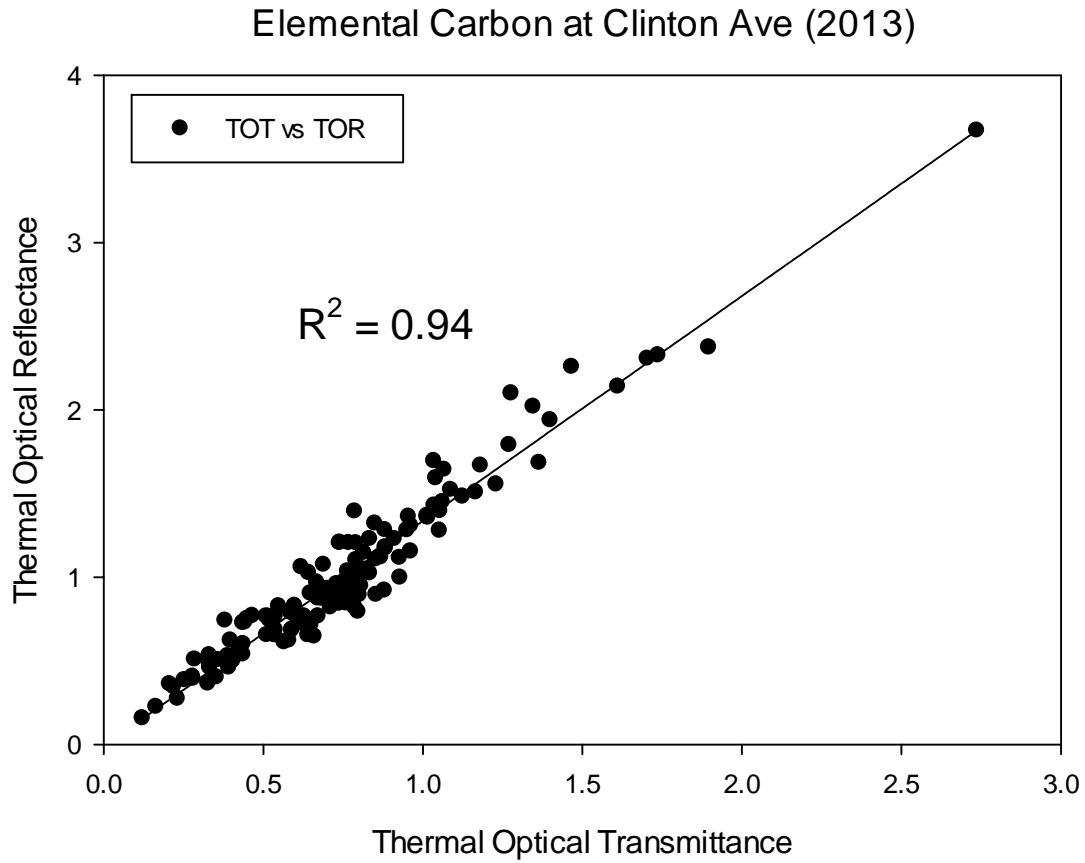
Figure 8. Comparison of elemental carbon measurements using thermal optical transmittance versus thermal optical reflectance. Data measuring in 2013 at the TCEQ Clinton Ave air monitoring site.
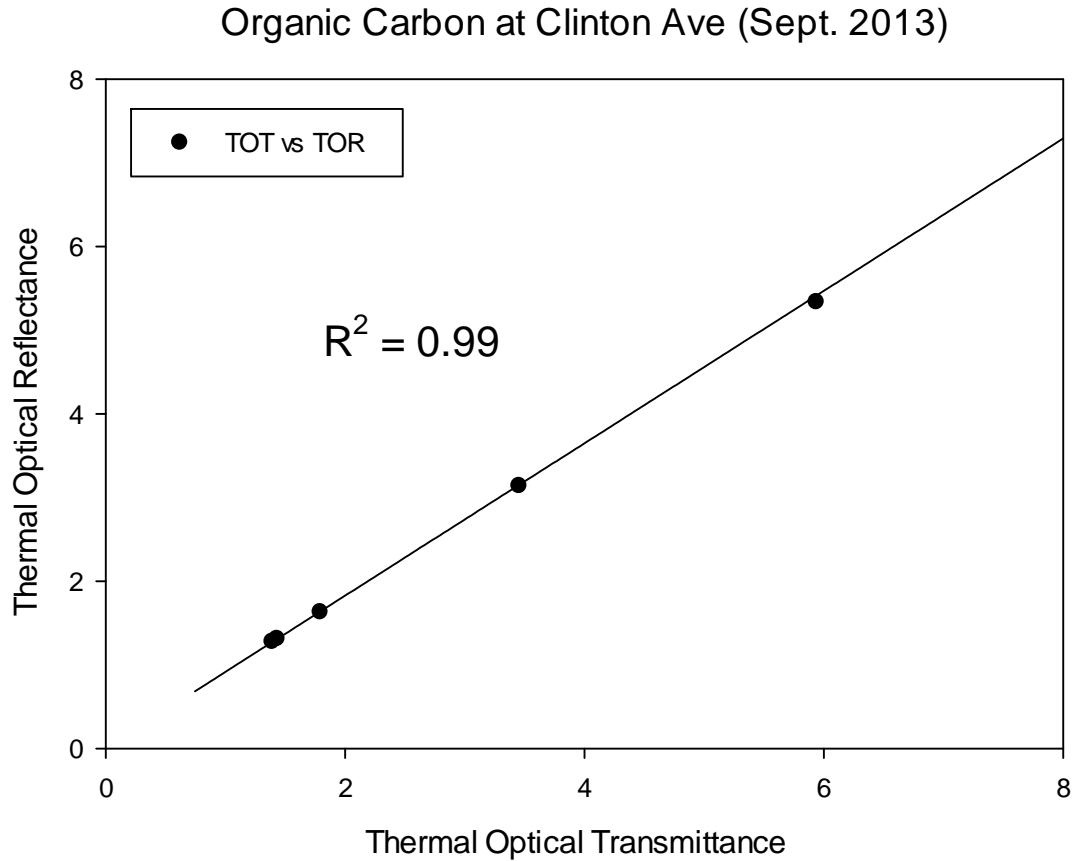
Figure 9. Comparison of organic carbon measurements using thermal optical transmittance versus thermal optical reflectance. Data measuring in September 2013 at the TCEQ Clinton Ave air monitoring site.

Elemental Carbon at Clinton Ave (Sept. 2013)
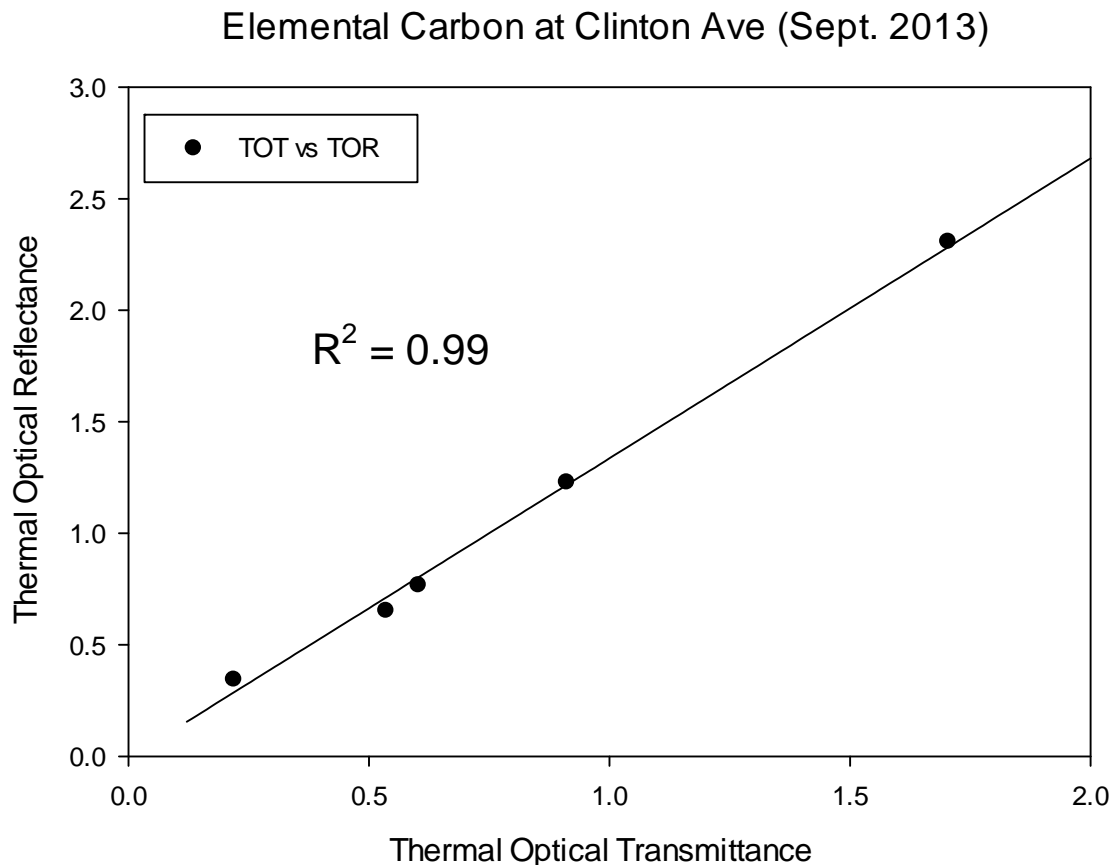
Figure 10. Comparison of elemental carbon measurements using thermal optical transmittance versus thermal optical reflectance. Data measuring in September 2013 at the TCEQ Clinton Ave air monitoring site.

Data reporting and sharing: Preliminary data has been shared with AQRP DISCOVER-AQ investigators. These results were reported at the American Geophysical Union conference in December 2014 in a poster titled "Spatial trends in surface-based carbonaceous aerosol, including organic, water-soluble and elemental carbon, during DISCOVER-AQ in Houston, TX". Discussion and inter-comparison of the trends for 9/21-9/28 with the other results from DISCOVER-AQ with NASA's Jim Crawford confirmed analytical decisions for detailed analysis (December 2014: at the American Geophysical Union conference).

Deliverable 2: Water Soluble Organic Carbon

Measure daily WSOC concentrations from PM samples collected from Moody Tower, Manvel Croix, and Conroe.

Overview: PM$_{2.5}$ samples from Moody Tower, Manvel Croix and Conroe and on TSP samples from La Porte were analyzed for water soluble organic carbon (Figures 11-14).

Results: WSOC was determined for 100% of samples analyzed. Figures 8-10 display the WSOC ambient concentrations for PM$_{2.5}$ for Moody Tower, Manvel Croix and Conroe. Figure 11 displays the WSOC ambient concentration for TSP for La Porte. For Conroe, the average WSOC was 1.9 µg/m³, with a range of 0.5 − 3.5 µg/m³. The average for daytime at Moody Tower for PM$_{2.5}$ was 2.0 with a range of 0.4 − 3.6 µg/m³. For Manvel Croix daytime PM$_{2.5}$ the average was 1.4 µg/m³with a range of 0.4 − 2.6 µg/m³. The average WSOC for TSP at La Porte was 2.6 µg/m³, with a range of 0.8 − 6.0 µg/m³.
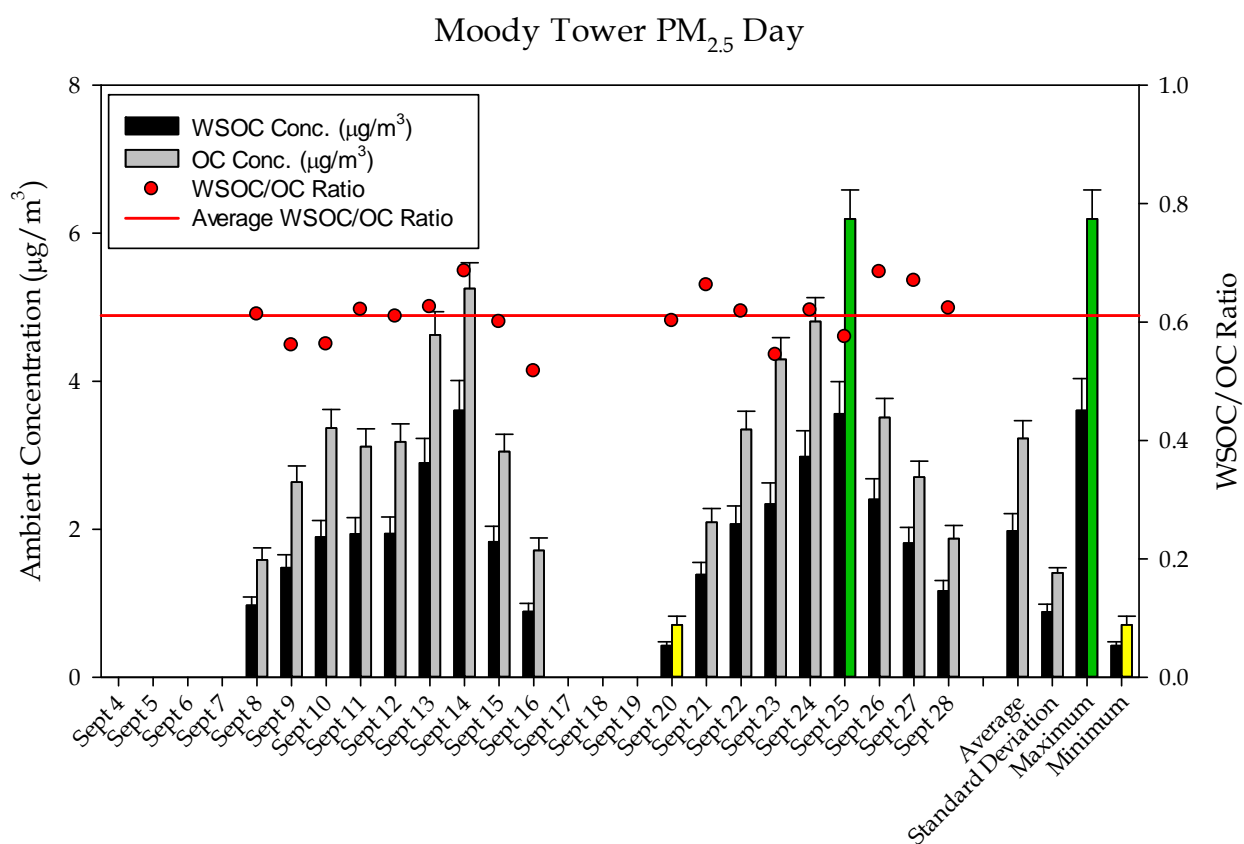
Figure 11. WSOC and WSOC/OC ratios at Moody Tower QFF HV PM$_{2.5}$. Day time samples collected from 6:30 to 20:00. Error bars denote the uncertainty in (µg/m³). Green and yellow bars highlight OC maximum and minimum, respectively.

Manvel Croix HV PM$_{2.5}$ Day
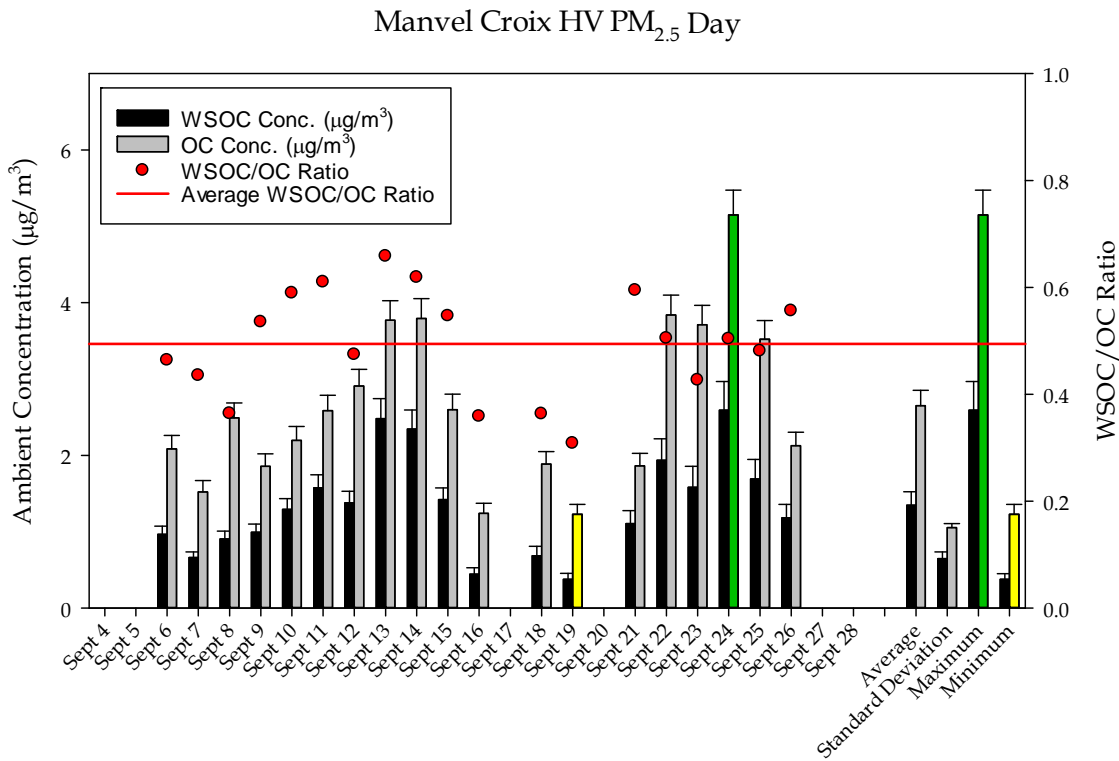
Figure 12. WSOC and WSOC/OC ratios at Manvel Croix QFF HV PM$_{2.5}$. Day time samples collected from 6:30 to 20:00. Error bars denote the uncertainty in (μg/m³). Green and yellow bars highlight OC maximum and minimum, respectively.

*PM2.5 summaries for Moody Tower and Manvel Croix*

Day concentrations for HV$_{2.5}$ samples are averages for the period 6:00-20:00. Average ambient WSOC concentration across the two sites was 1.65 +/- 0.83 μg/m³ with a range from 0.38 – 3.60 μg/m³. The WSOC/OC ratio ranged from 30.8% - 68.6% during the campaign. Across Moody Tower and Manvel Croix there is a strong correlation between WSOC and OC with an r² = 0.91.

Conroe PM$_{2.5}$
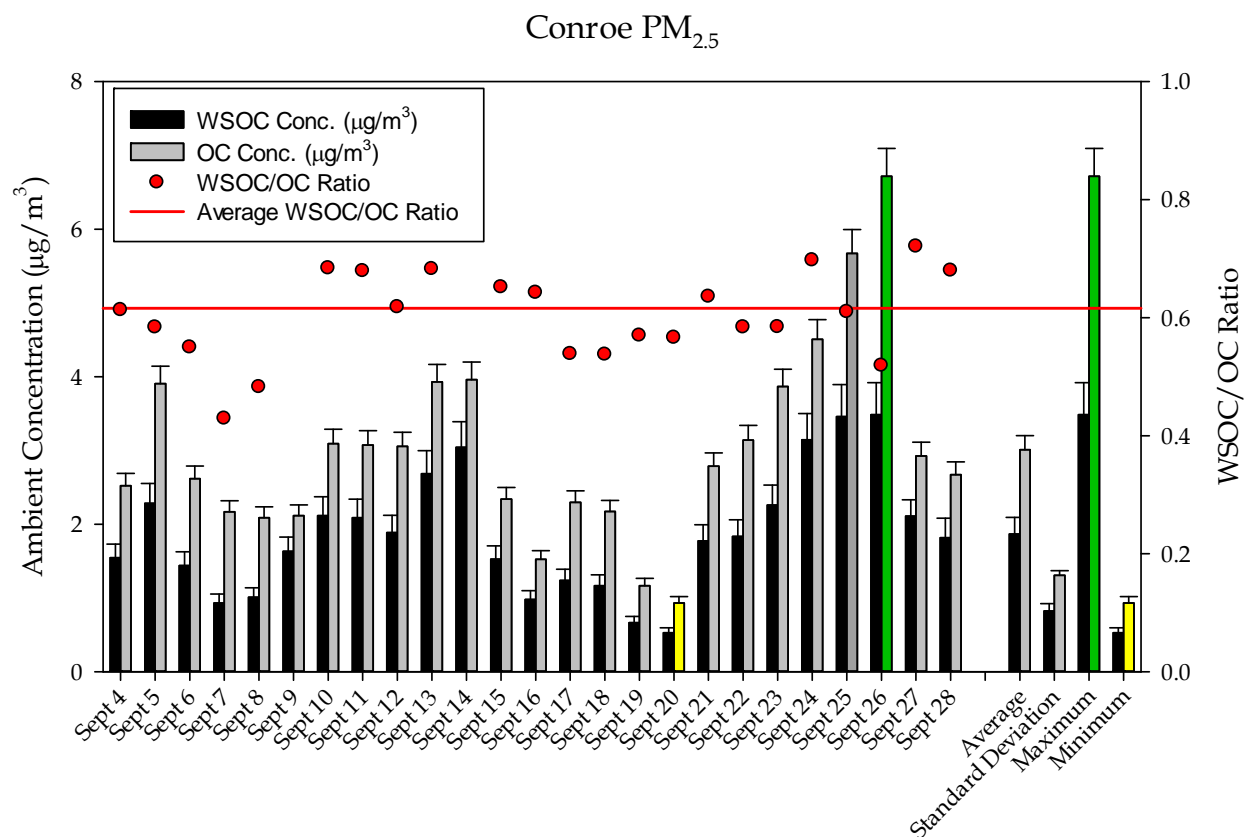
Figure 13. WSOC and WSOC/OC ratios at Conroe QFF HV PM$_{2.5}$. 24 hour samples collected from 6:00 to 5:30. Error bars denote the uncertainty in (µg/m³). Green and yellow bars highlight OC maximum and minimum, respectively.

PM2.5 summary for Conroe

Twenty four hour concentrations for HV$_{2.5}$ samples are averages for the period 6:00-5:30. WSOC ambient concentrations averaged 1.87 +/- 0.83 µg/m³ at Conroe. WSOC concentrations ranged from 0.53 – 3.49 µg/m³, with the minimum and maximum values occurring during September 20st and September 26th, respectively. The WSOC/OC ratios ranged from 42.9% - 77.2% for the month of September, with the minimum WSOC/OC ratio occurring on 9/7 and the maximum occurring on 9/9. There is a strong correlation between WSOC and OC concentrations at Conroe, with an r² = 0.90.
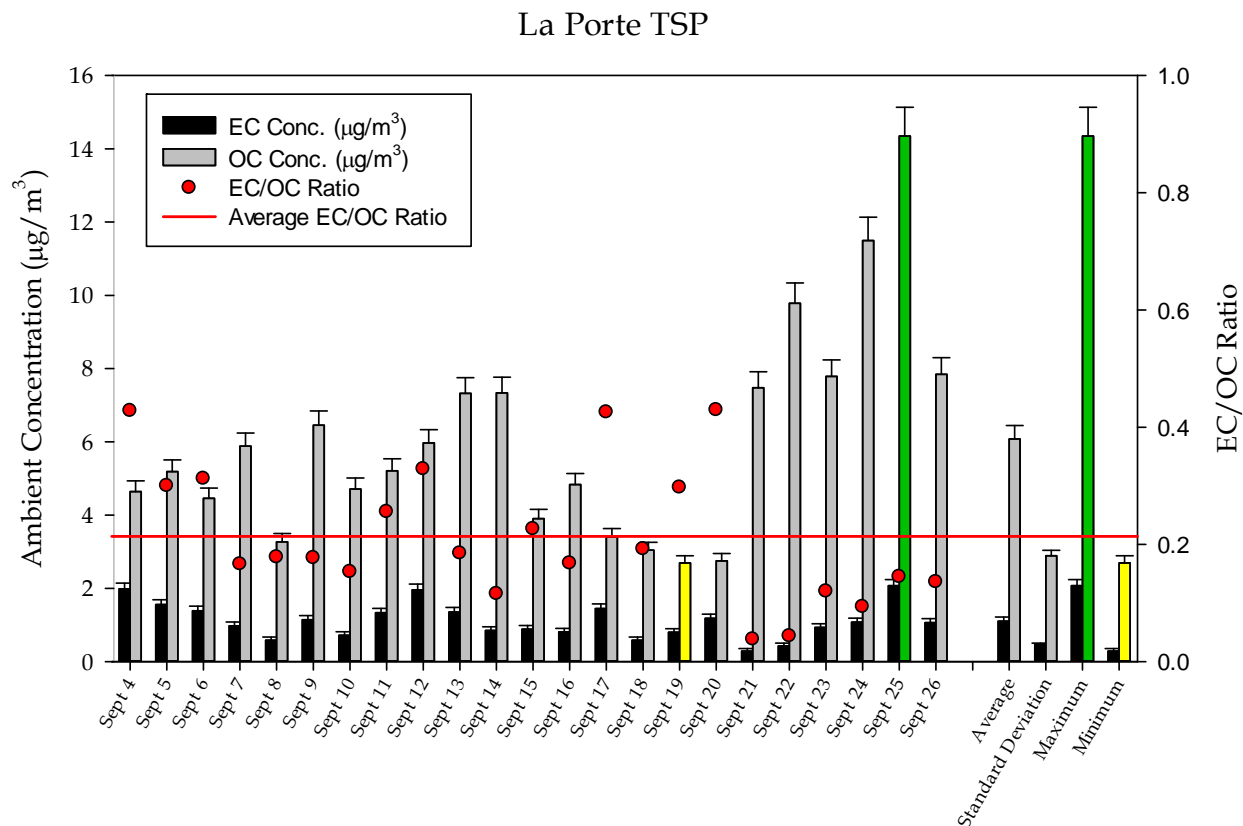
La Porte TSP

Figure 14. WSOC and WSOC/OC ratios at La Porte QFF TSP. 24 hour samples collected from 6:00 to 5:30. Error bars denote the uncertainty in (µg/m³). Green and yellow bars highlight OC maximum and minimum, respectively.

TSP summary for La Porte

Twenty four hour concentrations for TSP samples are averages for the period 6:30-6:00. The WSOC concentration averaged 2.58 +/- 1.40 µg/m³. WSOC concentrations ranged from 0.80 -6.06 µg/m³, with the minimum concentration occurring on 9/20 (light rain day in La Porte) and the maximum on 9/25 (high ozone event). The WSOC/OC ratio ranged from 28.1% - 54.8% at La Porte. There is a strong correlation between WSOC and OC concentrations at La Porte, with an r^2 = 0.93.

Data reporting and sharing: Preliminary data has been shared with AQRP DISCOVER-AQ investigators. These results were reported at the American Geophysical Union conference in December 2014 in a poster titled "Spatial trends in surface-based carbonaceous aerosol, including organic, water-soluble and elemental carbon, during DISCOVER-AQ in Houston, TX". Comparison of data and trends with the

Environmental Protection Agency (December 2014: at the American Geophysical Union conference) for La Porte.

Deliverable 3: Inorganic Ions

Measure inorganic ions (SO4, Cl, NO3, NH4 and K) concentrations at Moody Tower. Moody Tower dataset will be combined and compared with the PILS dataset collected from Manvel Croix (14-009) and inorganic ion dataset from Conroe PM filters samples (14-024).

Overview: Inorganic ion concentrations were completed for $PM_{2.5}$ samples at Moody Tower and Conroe using the contract laboratory DRI by ion chromatography for cations (potassium, sodium, ammonium) and anions (chloride, nitrate and sulfate) (Figures 15-17).

Results: The filter plans and preparatory work for this contract analysis was completed by grad students and PIs at Baylor University for both sites, while the contract service fees were charged to 14-029 for Moody Tower and to 14-024 for Conroe. Filter plans utilized inorganic ion data reported by TCEQ for Houston plus detection limits provided by DRI to estimate fraction of filter needed for analysis. For Manvel Croix, sulfate was the only inorganic ion that was reported; this enabled comparison of sulfate concentrations at three sites across Houston during DISCOVER-AQ (Moody Tower; IC by DRI, Conroe IC by DRI, and Manvel Croix; PILS by AQRP project 14-009).

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 March 2015. Raw inorganic ion mass was converted to ambient concentrations by Baylor grad students. Ambient concentrations were blank corrected, then normalized to the area of the filter to give total mass of the inorganic ions per sample (i.e. per filter). The mass of inorganic ions were then divided by the volume of air sampled. For this dataset the following anions and cations were reported: chloride, particulate nitrate, sulfate, ammonium, sodium and potassium. The four filter blanks had non-detectable results 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 were the following detectable results for each reported anion and cation: 16 detectable results for chloride, 23 detectable results for particulate nitrate, 27 detectable results for sulfate, 26 detectable results for ammonium, 26 detectable results for soluble sodium and 24 detectable results for soluble potassium (Figure 15).

Inorganic ion data from Conroe. Raw data was sent to Baylor grad students and PIs in March; this raw data was forwarded to PI Hildebrandt Ruiz (14-024). Raw inorganic

ion mass was converted to ambient concentrations by Baylor graduate students and shared with PI Hildebrandt Ruiz (14-024). Ambient concentrations were calculated as described above. For this dataset the following anions and cations were reported: chloride, particulate nitrate, sulfate, ammonium, sodium and potassium. The two filter blanks had non- detectable results for all ions. Of the 25 samples (9/4/2013 – 9/28/2013), there were 25 detectable results for all except particulate nitrate which only had detectable results on 14 of the 25 (Figure 16). 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.

Figures 15 and 16 display the inorganic ion ambient concentrations combined with EC and OC*1.2 for $PM_{2.5}$ for Moody Tower and Manvel Croix. The OC as measured by TOT carbon analysis represents only organic carbon, not the entire organic matter mass. A correction factor is needed to convert OC to organic matter. A minimum factor of 1.2 represents primary, hydrocarbon-like organic matter, but is most likely biased low for Conroe. Figure 17 integrates sulfate data across Moody Tower, Manvel Croix and Conroe. Conroe consistently has the highest ambient concentration of sulfate with the exception of 9/14 at Moody Tower.

HV2.5 Samples- Moody Tower and Conroe

Day concentrations for $HV_{2.5}$ samples are averages for the period 6:30-20:00 at Moody Tower (Figure 15). Chloride ambient concentrations ranged from 0.04-0.17 µg/m^3, with an average of 0.9 +/- 0.04 µg/m^3. Nitrate ambient concentrations ranged from 0.03-0.47 µg/m^3, with an average of 0.16 +/- 0.11 µg/m^3. Sulfate ambient concentrations ranged from 0.76-4.73 µg/m^3, with an average of 2.21 +/- 0.91 µg/m^3. Sulfate concentrations were the highest concentrations of inorganics at Moody Tower. Ammonium ambient concentrations ranged from 0.04-1.54 µg/m^3, with an average of 0.66 +/- 0.36 µg/m^3. Soluble Sodium ambient concentrations ranged from 0.03-0.42 µg/m^3, with an average of 0.19 +/- 0.10 µg/m^3. Soluble potassium ambient concentrations ranged from 0.02-0.19 µg/m^3, with an average of 0.04 +/- 0.03 µg/m^3. 24 hour sample concentrations for $HV_{2.5}$ samples are averages for the period 6:00-5:30 at Conroe (Figure 16). Sulfate ambient concentrations ranged from 0.81-4.44 µg/m^3, with an average of 2.93 +/- 1.12 µg/m^3.
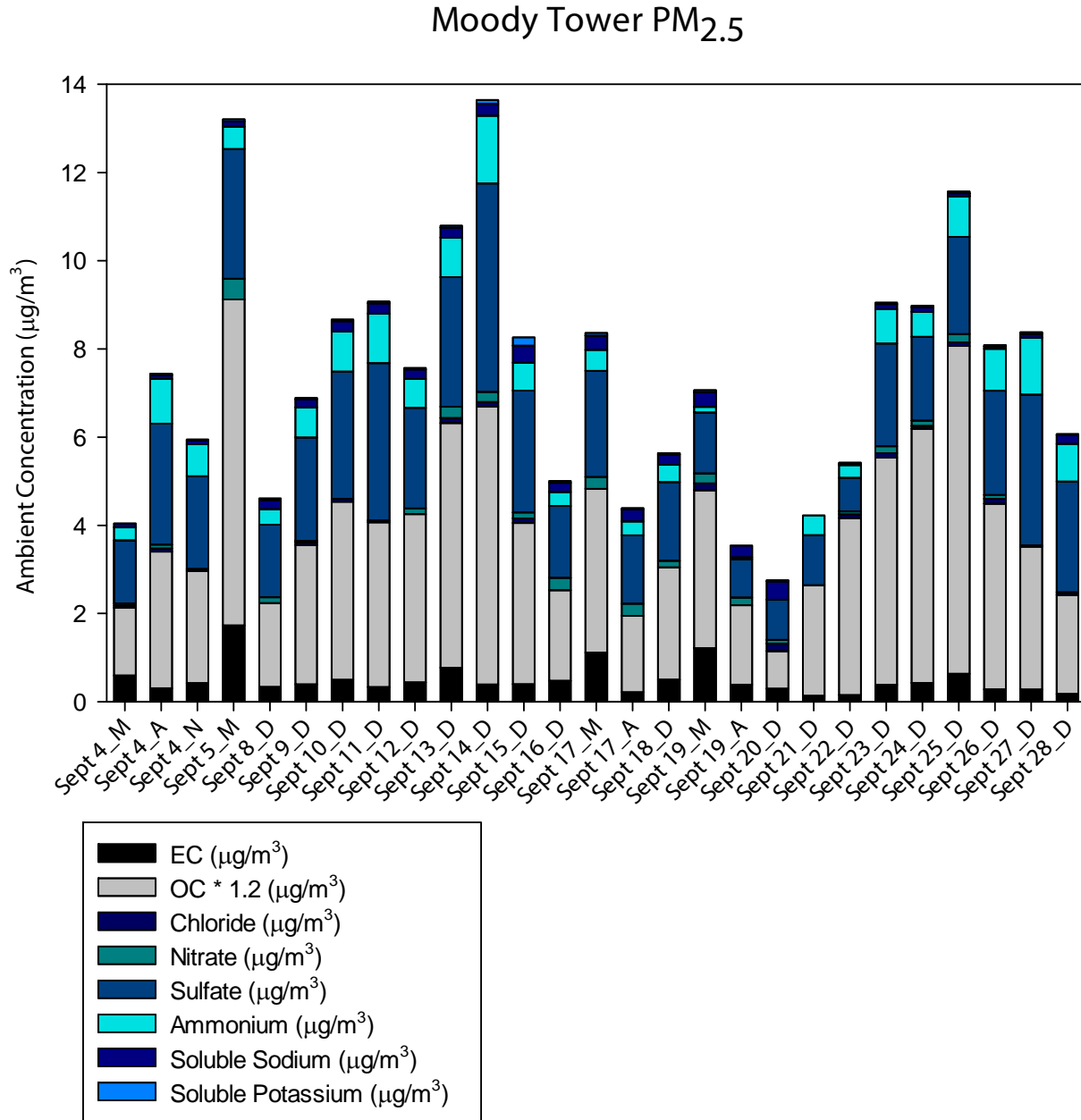
Moody Tower PM$_{2.5}$

Figure 15. Inorganic ion, EC, and OC ambient concentrations at Moody Tower (QFF HV PM$_{2.5}$) by date and time. "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.

Conroe PM$_{2.5}$
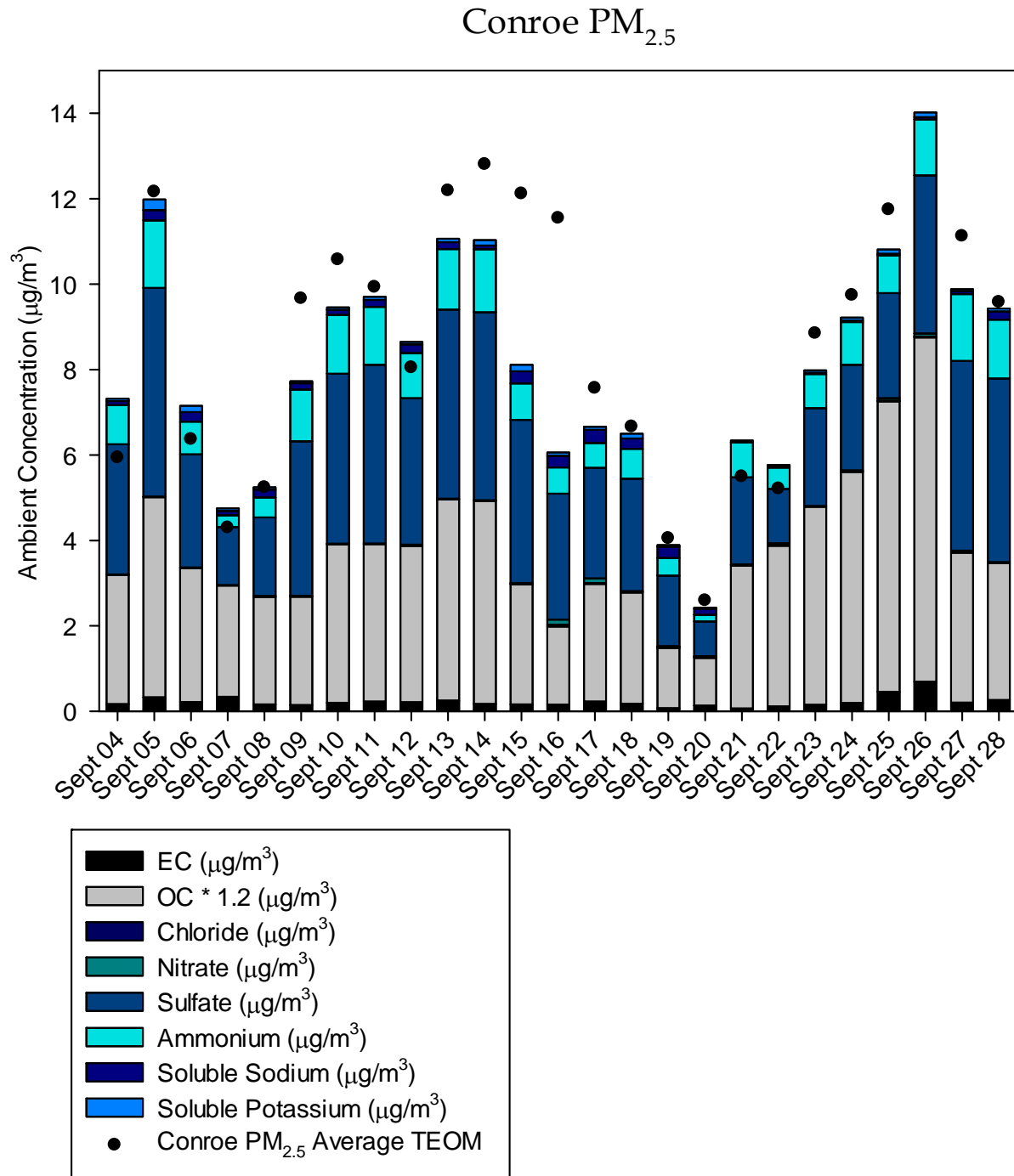
Figure 16. Inorganic ion, EC, and OC ambient concentrations at Conroe (QFF HV PM$_{2.5}$). 24 hour samples were collected from 6:00 to 5:30.

Ambient Sulfate Concentrations
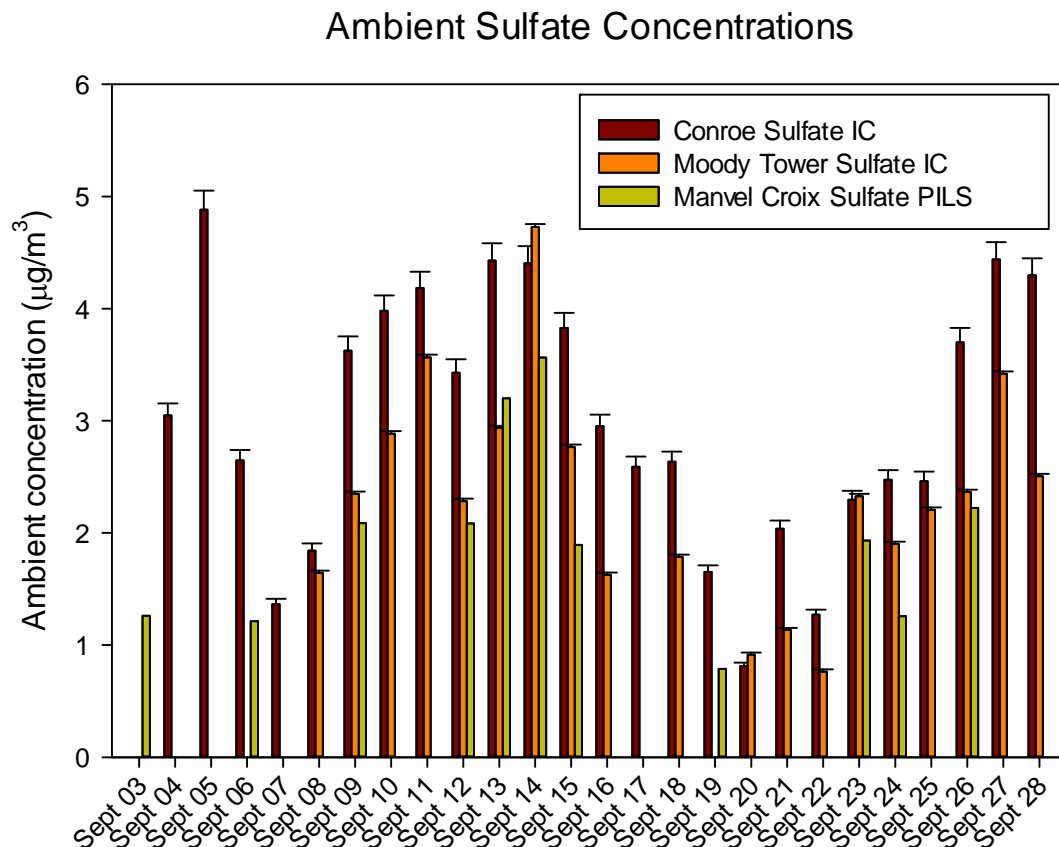
Figure 17. Ambient concentrations (μg/m³) of sulfate from Moody Tower, Manvel Croix, and Conroe. Sulfate measured at Moody Tower and Conroe were measured using ion chromatography (DRI; 14-024 and 14-029), while at Manvel Croix, the sulfate concentrations were determined using particle into liquid sampler (PILS; 14-009).

Data reporting and sharing: Inorganic ion data collected from Moody Tower was made available with other AQRP DISCOVER-AQ projects PIs, specifically PIs associated with AQRP projects 14-024 and with 14-005. The sulfate data for Manvel Croix was shared by 14-009. These results are presented at Regional meeting of the Society for Environmental Toxicology and Chemistry, May 29-30, 2015 in a poster "Spatial trends in inorganic atmospheric particulate matter composition during DISCOVER-AQ in Houston, TX".

Deliverable 4: Elemental Tracers

Daily concentrations of 51 elemental tracers will be reported for Teflon PM Filters collected at Moody Tower.

Overview: Daily, 24 h $PM_{2.5}$ samples collected at Moody Tower were analyzed for 51 elemental tracers by DRI.

Results: Filter Plans for Metal (Elemental Tracers) Analysis. Metals were measured at Moody Tower from Teflon filters. Baylor PIs and student shipped 25 samples (9/4/2013 – 9/28/2013) and 3 blanks (following project's approved QAQC plan) to DRI for metal analysis using X-ray fluorescence. The entire filter was used for this analysis. XRF is a non-destructive method and the filters were returned to Baylor (Figures 18-20).

Metals data from Moody Tower. Raw metal mass per filter was blank subtracted using site-specific field blanks and converted to ambient concentrations by Baylor grad students. For this dataset the following 51 metals were reported, with the number of detectable results 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 are included in Appendix A. In addition, select metals, when detected, are used as quantitative and semi-quantitative molecular tracers. Iron ambient concentrations ranged from 0.03-0.4 μg/m^3, with an average of 0.11 +/- 0.09 μg/m^3. Copper and Zine ambient concentrations ranged from non-detect-0.2 μg/m^3 and non-detect-0.61 μg/m^3, with an average of 0.01 μg/m^3 and 0.11 μg/m^3, respectively. Sodium and Magnesium ambient concentrations ranged from 0.28-5.2 μg/m^3 and 0.01-0.14 μg/m^3, with an average of 1.60 +/- 1.25 and 0.07 +/- 0.05, respectively. For the current study, the week of interest (9/21 – 9/28) was chosen based on high ozone and high potential for secondary OC. Trace metal concentrations during that week were very low or below detection, so these tracers were not included in the source apportionment modeling. Vehicular tracers were consistent for the month (Figure 18). Future efforts should include detailed investigation of the high trace metal event period (9/10 – 9/15), which was sea salt tracers 9/12-13 (Figure 20) and crustal elements for 9/15-9/16 (Figure 19).

Figure 18. Ambient concentrations of select vehicular tracers and elemental carbon at Moody Tower PM$_{2.5}$ Teflon filter. 24 hour samples collected from 6:00 to 5:30.

Figure 19. Ambient concentrations of select crustal tracers at Moody Tower PM2.5 Teflon filter. 24 hour samples collected from 6:00 to 5:30.

Sea-Salt: Moody Tower MV$_{2.5}$ 24 hr (Teflon)
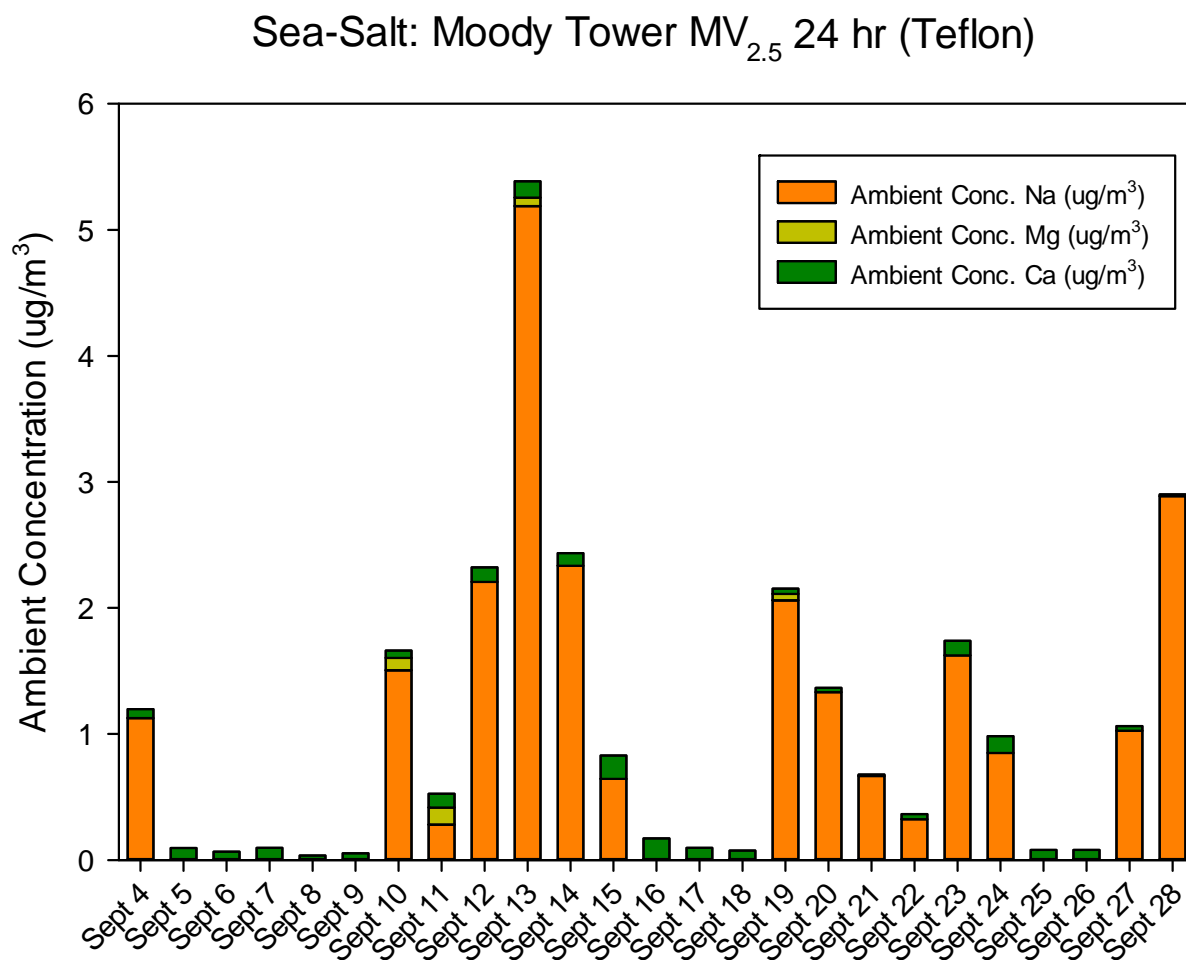
Figure 20. Ambient concentrations of select sea-salt tracers at Moody Tower PM$_{2.5}$ Teflon filter. 24 hour samples collected from 6:00 to 5: 30.

Deliverable 5: Organic Tracers

A detailed characterization of relative high OC (relative to EC) and ozone days (9/21-9/28) will be provided using organic tracers.

Overview: The primary objective was to characterize sources and atmospheric transformation of high particulate OC concentrations during the final week of the DISCOVER-AQ campaign (9/21-28/13). To accomplish this goal, analysis was first completed on samples from 9/11-14/13 and 9/4-6/13 for two reasons 1) to establish site- and particle size-specific organic tracer to OC ratios 2) to provide comparison with

tracer concentrations and ratios in the high ozone event from 9/25/13. The organic tracer analysis for Moody Tower, Manvel Croix and Conroe was focused on $PM_{2.5}$, to match WSOC and radiocarbon analysis of the same filter samples. Organic tracer analysis for La Porte was completed on TSP, which matched WSOC and radiocarbon for that site.

Complete organic tracer dataset for 9/21-28/13 plus initial findings from 9/4-6 and 9/11-14 are included in the AQRP data archive. Example figures, Figure 21-28, display the ambient concentration of representative organic compounds in each measured compound class for Conroe, Manvel Croix, Moody Tower and La Porte for 9/21 to 9/28/13.

HV PM2.5 and TSP Samples- n-alkanes

Ambient concentrations of n-alkanes are used as tracers to identify PM from both combustion and biogenic sources. A total of 19 alkanes (sum of C_{16} to C_{34}) were analyzed in $PM_{2.5}$ and TSP samples at all sites. TSP sample from La Porte and Moody Tower, average ambient concentrations were 23.74 ± 6.13 ng/m³ and 15.79 ±2.01 ng/m³, respectively. The average ambient concentration of n-alkanes for Manvel Croix and Conroe (both HV $PM_{2.5}$) were 10.16 ±2.60 ng/m³ and 7.78 ±4.00 ng/m³, respectively.

Carbon preference index (CPI) utilized ambient alkane concentrations, to determine the relative influence of biogenic to anthropogenic alkane sources to ambient environment. Biogenic sources express a strong odd-number alkane preference while anthropogenic sources show no enrichment of odd carbon alkanes. Sources of biogenic contribution can be from plant wax particles while anthropogenic sources are mainly from fossil fuel combustion. The CPI values were calculated as

$$\text{CPI} = \frac{(C_{27}+C_{29}+C_{31}+C_{33})}{(C_{26}+C_{28}+C_{30}+C_{32})}.$$

CPI values greater than 3 represent concentrations predominantly from biological materials while values near 1 indicate a dominance of fossil fuel combustion sources [18]. Of the four sites, Conroe had the highest CPI value of 3.18, followed by La Porte and Moody Tower with very similar CPI values, 2.84 and 2.72, respectively. Manvel Croix had the lowest CPI of 1.71.

HV PM2.5 and TSP Samples- polycyclic aromatic hydrocarbons

Chrysene, benzo[a]pyrene, and benzo[ghi]perylene are three of the 17 PAH compounds analyzed. PAHs are used as molecular markers for source apportionment studies for incomplete combustion. They were detected at all of the four sites. Aside from TSP Moody Tower Samples, concentrations of PAH compound classes varied largely by sampled date for La Porte, Conroe, Moody Tower (HV PM$_{2.5}$) and Manvel Croix. Sampling dates 9/24- 9/26 showed elevated concentrations of ΣPAHs at each site and were excluded from mean concentrations (± standard deviation). TSP samples of Moody Tower (0.99 ±0.33 ng/m^3) and La Porte (0.31 ±0.07 ng/m3) had higher mean ambient concentrations of ΣPAHs than HV PM$_{2.5}$ samples, in receding order, from Conroe (0.19 ±0.07 ng/m^3), Manvel Croix (0.12 ±0.02 ng/m^3) and Moody Tower (0.10 ±0.04 ng/m^3). In La Porte samples, an elevated ambient concentration of 0.87 ng/m^3 was observed on the 9/25, relative to the mean concentration of 0.31 ±0.07 ng/m3. Conroe had peak concentration on the 9/25 (1.32 ng/m^3) and still elevated concentration on the 9/26 (0.76 ng/m3). On the September 25-26, samples from Manvel Croix observed a mean concentration of 0.27 ±0.03 ng/m3 for those two elevated ΣPAH concentration days. Moody Tower experienced higher ΣPAH concentrations on the 9/24-9/25, mean concentration of 0.43 ±0.08 ng/m3. These increased activity days was observed in organic tracer analysis.

Select Polycyclic Aromatic Hydrocarbons
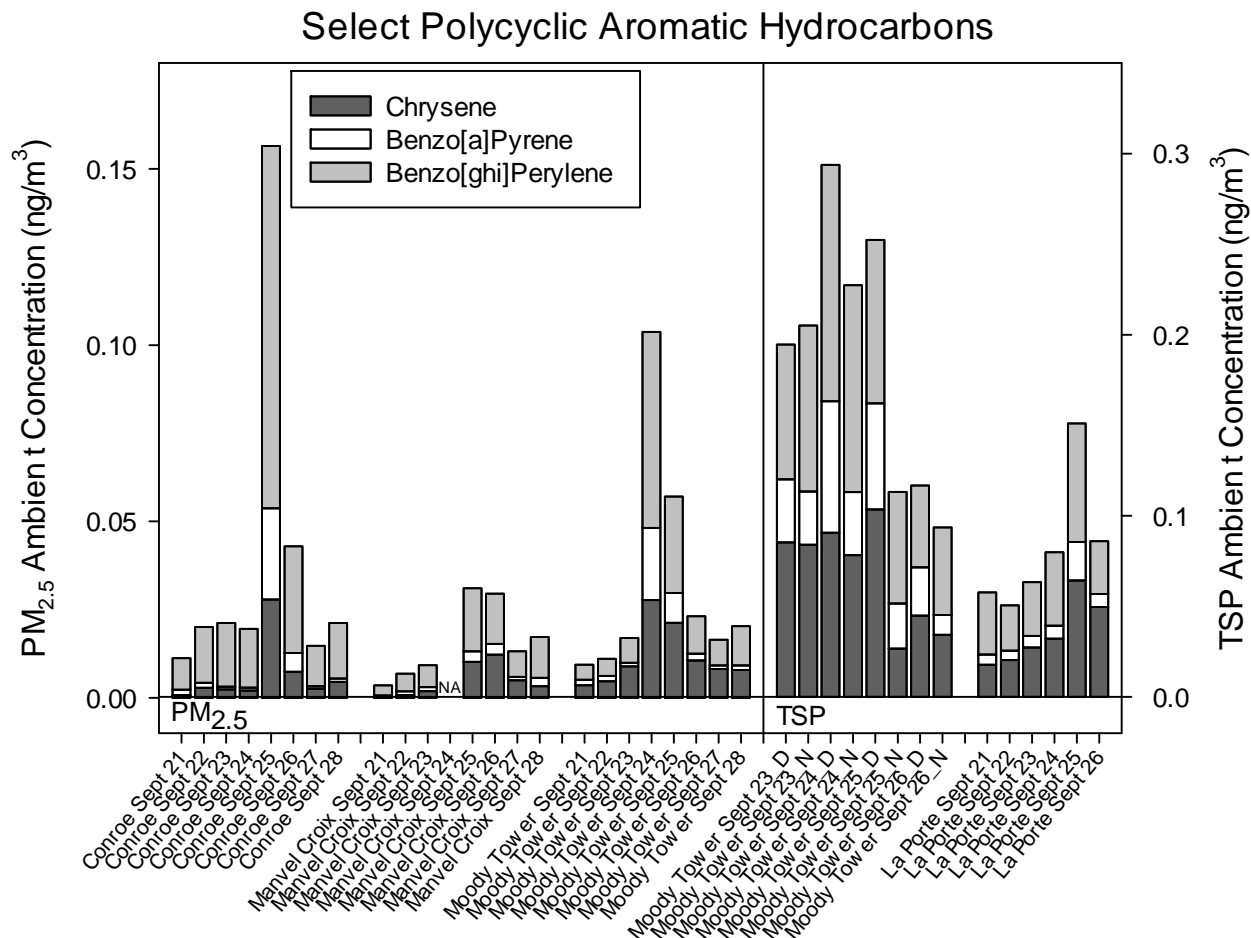
Figure 21. Ambient concentrations of PAHs (ng/m³) for Moody Tower, Manvel Croix, Conroe, and La Porte measured from PM$_{2.5}$ and TSP samples. Representative compounds are included for a range of molecular weights including 228 (chrysene), 252 (benzo[a]pyrene) and 276 (benzo[ghi]perylene). TSP and PM$_{2.5}$ are plotted on separate axis.

HV PM2.5 and TSP Samples- hopanes and steranes

Hopane and steranes are molecular markers for petroleum that can track emissions from vehicle sources. Similarly, to the alkanes and PAHs, average concentration of both hopane and sterane compounds were highest in the TSP samples. Moody Tower mean ambient concentrations (± standard deviation) of hopanes and steranes were 0.82 ±0.3 ng/m³ and 0.18 ±0.08 ng/m³, respectively. Average ambient hopane and sterane concentrations for La Porte were 0.55 ±0.17 ng/m³ and 0.11 ±0.05 ng/m³, respectively. Hopane and sterane concentrations for HV PM$_{2.5}$ were in order from Moody Tower (0.32 ±0.1 and 0.06 ±0.02 ng/m³, respectively); Conroe (0.15 ±0.1 and 0.02 ±0.02

ng/m³, respectively); and Manvel Croix (0.02 ±0.01 and 0.13 ±0.04 ng/m³, respectively). The order of highest to lowest concentration levels at each site for the two compound classes were the same. Contribution of vehicle emissions was highest in Moody Tower, both size fraction samples, relative to the other three sites. This is in agreement with the fact that Moody Tower sampling site was an urban site in close proximity to many of the central highways in Houston.

Figure 22. Ambient concentrations of two hopanes (ng/m³) for Moody Tower, Manvel Croix, Conroe, and La Porte measured from HV PM₂.₅ and TSP samples. TSP and HV PM₂.₅ are plotted on separate axis.

Levoglucosan is an organic tracer for biomass burning and was measured in all sites, and in both HV PM2.5 and TSP samples. Highest ambient concentrations (~350

ng/m3) were measured at La Porte (TSP 24 hours samples) on 9/24. The highest ambient concentrations measured in HV $PM_{2.5}$ samples were at Conroe (9/22 and 9/23) and were greater than 70 ng/m3. Average concentration of all HV $PM_{2.5}$ was 27.12 ng/m3. In comparison, this value is below levels measured of a similar study in Houston (sites included are Aldine, HRM-3 and La Porte) in 2000 (234.07 ng/m3) [19].
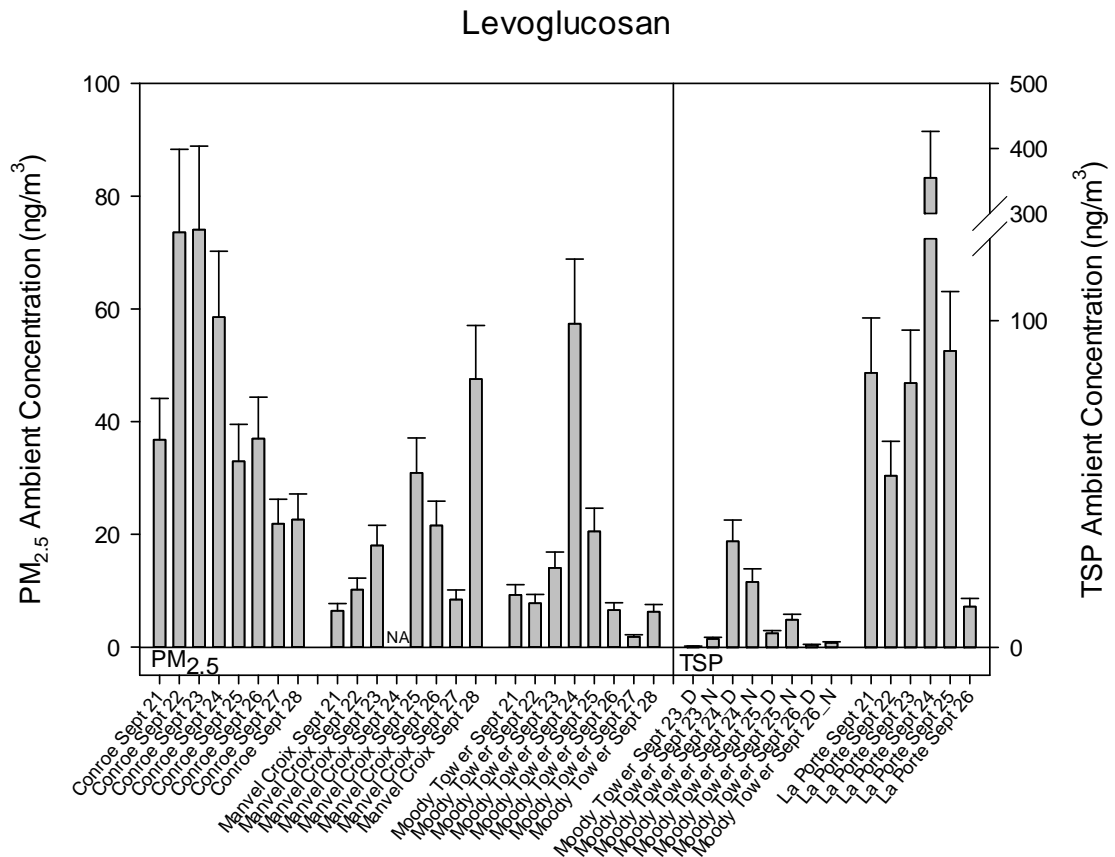
Figure 23. Ambient concentrations of levoglucosan (ng/m3) for Moody Tower, Manvel Croix, Conroe, and La Porte measured from HV PM2.5 and TSP samples. TSP and HV PM2.5 are plotted on separate axis.

Permethrin and malathion are commonly used to control adult mosquito populations and were detected at all four sites. Permethrin is a current-use pyrethroid pesticide, while malathion is a current-use organophosphate pesticide. These two pesticides were used in conjunction by Harris County in an alternating week usage pattern. Harris County officials identified 9/21 to 9/27 and 9/28 to 10/4 as Permethrin and Malathion usage week, respectively.

Permethrin was detected in 100% of PM samples analyzed at all four sites (week of September 21-28) with concentrations ranging from 0.025 to 60 ng/m^3 (Figure 24). Of these samples, the highest pesticide concentration was measured at 60 ng/m^3 on the 24th of September at the La Porte site. Permethrin was still detected at the two rural/suburban sites Conroe and Manvel Croix with concentrations ranging from 0.025 to 0.25 ng/m^3.

The transition from Permethrin to malathion was scheduled to occur on 9/27 or 9/28, however the highest concentration of malathion was measured on 9/26 (night sample) at 12000 pg/m^3 (Figure 25). Malathion is known to oxidize to malaoxon in the atmosphere with half-lives ranging from hours to days. Malaoxon is considerably more toxic than Malathion. The highest atmospheric concentrations of Malaoxon were detected at Moody Tower on 9/27 and 9/28 at approximately 12000 pg/m^3. Additionally, the Malaoxon to Malathion ratio was calculated as an indication of degradation of Malathion and atmospheric processing. Malaoxon to Malathion ratio measured at Conroe, La Porte, and Manvel Croix were significantly lower than ratios measured at Moody Tower (over 25 to 1). This suggest that applications of Malathion occurred near Moody Tower and that during the following days malathion was oxidized to malaoxon.

In addition three current-use pesticides, bifenthrin, λ-cyhalothrin, and chlorothalonil were frequently detected at all four sites (Figure 26). The most abundant pesticide was bifenthrin at La Porte on September 26th, with a concentration of over 1000 pg/m^3. Each site displayed different usage patterns, with bifenthrin being most used at all the sites except Conroe, which had higher amounts of λ-cyhalothrin. Measured atmospheric concentrations were less than Permethrin and Malathion.
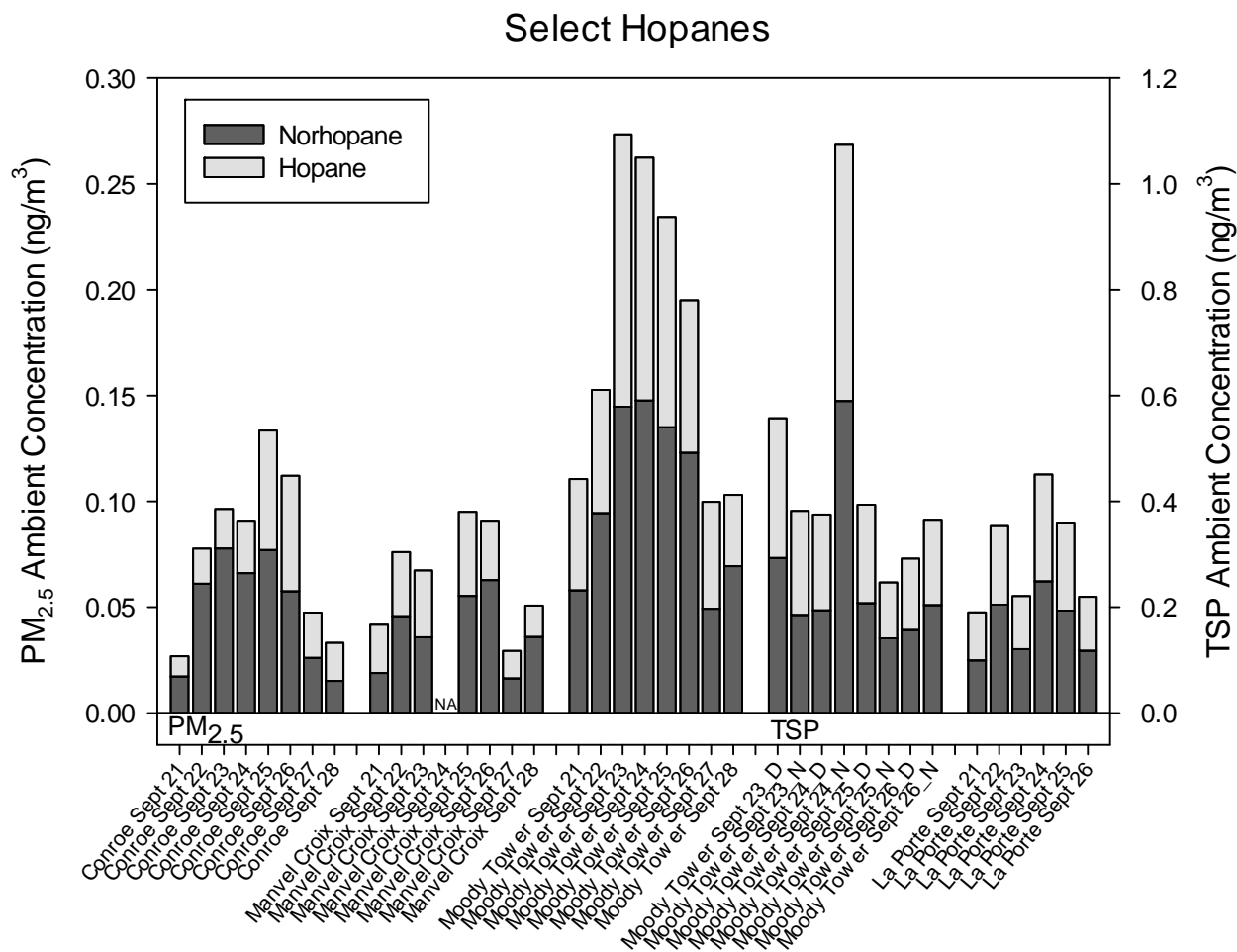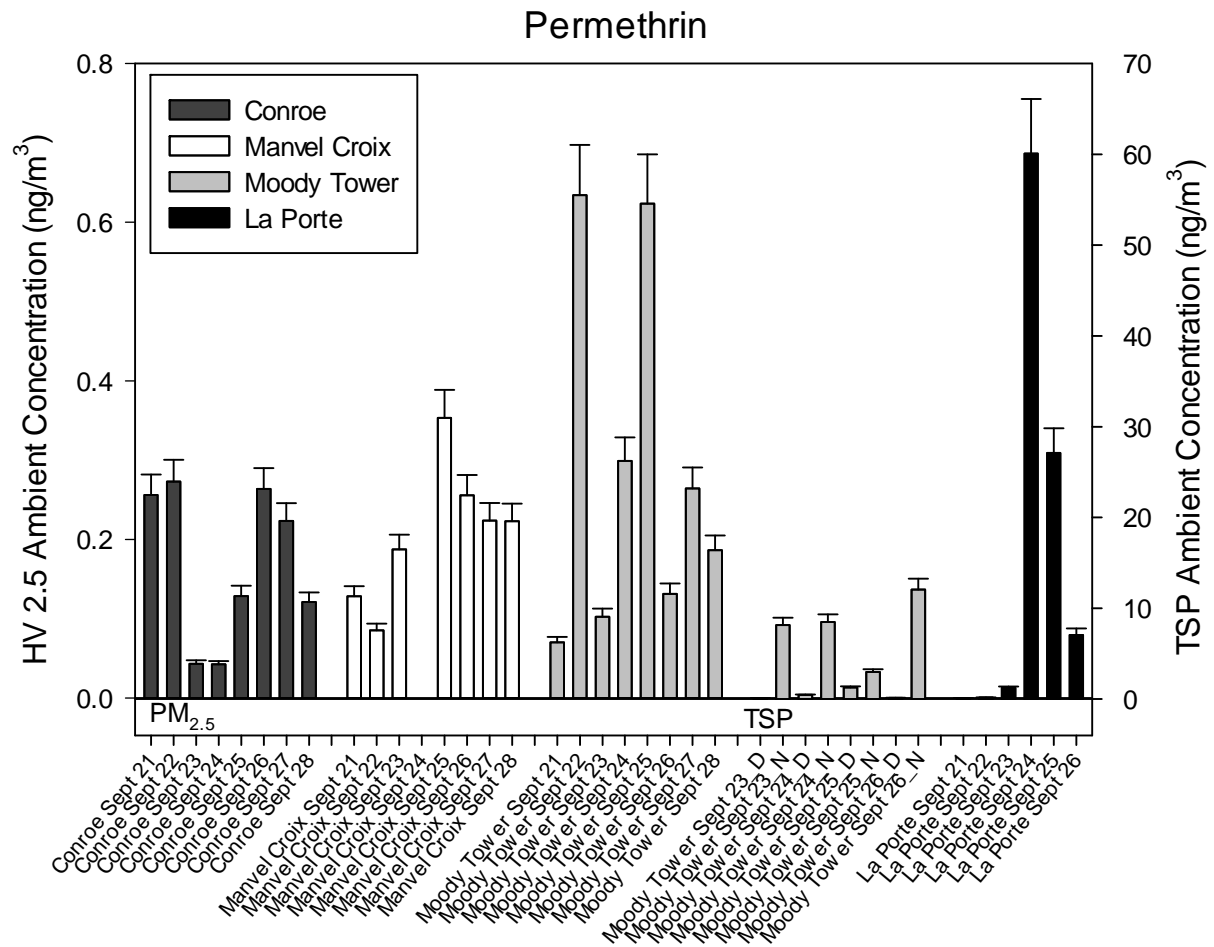
Figure 24. Ambient concentrations of Permethrin (ng/m³) at for Moody Tower, Manvel Croix, Conroe, and La Porte measured from HV PM₂.₅ and TSP samples.
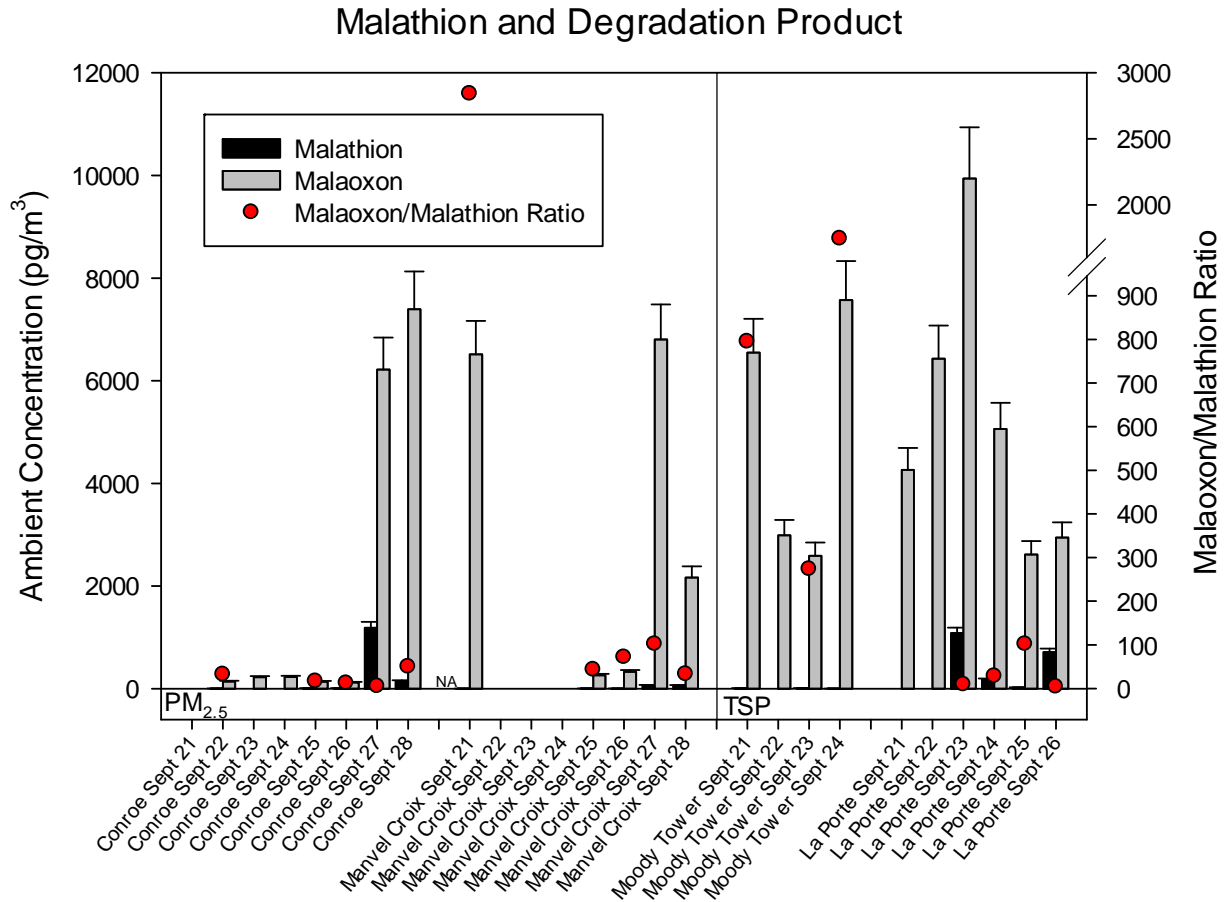
Figure 25. Ambient concentrations of Malathion and its degradation Malaoxon (pg/m³) at for Moody Tower, Manvel Croix, Conroe, and La Porte measured from HV PM₂.₅ and TSP samples. Malaoxon/Malathion ratios are also present highlighting different levels of atmospheric degradation.

ΣSelect Current-Use Pesticides
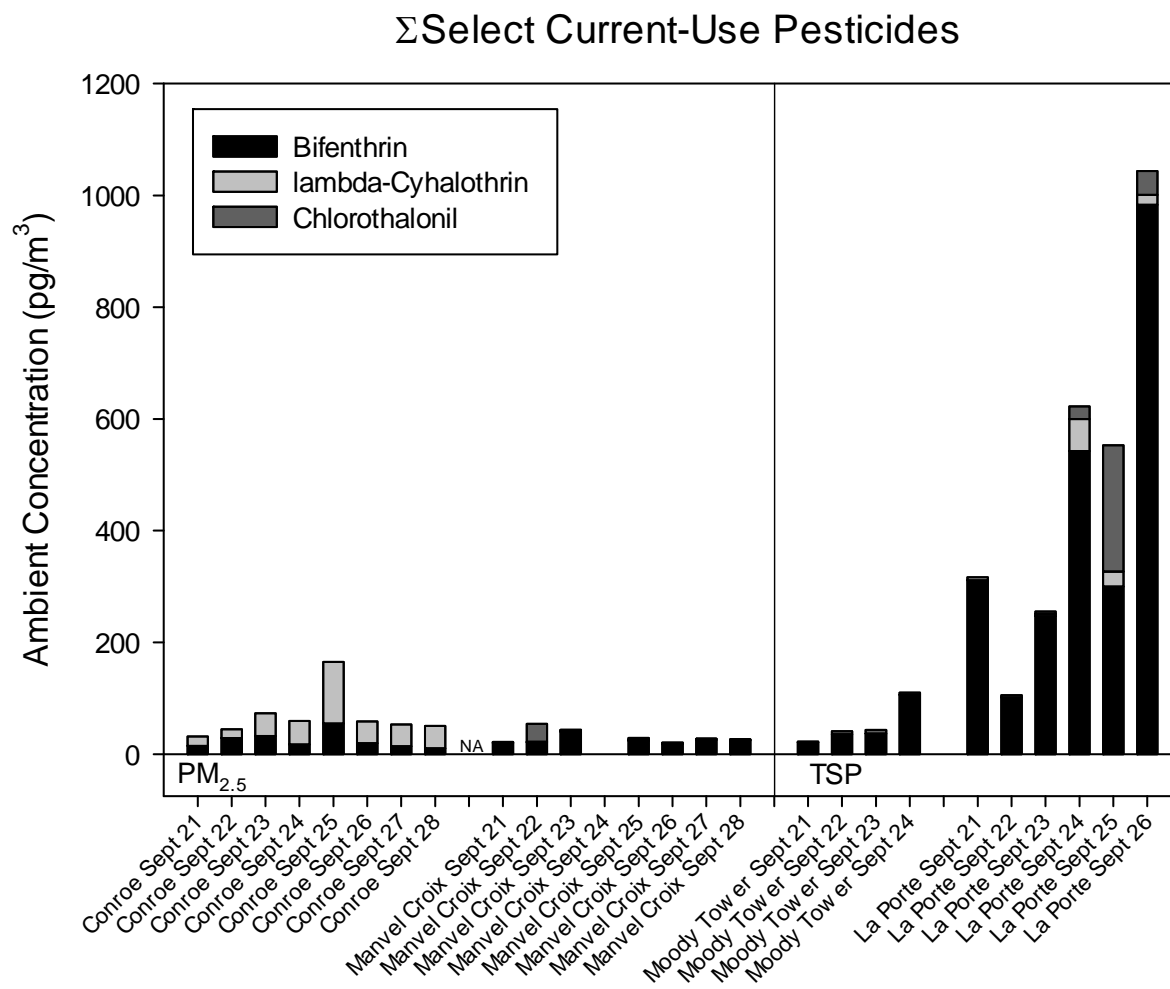
Figure 26. Ambient concentrations of Bifenthrin, lambda-Cyhalothrin, and Chlorothalonil (pg/m3) at for Moody Tower, Manvel Croix, Conroe, and La Porte measured from HV PM2.5 and TSP samples.

Organophosphate ester (OPEs), an emerging contaminant, were detected at all four sites. ΣOPEs atmospheric concentrations (HV PM$_{2.5}$ and TSP) ranged from 160 pg/m³to 3400 pg/m³. The four sites exhibited different OPE profiles of chlorinated (*tris* (2-chloroethyl)phosphate (TCEP), *tris* (1-chloro-2-propyl) phosphate (TCPP), and *tris* (1,3-dichloro-2-propyl) phosphate (TDCPP)) and non-chlorinated (triphenyl phosphate (TPP), *tris* (2-ethylhexyl) phosphate (TEHP), 2-ethylhexyl-di-phenylphosphate (EHDPP), tri-*n*-butyl phosphate (TBP)) congeners. Average atmospheric concentrations of ΣOPEs were calculated for all four sites (see Figure 27 for specific periods) For example, average atmospheric ΣOPEs concentrations (1,400 ± 600 pg/m³) for Moody Tower HV PM$_{2.5}$ were calculated from samples collected from 9/21 – 9/28.

Generally, for chlorinated congener concentrations, TCPP>TCEP>TDCPP, except at the Conroe site where TCPP>TDCPP>TCEP. Maximum TCPP (chlorinated congener) concentrations were seen in TSP samples taken at Moody Tower on the night of September 26th (over 2000 pg/m3). The chlorinated congeners are thought to have a shorter atmospheric half-life than the non-chlorinated congeners, and can be used to indicate plume age. Non-chlorinated congeners detected at all four sites provided no specific trends and the most abundant congener varied from site-to-site. The highest concentration of a non-chlorinated congener was TPP measured at Moody Tower in a TSP sample on the day of September 23rd (over 2300 pg/m3). Results were normalized to the mass of organic carbon in each sample and showed similar results to non-normalized atmospheric concentrations (Figure 28).

Preliminary results from this study were compared to a Great Lakes study by Salamova et al [20] that examined atmospheric OPE concentrations and profiles (chlorinated to non-chlorinated OPEs). The average atmospheric concentrations and fraction of chlorinated OPE congeners was calculated for the Great Lake study using 1 in 6 day 24 hours TSP samples from March 2012 to December 2012 (Figure 27). Atmospheric concentrations of ΣOPE for six overlapping congeners (2,000 ± 700 pg/m3) at Moody Tower (9/23 – 9/26) is more than 1.5 times higher than atmospheric ΣOPE concentrations reported in Chicago (1,300 ± 200 pg/m3) and similar to atmospheric ΣOPE concentrations reported in Cleveland (1,900 ± 300 pg/m3, urban site).[20] At La Porte, the average atmospheric concentrations of ΣOPE for six overlapping congeners (1,200 ± 400 pg/m3) are similar to Chicago.[20] The average fraction of chlorinated OPE congeners calculated at Moody Tower and La Porte (TSP samples) were similar to average fraction of chlorinated OPEs measured in Chicago (an urban area).[20]
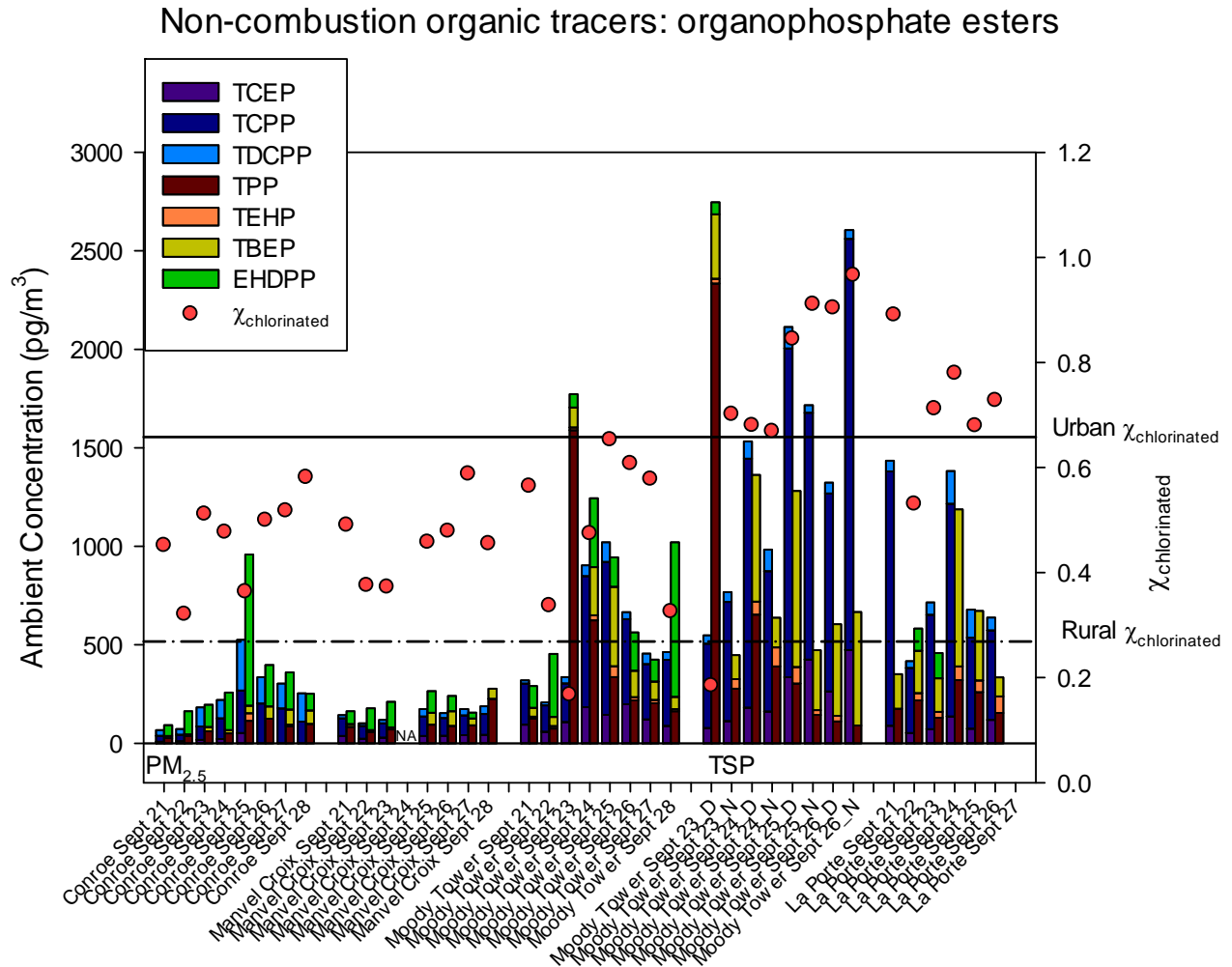
Figure 27. Ambient concentrations of OPEs (pg/m³) across Houston Ambient at for Moody Tower, Manvel Croix, Conroe, and La Porte measured from HV PM₂.₅ and TSP samples. Red circles describe the fraction of OPE that were chlorinated with the sample (y-axis). The solid and dashed horizontal line describes the fraction chlorinated determined in an urban site (Chicago, IL) and a remote site (Eagle Harbor, MI) [20].

Non-combustion organic tracers: organophosphate esters
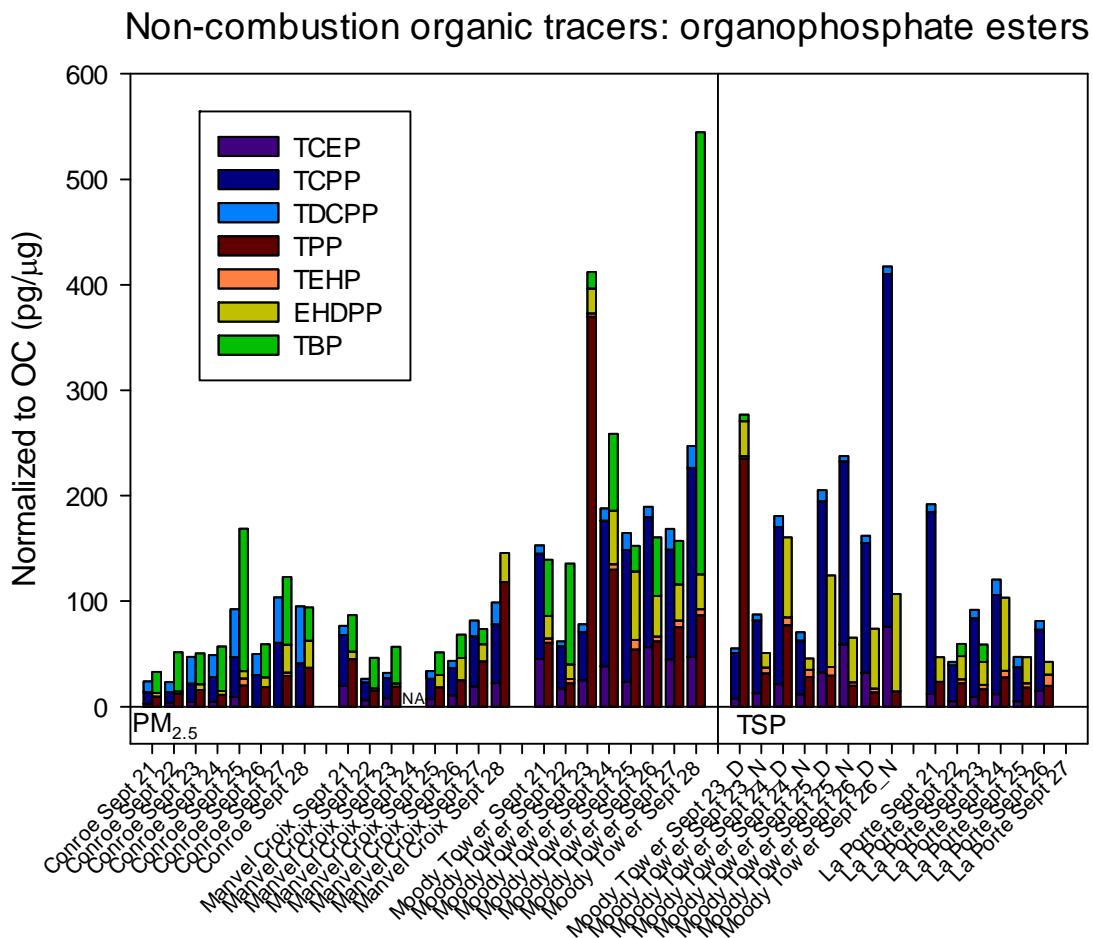
Figure 28. Ambient concentrations of OPEs normalized to the mass of organic carbon (pg/μg). Ambient concentrations for Moody Tower, Manvel Croix, Conroe, and La Porte measured from HV PM₂.₅ and TSP samples.

Deliverable 6: Radiocarbon Measurements

Radiocarbon measurements were made on samples collected from all four ground-based sites during 9/21-9/28.

Overview: Samples from 9/21-28/13 from Moody Tower, Manvel Croix, Conroe and La Porte were prepped at Baylor University as described in the Analytical Methods and radiocarbon analysis was performed by NOSAMS (Figure 29).

Results: A total of 50 particulate matter samples were analyzed for radiocarbon analysis including 4-24 hour samples. These included PM₂.₅ and TSP samples from Moody Tower, Manvel Croix, Conroe and La Porte (see Table 2). All results have been blank

subtracted using field blanks for each filter type. The field blanks represented < 25% of the submitted mass for all samples, averaging 8% of the submitted TOC. The contemporary end member that was utilized for the current study was an average of woodsmoke and biogenic ($\Delta^{14}C$ = 67.5 ‰)[21]. Contemporary TOC includes biomass burning, primary biogenic particulate emissions and secondary biogenic and biomass burning organic aerosol. The range in fraction contemporary for TOC is as follows for $PM_{2.5}$: 48-78% for Moody Tower, 59-86% for Manvel Croix, 66-89% for Conroe. The range in fraction contemporary for TOC is as follows for TSP: 51-65% for Moody Tower and 51-83% for La Porte. These results are plotted in Figure 29. Conroe consistently has the highest contribution from contemporary TOC in the $PM_{2.5}$. Moody Tower consistently has the lowest contemporary TOC contribution in $PM_{2.5}$ and TSP. La Porte has the widest range in contemporary TOC contribution during the last week of the campaign. Additional discussion is included in Deliverable 8.
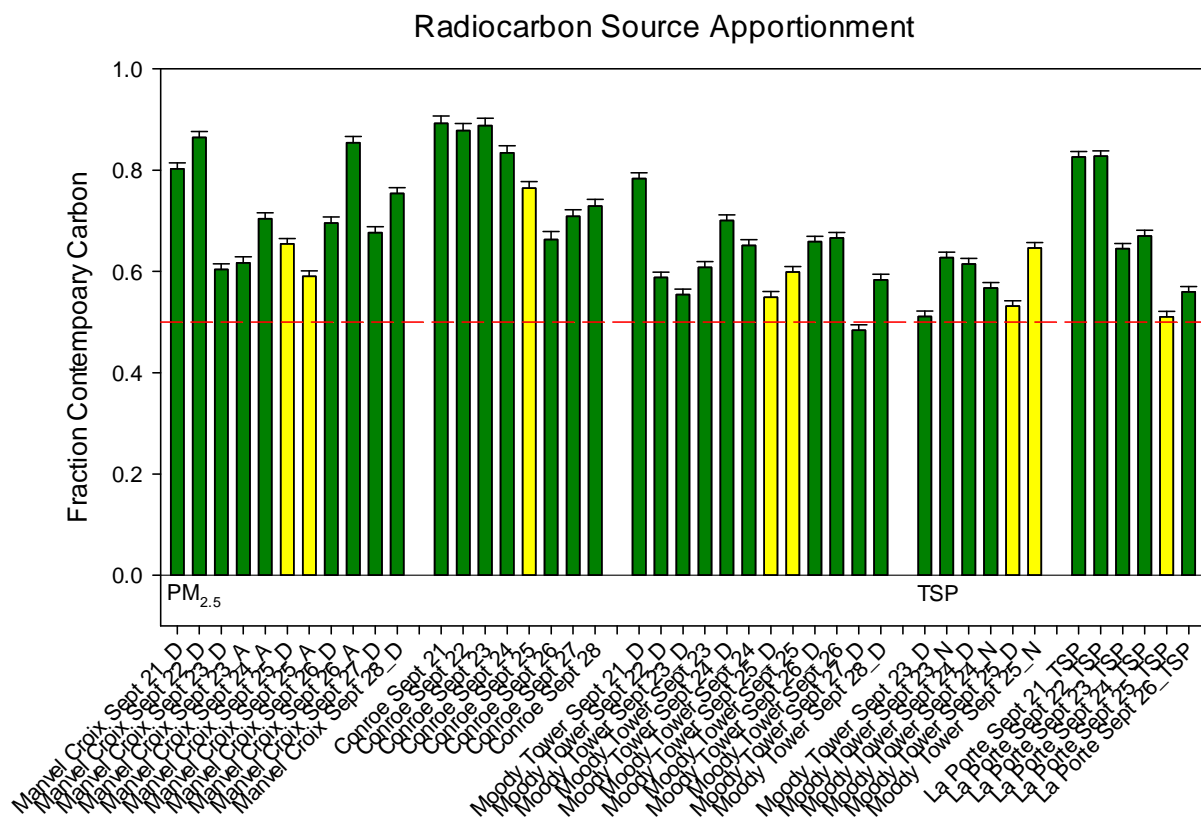
Figure 29. Fraction of contemporary organic carbon determined using ^{14}C measurements. "D" denotes day sample collected from 6:30 to 20:00. "A" denotes afternoon sample collected from 10:00 to 20:00. Yellow bars indicate samples were collected on September 25th. Red dashed line denotes the 50 percent line.

Deliverable 7: Chemical Mass balance Modeling

Organic tracers and select elemental tracers will be used to apportion the POA at each site by molecular marker chemical CMB using known profiles.

Overview: Organic and elemental tracer ambient concentrations were combined to model contribution of primary emission sources of organic carbon at Moody Tower, Manvel Croix, Conroe, and La Porte during the week of 9/21-28/13. This was accomplished with the Chemical Mass Balance Model (EPA v8.2) and primary emission source profiles from the literature[22-25] (Figure 30-33).

Results: As with the organic tracer analysis, the initial runs of the CMB model were completed with 9/11-9/14 samples. For the model runs, hopanes, polycyclic aromatic hydrocarbons, alkanes, levoglucosan and elemental carbon were used as tracers. The elemental tracers had inconsistent detection for the 9/21-28/13 and were not included in the modeling. The final model input included three motor vehicle profiles (diesel-powered motor vehicle exhaust, gasoline-powered motor vehicle exhaust and lubricating oil-impacted motor vehicle exhaust) which were all reported in Lough and Schauer [22]. These three were summed to give the total primary motor vehicle emission contribution as the lubricating oil exhaust can include contributions from visible smokers that are both gasoline- and diesel-powered [23]. The wood smoke profile used in this study was reported in Fine et al [24]. Vegetative detritus was reported by Rogge et al [25]. The profiles were originally defined for $PM_{2.5}$ and were used in this project for both $PM_{2.5}$ and TSP. Combustion emissions are dominated by fine particles, however there is a potential for underestimation of source contribution to TSP using this assumption. All TSP results should be considered lower bounds for source contributions. To determine model performance, fitting statistics including the r^2 and χ^2 were monitored. For all runs, r^2 averaged 0.75 ± 0.09 and χ^2 averaged 6.15 ± 2.32. The percent mass apportioned ranged from 12-52%, with an average of 23% (Figure 31 and 33). CMB data is included in the Appendix.
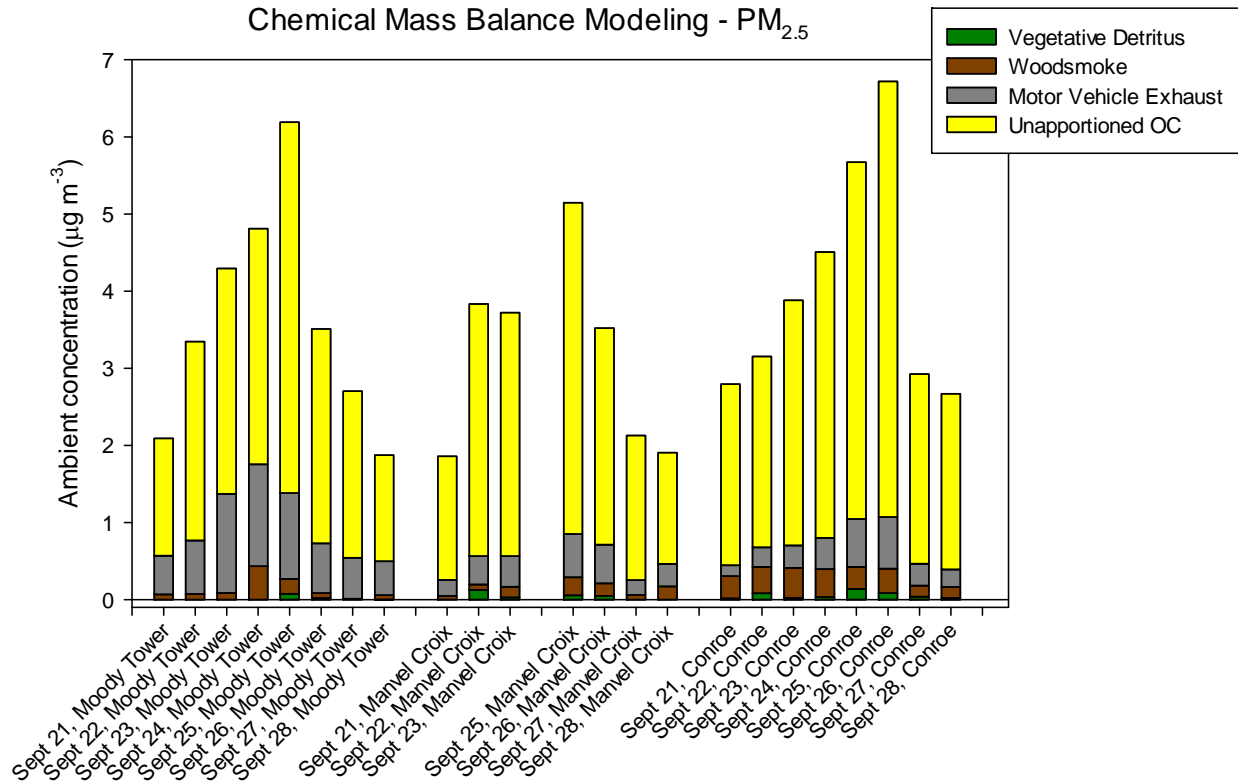
Figure 30. Apportioned and unapportioned organic carbon modeled using the Chemical Mass Balance model (OC fraction of PM$_{2.5}$). Ambient concentrations (µg/m³) for Moody Tower, Manvel Croix, and Conroe are presented.
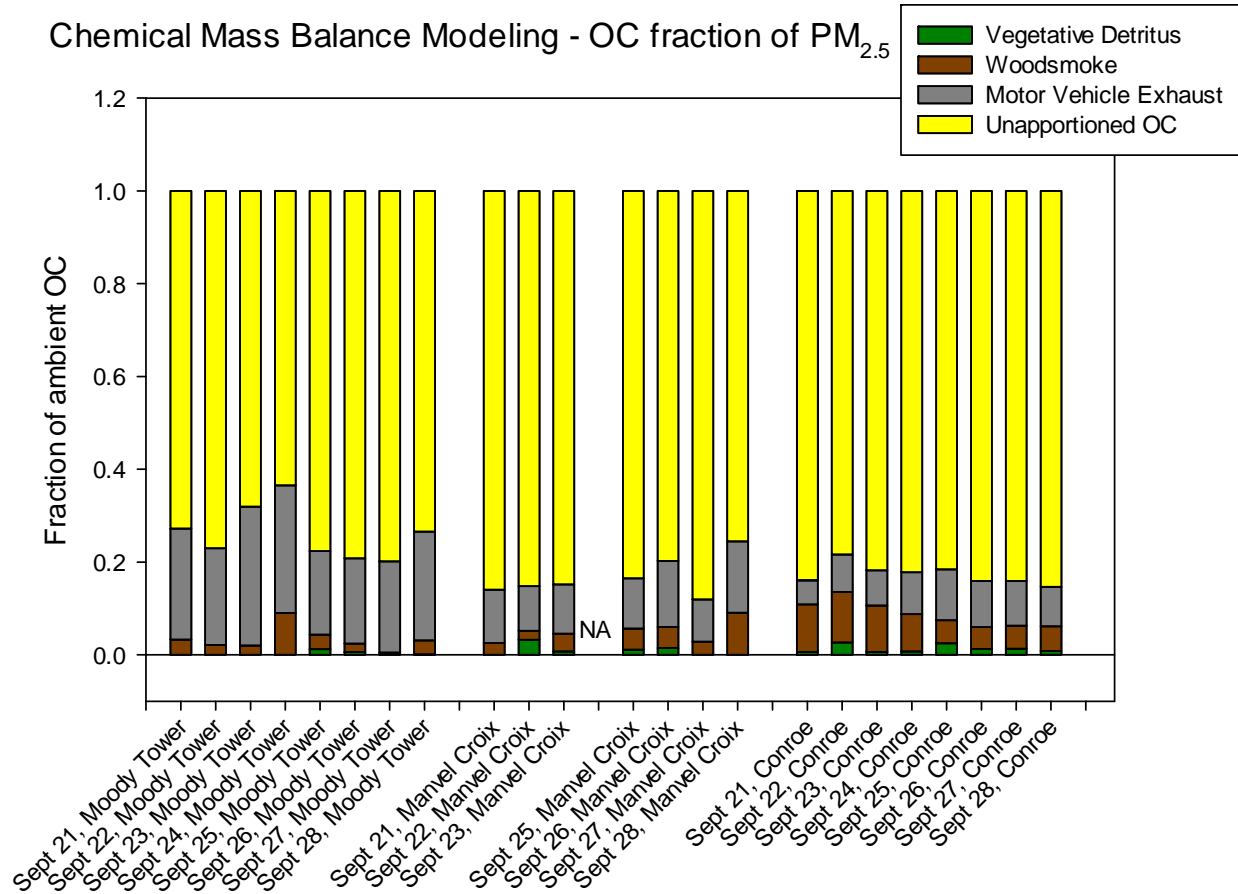
Figure 31. Fraction of apportioned and unapportioned organic carbon modeled for Moody Tower, Manvel Croix, and Conroe using the Chemical Mass Balance model (OC fraction of PM$_{2.5}$).
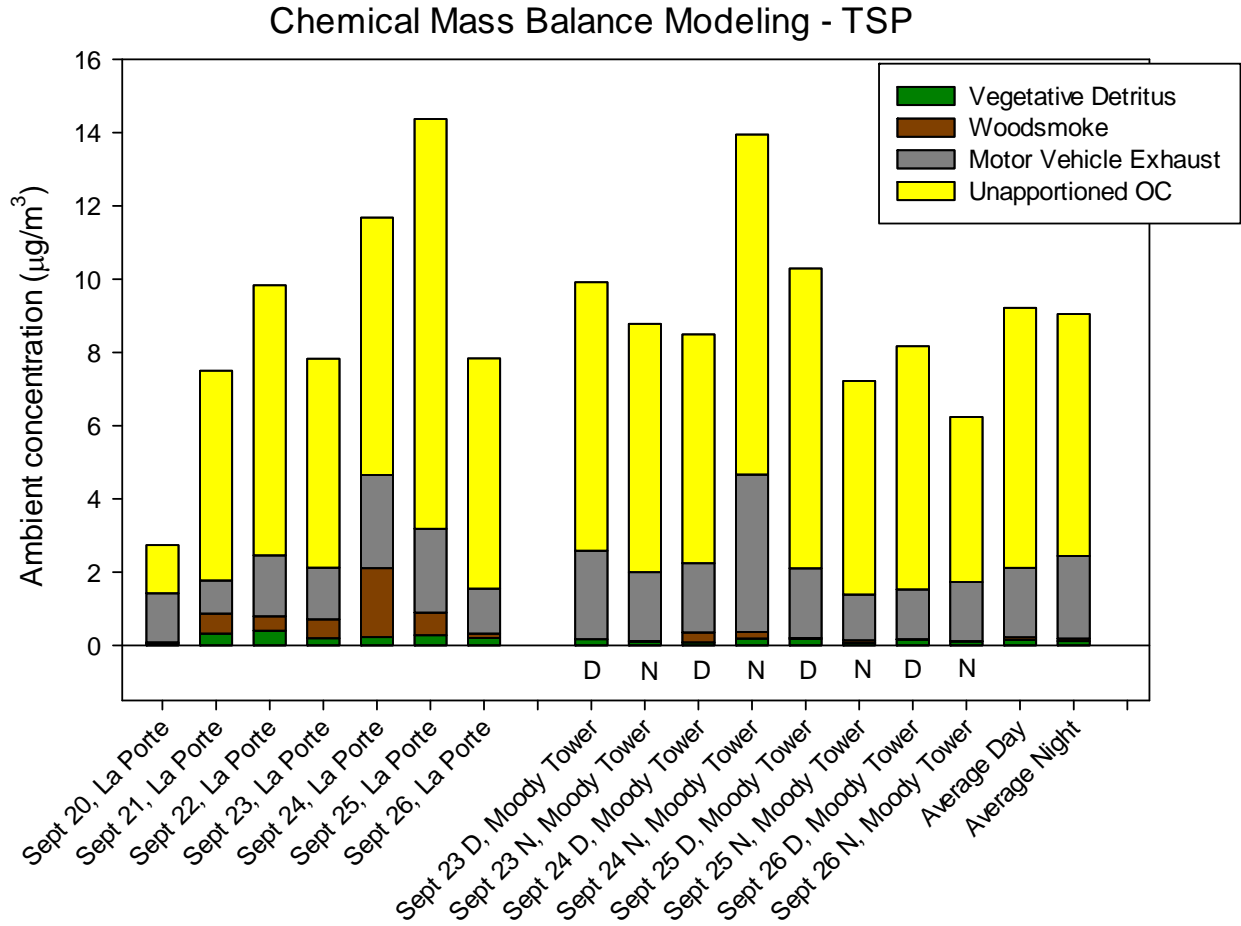
Figure 32. Apportioned and unapportioned organic carbon modeled using the Chemical Mass Balance model (TSP). Ambient concentrations (μg/m³) for Moody Tower and La Porte are presented. "D" denotes day sample collected from 6:30 to 20:00. "N" denotes night samples collected from 20:00 to 6:30.
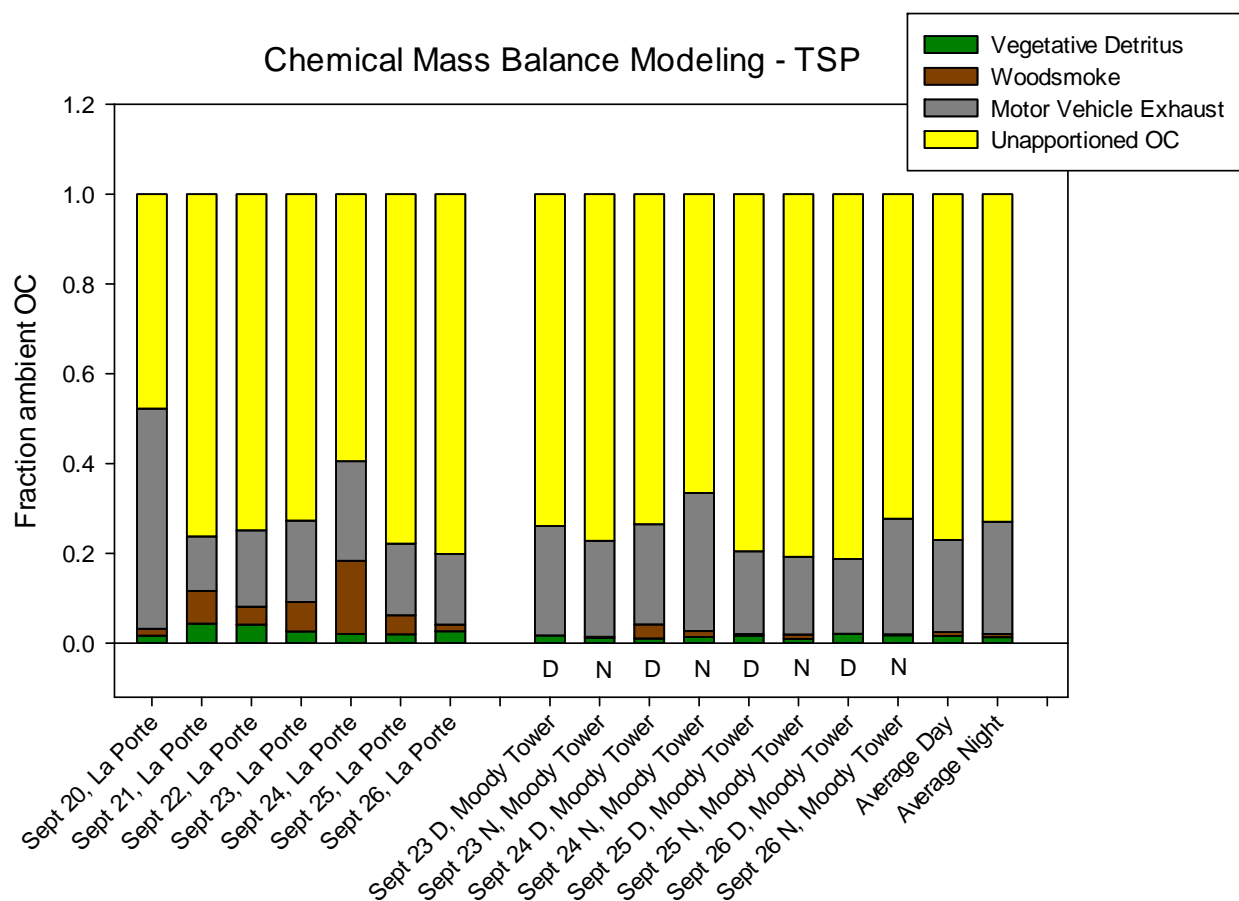
Figure 33. Fraction of apportioned and unapportioned organic carbon modeled for Moody Tower and La Porte using the Chemical Mass Balance model (PM$_{2.5}$). "D" denotes day sample collected from 6:30 to 20:00. "N" denotes night samples collected from 20:00 to 6:30.

Deliverable 8: Fossil Combustion-Derived Primary Organic Aerosol

Fossil combustion-derived POA constrained by radiocarbon analysis

Overview: The radiocarbon results for 9/21-28/13 samples from Moody Tower, Manvel Croix, Conroe and La Porte are utilized for radiocarbon source apportionment (Figure 34-39). The radiocarbon source apportionment gives a definitive split between fossil and contemporary carbon sources. Fossil sources of atmospheric carbon in PM$_{2.5}$ and TSP include all types of primary fossil fuel combustion and SOA produced in the atmosphere from fossil-derived volatile organic carbon. Contemporary sources of atmospheric carbon in PM$_{2.5}$ and TSP include primary biogenic emissions, biomass combustion and SOA produced in the atmosphere from biogenic- and biomass combustion-derived volatile organic carbon.

Results: ^{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 are used to define biogenic vs. wood smoke split. The levoglucosan-based estimate of the concentration of OC from biomass burning plus the alkane-based estimate of vegetative detritus is subtracted from the radiocarbon-derived concentration of contemporary carbon to quantify the biogenic SOA contribution. The organic tracer-based estimate of primary motor vehicle exhaust contribution to OC is subtracted from the radiocarbon-derived concentration of fossil carbon to quantify the fossil carbon-derived SOA. This combination of CMB and ^{14}C source apportionment gives an upper bound to the biogenic and fossil SOA estimate at each site during a week of high photochemical activity.
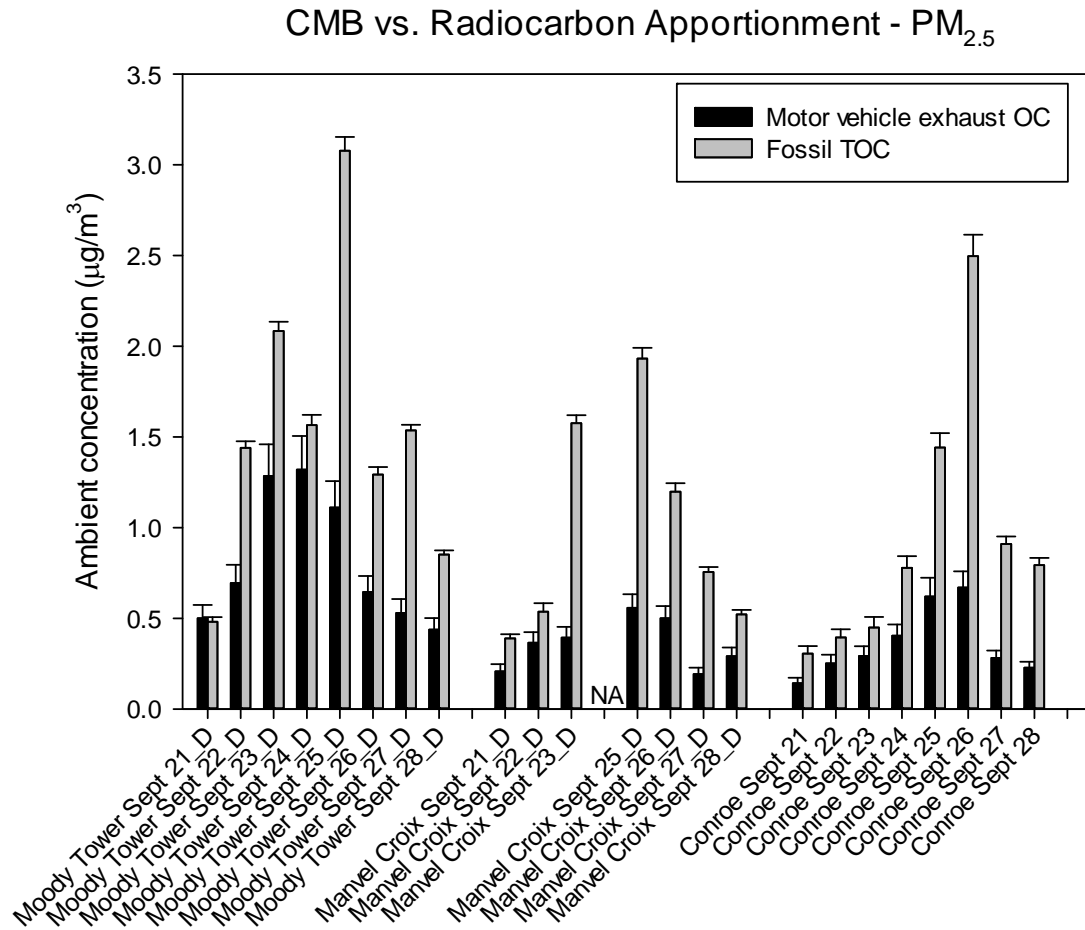
Figure 34. A comparison of apportioned fossil organic carbon (PM$_{2.5}$) using CMB and radiocarbon. Comparison presented for Moody Tower, Manvel Croix, and Conroe in terms of ambient concentrations (μg/m³). "D" denotes day sample collected from 6:30 to 20:00. Error bars denote the uncertainty in (μg/m³).
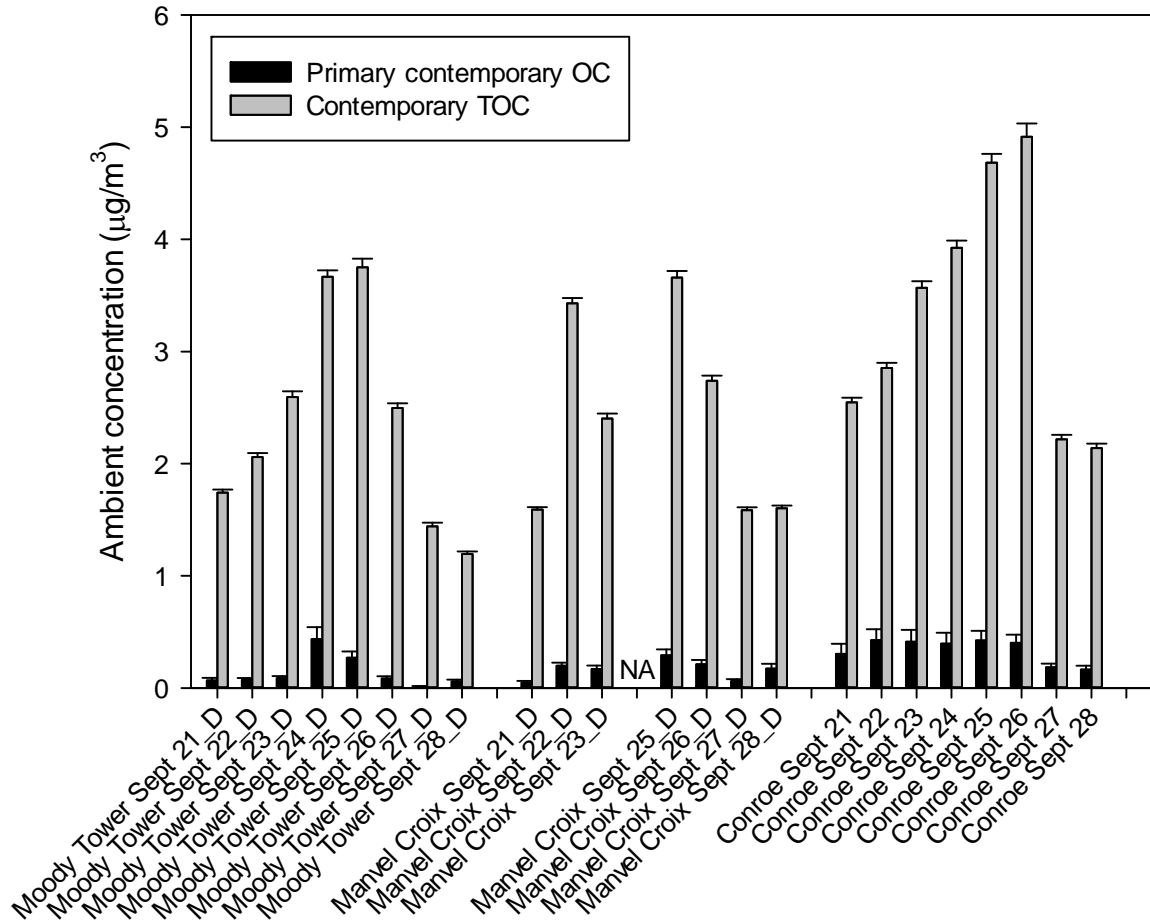
Figure 35. A comparison of apportioned contemporary organic carbon (PM$_{2.5}$) using CMB and radiocarbon. Comparison presented for Moody Tower, Manvel Croix, and Conroe in terms of ambient concentrations (µg/m³). "D" denotes day sample collected from 6:30 to 20:00. Error bars denote the uncertainty in (µg/m³).
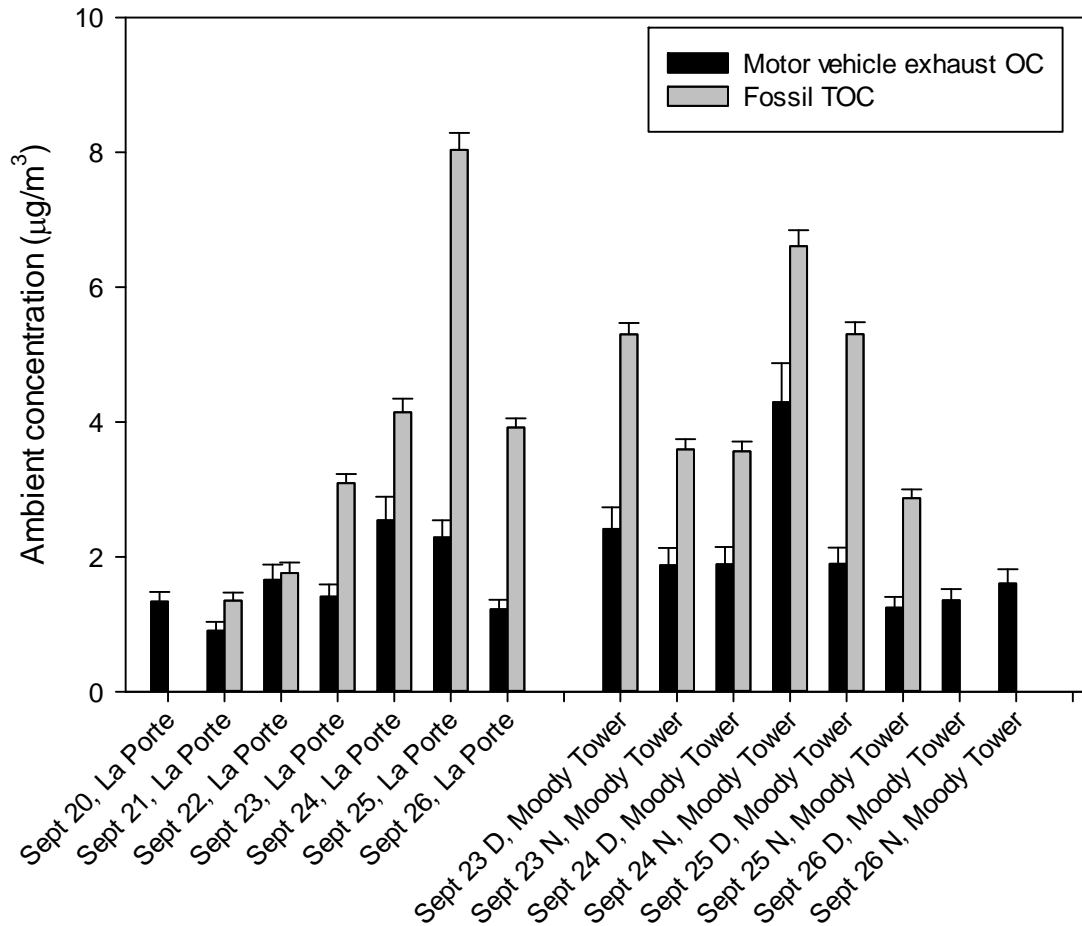
Figure 36. A comparison of apportioned fossil organic carbon (TSP) using CMB and radiocarbon. Comparison presented for Moody Tower and La Porte in terms of ambient concentrations (μg/m³). "D" denotes day sample collected from 6:30 to 20:00. "N" denotes night samples collected from 20:00 to 6:30. Error bars denote the uncertainty in (μg/m³).
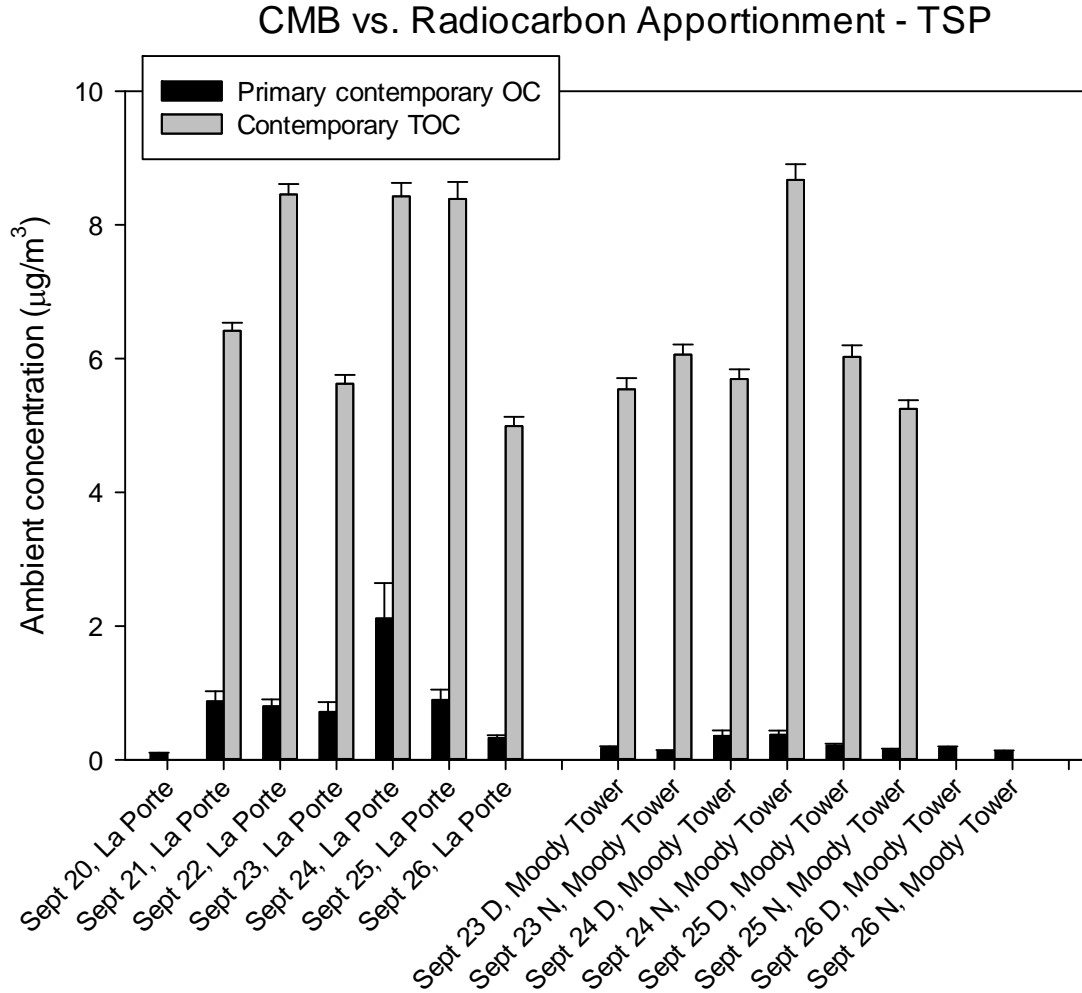
Figure 37. A comparison of apportioned contemporary organic carbon (TSP) using CMB and radiocarbon. Comparison presented for Moody Tower and La Porte in terms of ambient concentrations (μg/m³). "D" denotes day sample collected from 6:30 to 20:00. "N" denotes night samples collected from 20:00 to 6:30. Error bars denote the uncertainty in (μg/m³).
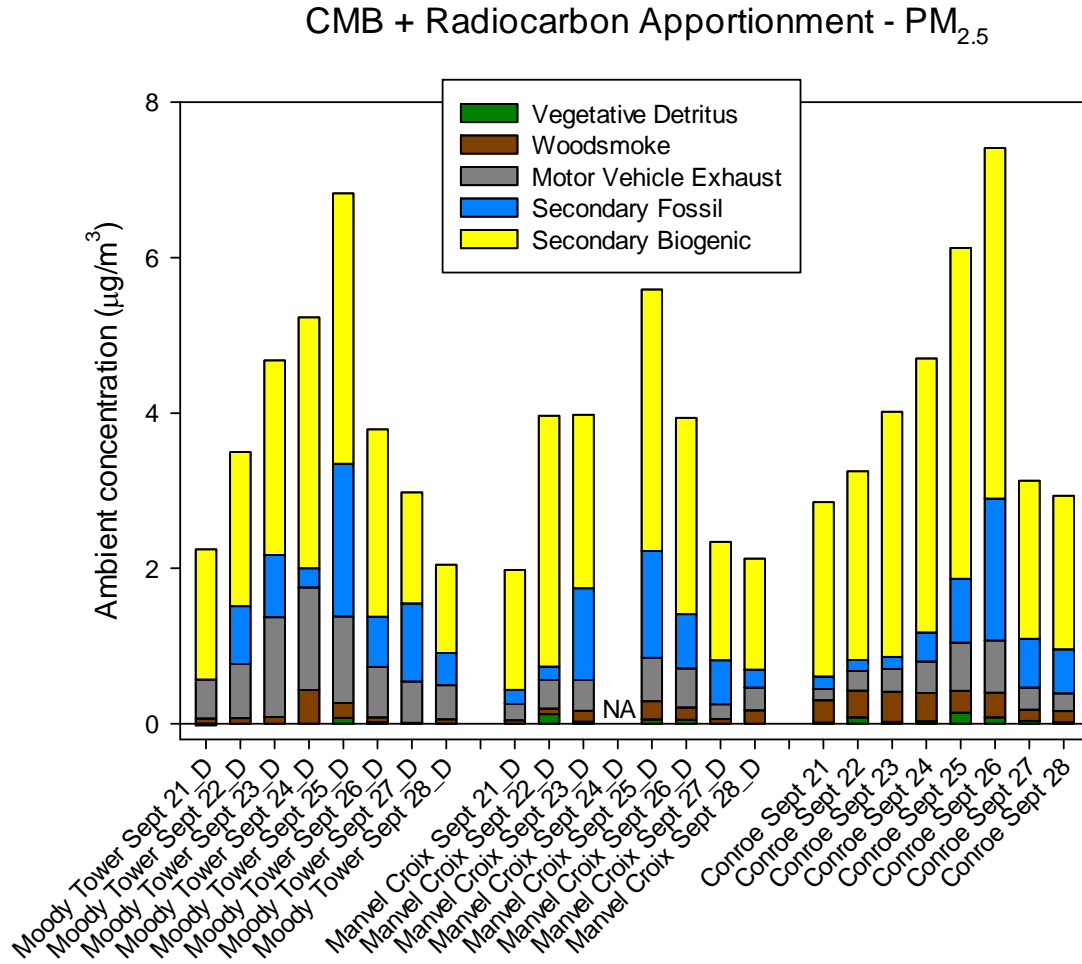
Figure 38. Apportioned primary and secondary organic carbon modeled using the Chemical Mass Balance model and radiocarbon (PM$_{2.5}$). Ambient concentrations (μg/m³) for Moody Tower, Manvel Croix, and Conroe are presented. "D" denotes day sample collected from 6:30 to 20:00.
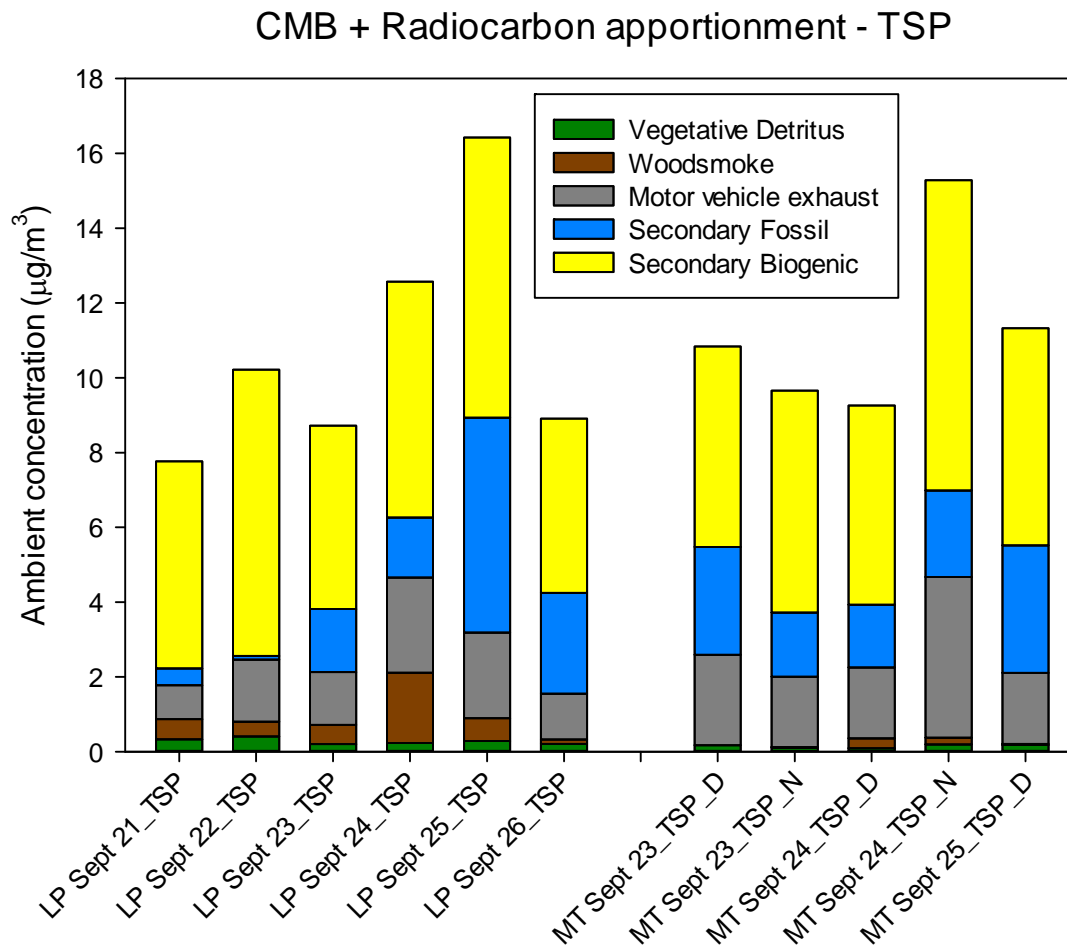
Figure 39. Apportioned primary and secondary organic carbon modeled using the Chemical Mass Balance model and radiocarbon (PM$_{2.5}$). Ambient concentrations (μg/m³) for Moody Tower and La Porte are presented. "D" denotes day sample collected from 6:30 to 20:00. "N" denotes night samples collected from 20:00 to 6:30.

Deliverable 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 CMB modeling to examine the efficacy of regulatory efforts and fleet modernization.

Overview: The CMB model results from the current study were compared with results from 1997-98 study[28] to characterize which primary emission sources achieved reductions in contribution to ambient PM$_{2.5}$ (Figure 40-41).

Results: The organic carbon CMB modeling from Deliverable 7 was transformed to source apportionment of total PM$_{2.5}$ mass using the OC to PM$_{2.5}$ ratios from the source profiles; this method has been utilized in previous published studies including the 1997-98 study defined in the 14-029 proposal and work plan [26-28]. Briefly, source profiles are normalized to OC emissions for CMB modeling. To transform results to PM$_{2.5}$, the reported ratios of OC/PM$_{2.5}$ from the emission profiles are used to scale up the OC contributions to PM$_{2.5}$ contributions. In this section of the project, the motor vehicle exhaust sources are listed separately to enable better comparison with the 1997-98 study[28] (Figure 41). The three motor vehicle exhaust sources are: Diesel exhaust, gasoline exhaust and lubricating oil-impacted exhaust. Nominally speaking, the diesel exhaust source is dominated by elemental carbon. It has been recently shown that lubricating oil is a common factor in the OC emissions across both gasoline and diesel-powered motor vehicles with visible plumes [23]. The lubricating oil exhaust source represents this source.

Chemical Mass Balance Modeling of total PM$_{2.5}$ mass
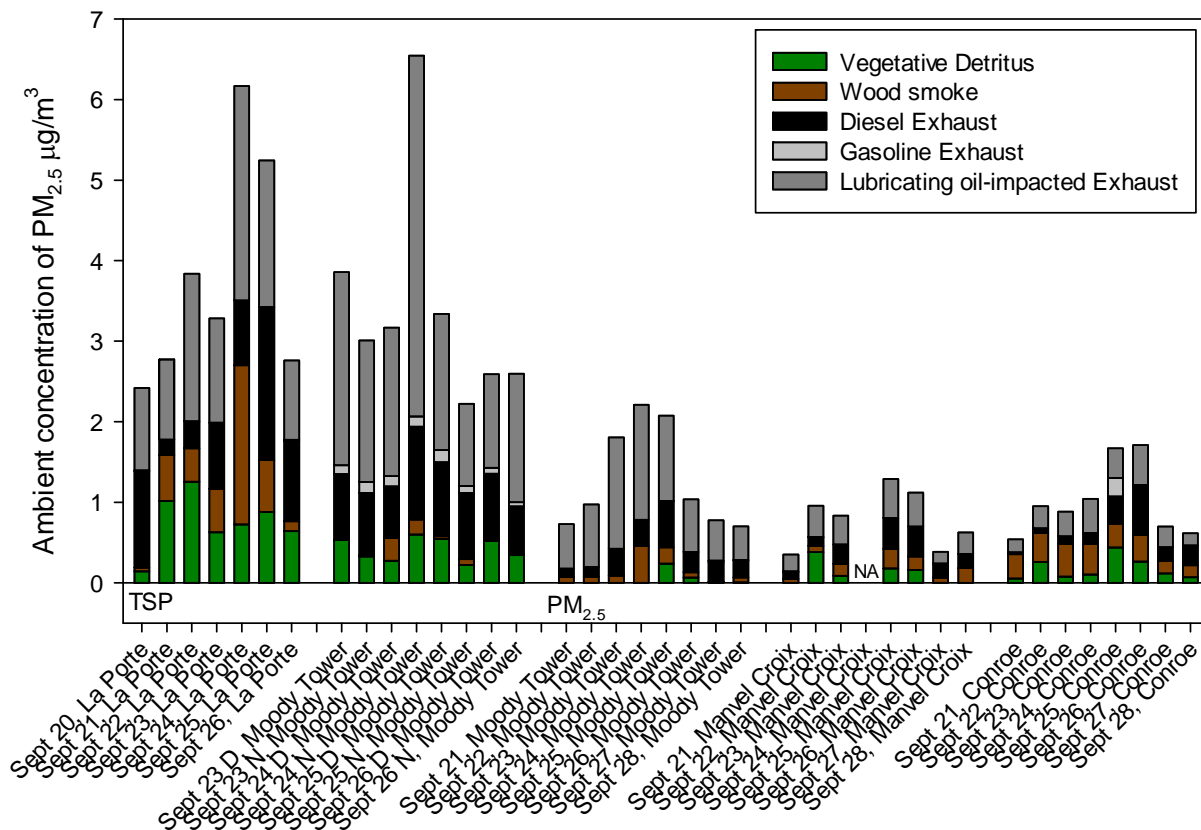
Figure 40. CMB modeling of primary OC transformed to contributions to PM$_{2.5}$ mass using source profiles for La Porte, Moody Tower, Manvel Croix and Conroe.
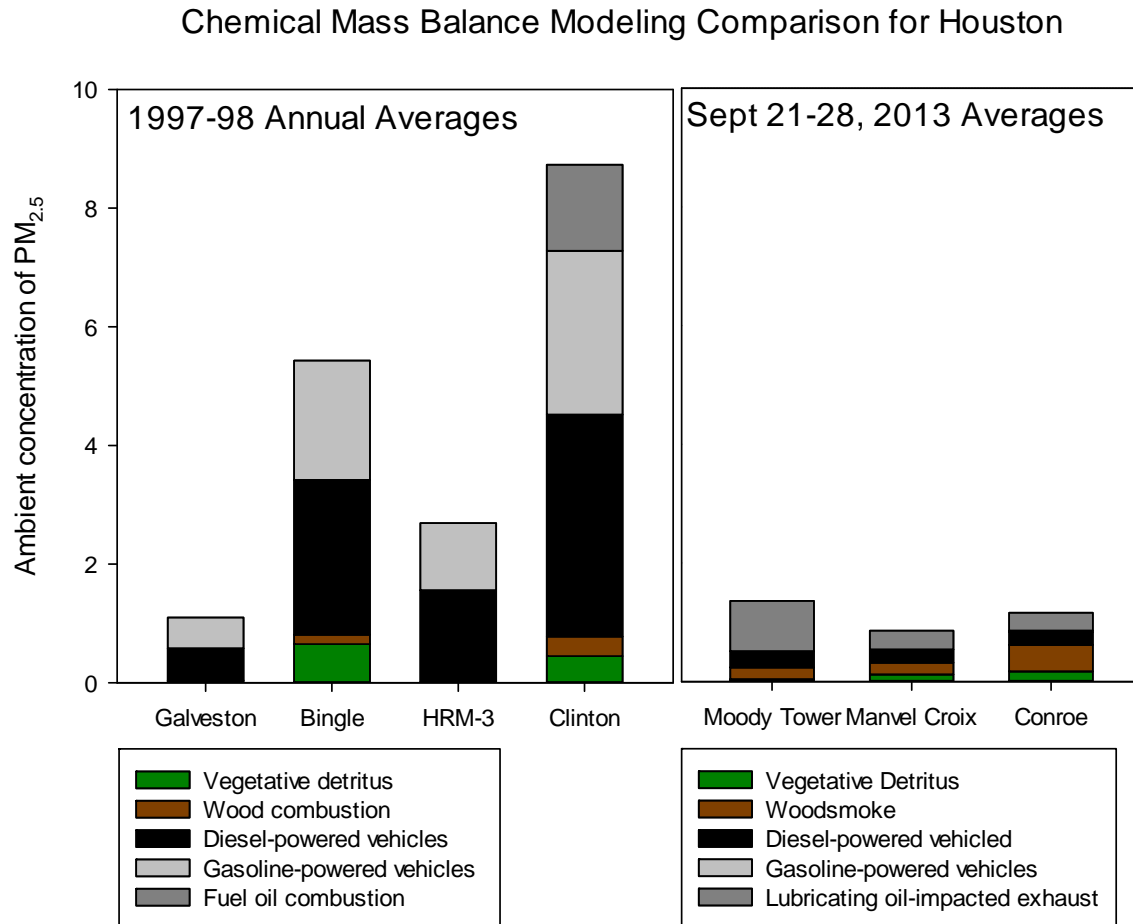
Figure 41.

Figure 41. Comparison of CMB modeling of OC transformed to PM$_{2.5}$ for an annual average of four Houston metro area sites in 1997-98 (Galveston, Bingle, HRM-3 and Clinton Avenue) and Sept 21-28, 2013 (Moody Tower, Manvel Croix and Conroe). The 1997-98 CMB includes Fuel oil combustion, while the 2013 CMB includes a lubricating oil-impacted motor vehicle exhaust profile.

The CMB modeling for Sept, 2013 PM2.5 at three sites in Houston were compared with the results of CMB modeling done for four sites in Houston in 1997-98 by Fraser et al [28](Figure 41). In the Fraser et al study [28], published in 2003 based on data from 1997-98, 2-9 µg/m³ of $PM_{2.5}$ were apportioned to the following primary sources: vegetative detritus, wood combustion, diesel-powered motor vehicle exhaust, gasoline-powered motor vehicle exhaust and fuel oil combustion. Additional sources including meat cooking and paved road dust were reported but are not included here.   These are compared to vegetative detritus, wood combustion, diesel-powered motor vehicle exhaust, gasoline-powered motor vehicle exhaust and lubricating oil-impacted motor vehicle exhaust for the 2013 study reported here. There were large reductions in motor vehicle exhaust compared to all three 1997-98 Houston sites. For 2013, only 0.9 to 1.4 µg/m³ are apportioned to primary sources, with motor vehicles representing 0.5 to 1.1 µg/m³. In contrast, there is no reduction in the wood smoke contribution. Future sampling and analysis efforts are needed to understand the full annual reduction of source impacts due to primary emissions.

Deliverable 10: Complement on-going PM characterization efforts at TCEQ monitoring sites by increasing the spatial extent and specificity of carbon apportionment.

Overview: OC and EC concentrations determined in the current study were combined with available results from TCEQ for Clinton Drive (Houston), Galveston and Deer Park. For the spatial intercomparison in the current study, the TOT carbon results for OC and EC were used (Figures 42-44).

Results:

TOR results for Moody Tower, Manvel Croix, Conroe and La Porte: The TOT OC and EC for all sites from the current project was corrected to TOR OC and EC using the linear regression from the Clinton Avenue, Houston monitoring site as commissioned by TCEQ.

Spatial intercomparison: OC and EC ambient concentrations were compared across Houston using TCEQ data for Deer Park and Clinton Avenue and using Baylor data for Moody Tower, Manvel Croix, Conroe and La Porte. Galveston concentrations were included as background for Houston, when applicable. The following datasets were available from TCEQ and of high interest to the project:

    i.   Deer Park: black carbon and continuous OC and EC for the duration of the project

ii.   Clinton Drive: 24h OC and EC, every sixth day measurements for the duration of the project.

iii.   Galveston: 24h OC and EC, every sixth day measurements for the duration of the project.

DISCOVER AQ- OCEC Ambient Concentrations- September 7, 2013
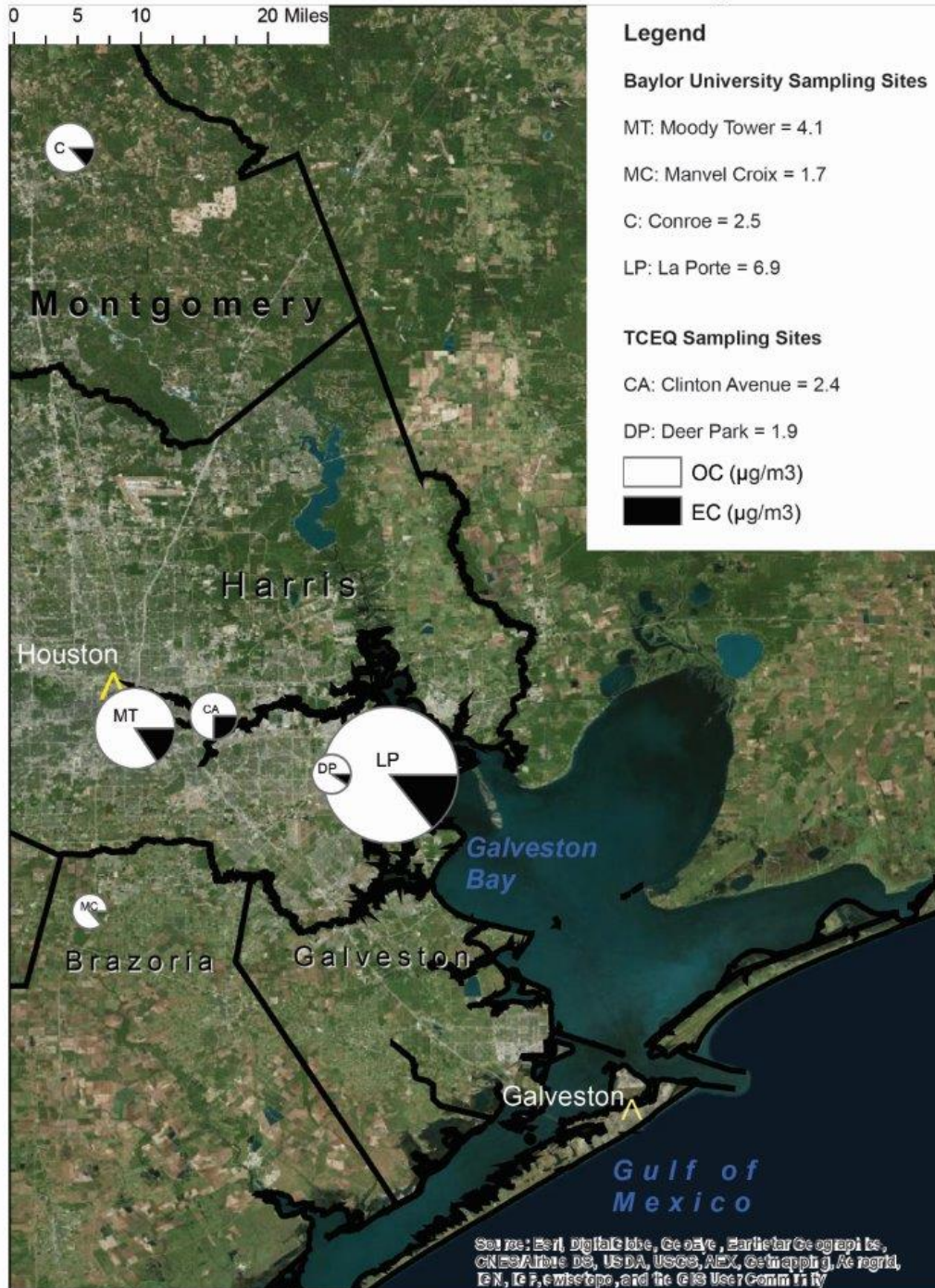
Figure 42. Spatial distribution of organic and elemental carbon (μg/m3) across Houston, TX during September 7th 2013.   Distribution covers four DISCOVER-AQ ground based sites (Moody Tower, Manvel Croix, Conroe, and La Porte) as well as two TCEQ air monitoring sites (Clinton Ave and Deer Park).
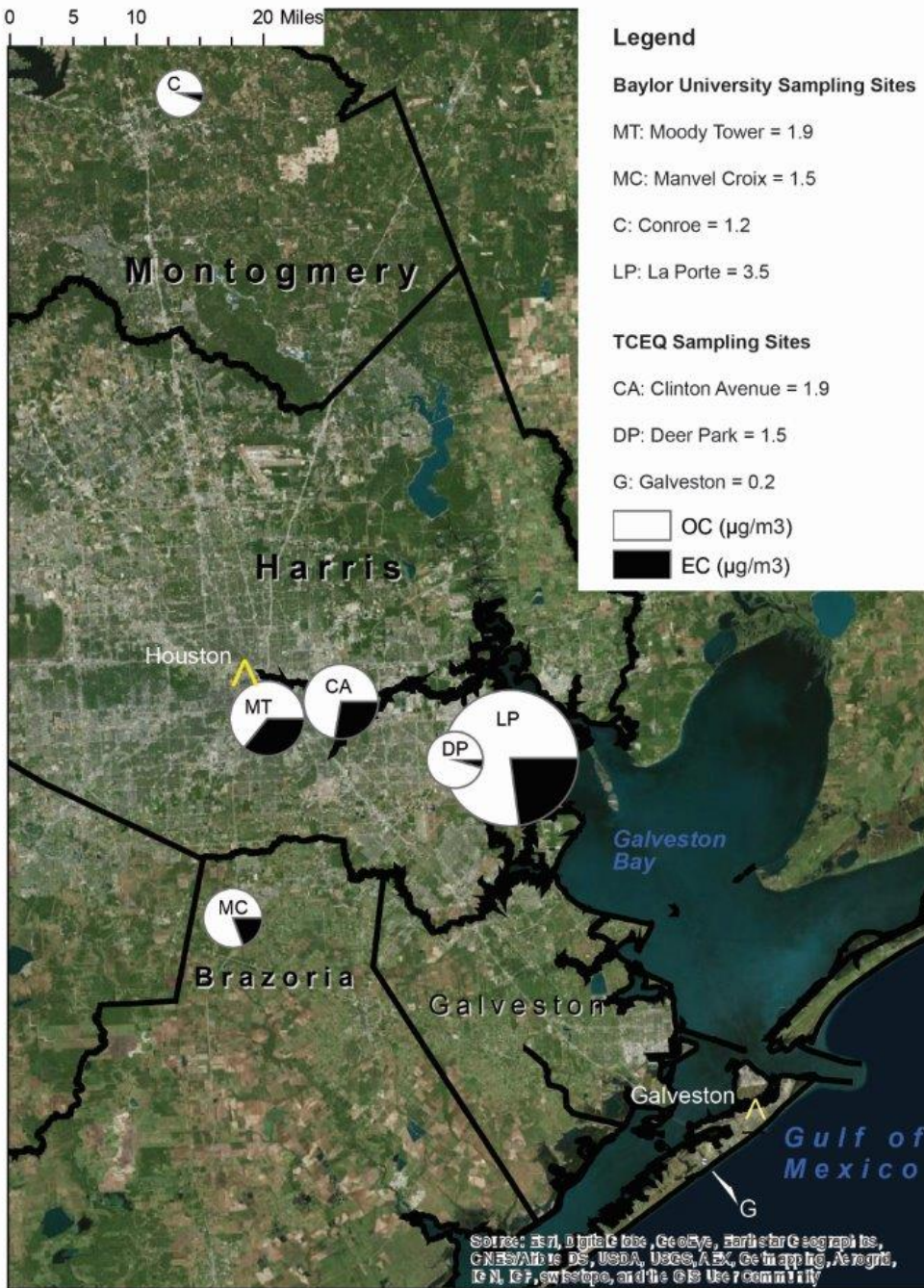
Figure 43. Spatial distribution of organic and elemental carbon (µg/m3) across Houston, TX during September 19th 2013.   Distribution covers four DISCOVER-AQ ground based sites (Moody Tower, Manvel Croix, Conroe, and La Porte) as well as two TCEQ air monitoring sites (Clinton Ave and Deer Park).

Figure 44. Spatial distribution of organic and elemental carbon (μg/m3) across Houston, TX during September 25th 2013. Distribution covers four DISCOVER-AQ ground based sites (Moody Tower, Manvel Croix, Conroe, and La Porte) as well as two TCEQ air monitoring sites (Clinton Ave and Deer Park).

The spatial continuity of PM across Houston was examined using 24 hour and day (6:00 to 20:00) EC and OC concentrations from Moody Tower, Manvel Croix, Conroe, and La Porte and Deer Park (TCEQ air monitoring site). Figure 45 provides the R^2 values associated with individual linear correlations between OC and EC (separately) from five different ground-based sites across Houston. Day (6:00 to 20:00) and 24 hours samples were also examined. The highest R^2 value was 0.80 and was for Daytime OC concentrations measured at Moody Tower and Manvel Croix. Both EC and OC were examined between La Porte (DISCOVER-AQ) and Deer Park (TCEQ site). OC concentrations measured at these two sites provided a linear correlation with a R^2 = 0.43, while EC concentrations measured at these two sites provided a linear correlation with a R^2 = 0.09. It is important to recognize that La Porte utilized TSP filters and Deer Park examined $PM_{2.5}$. Despite this difference, the lack of a strong correlation between two relative close sites suggest the relative strong impact of local OC and EC emission sources. Interestingly, there are stronger correlations among the day samples than 24 h samples; this may indicate that the impact of local sources is greater at night.

A. Day Samples

		Elemental Carbon	
	Moody Tower	Manvel Croix	Deer Park
Moody Tower	1	**0.51**	**0.50**
Manvel Croix	**0.80**	1	0.30
Deer Park	0.27	0.20	1

(Organic Carbon)

B. 24h Samples

			Elemental Carbon	
	Moody Tower	Conroe	La Porte	Deer Park
Moody Tower	1	0.01	0.32	0.32
Conroe	**0.50**	1	0.15	0.005
La Porte	0.39	**0.55**	1	0.09
Deer Park	0.14	0.01	0.43	1

(Organic Carbon)

Figure 45. Linear correlation examining the spatial relationship between EC and OC across Houston. DISCOVER-AQ ground based sites including Moody Tower, Manvel Croix, Conroe, and La Porte. TCEQ air monitoring sites including Clinton Ave and Deer Park. 6 in 1 sampling (i.e. Clinton Ave) data was not included due to the low number of samples collected during the DISCOVER-AQ sampling campaign. Day time samples collected from 6:30 to 20:00. 24 h samples were collected from 6:00 to 5:30.

Collaboration and Data Sharing

Collaboration and data sharing was critical to the success of this project. PIs collaborated and shared data with PIs from concurrent AQRP DISCOVER-AQ aerosol focus projects. Specifically, Robert Griffin - Rice University (PILS; Manvel Croix; 14-009) and Lea Hildebrandt Ruiz – University of Texas at Austin (Inorganic Ions; Conroe; 14-024). Baylor PIs provided access to EC, OC, and inorganic ions to concurrent AQRP DISCOVER-AQ aerosol focus projects.
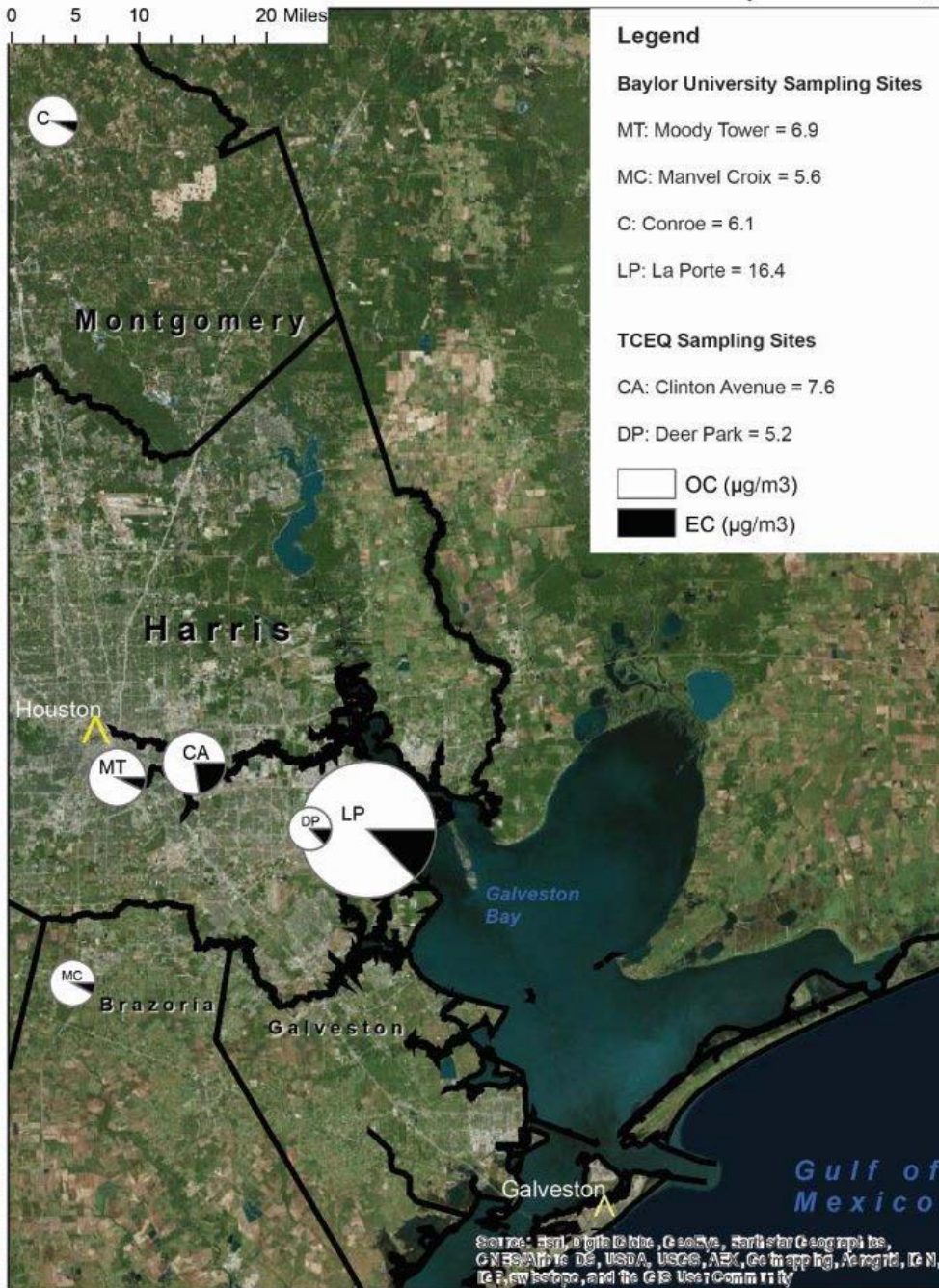
Summary Statement

This project builds on a previously-funded AQRP project (AQRP 12-032).   Over the course of this project which operated from July 2014 to June 2015, the project PIs expanded the initial characterization of particulate matter (PM) during DISCOVER-AQ. The enhanced characterization expanded the initial elemental carbon (EC) and organic carbon (OC) characterization including the radiocarbon, WSOC, organic and elemental tracers and inorganic ions. A majority of the analysis focused on samples collected during 9/21/13-9/28/13; however the scope of the project also expanded to La Porte and Conroe. In addition, different PM fractions (TSP and $PM_{2.5}$) and samples periods (e.g. 24 hour and day samples) were examined.

For the OC and EC, there were several trends for the September 2013 campaign. The maximum OC concentration for all four sites occurred between 9/24-9/26, which coincided with the peak ozone concentration on 9/25 in Houston. The maximum EC concentration at Conroe and La Porte was also 9/25-9/26. However, the maximum EC concentration at Moody Tower and Manvel Croix was 9/12-9/13, indicating that different spatial trends during the campaign. OC had higher correlation among sites than EC when comparing within the Baylor sites and between Baylor and TCEQ monitoring sites. Also, stronger correlations were seen with daytime samples than 24h samples across sites. This difference between correlation among day samples and

correlation among 24 h samples at the same sites seems to indicate larger local impacts at night as compared to the daytime when the boundary layer is higher.

For the remaining bulk species (WSOC and inorganic ions) there were the following trends during the September 2013 campaign. WSOC concentrations were strongly correlated with OC for all four sites with r^2 near 0.9. There were site-to-site differences in the WSOC/OC ratio. Conroe had the highest fraction of WSOC ranging from 40-80%. Manvel Croix and Moody Tower were lower with a range of 30-70%, while La Porte (TSP) had the lowest fraction at 30-55%. Higher percentages of WSOC may indicate that the sites had higher contributions of SOA. For the inorganic composition, sulfate contributed the highest concentration at Moody Tower and Conroe. The reconstructed mass (including OC*1.2, EC, sulfate, nitrate, ammonium, potassium, chloride) for the 24 h samples at Conroe closely followed measured $PM_{2.5}$ from TCEQ, except on 9/15-9/16. Of Moody Tower, Manvel Croix, and Conroe, the highest consistent concentrations of sulfate were measured at Conroe for September 2013.

Trace metals were measured at Moody Tower with 24 h samples. Vehicular tracers were consistent for the month (Figure 18). Future efforts should include detailed investigation of the high trace metal event period (9/10 – 9/15), which was sea salt tracers 9/12-13 (Figure 20) and crustal elements for 9/15-9/16 (Figure 19). Because many of the metals were below detection for a majority of the month, a monthly average would not properly represent the data. A few metals had consistent detectability, including Fe, which had a monthly average of 0.11 +/- 0.09 µg/m³, Zn, which had a monthly average of 0.11 +/- 0.14 µg/m³, and Na, which had a monthly average of 1.6 +/-1.25 µg/m³. Fe can be emitted by motor vehicles and can also be a crustal component. Zn is emitted by motor vehicles and Na is a component of sea salt.

Organic tracers including alkanes, PAHs, hopanes, steranes and levoglucosan were measured during the week of 9/21-9/28 at the four sites. For alkanes, Conroe had the highest CPI value of 3.18, followed by La Porte and Moody Tower with very similar CPI values, 2.84 and 2.72, respectively. Manvel Croix had the lowest CPI of 1.71. Higher CPI indicates greater impact from primary biogenic OC. Sampling dates 9/24- 9/26 showed elevated concentrations of ΣPAHs at each site. TSP samples of Moody Tower (0.99 ±0.33 ng/m³) and La Porte (0.31 ±0.07 ng/m³) had higher mean ambient concentrations of ΣPAHs than HV $PM_{2.5}$ samples, in receding order, from Conroe (0.19 ±0.07 ng/m³), Manvel Croix (0.12 ±0.02 ng/m³) and Moody Tower (0.10 ±0.04 ng/m³). Hopane and sterane concentrations for HV $PM_{2.5}$ were in order from Moody Tower (0.32 ±0.1 and 0.06 ±0.02 ng/m³, respectively); Conroe (0.15 ±0.1 and 0.02 ±0.02 ng/m³, respectively); and Manvel Croix (0.02 ±0.01 and 0.13 ±0.04 ng/m³, respectively). Levoglucosan is an organic tracer for biomass burning and was measured in all sites, and in both HV PM2.5 and TSP samples. Highest ambient concentrations (~350 ng/m³) were measured at La Porte (TSP 24 hours samples) on 9/24. The highest

ambient concentrations measured in HV PM$_{2.5}$ samples were at Conroe (9/22 and 9/23) and were greater than 70 ng/m3. Average concentration of all HV PM$_{2.5}$ was 27.12 ng/m3. In comparison, this value is below levels measured of a similar study in Houston (sites included are Aldine, HRM-3 and La Porte) in 2000 (234.07 ng/m3) [19].

Organic tracers such as current-use pesticides and OPEs, non-combustion based tracers, are often not monitored and therefore not included in atmospheric particulate matter processing and source apportionment studies. However, many non-combustion based tracers show strong correlations with organic carbon. Non-combustion based tracers provide an additional opportunity to examine aerosol chemistry due to their specific emissions and known degradation rates and degradation processes. A number of non-combustion based organic tracers were detected in PM samples from all four sites including current-use pesticides, flame retardants, and plasticizers. For example, Permethrin, a commonly used mosquitocide, was detected in 100% of PM samples analyzed at all four sites (week of September 21-28) with concentrations ranging from 0.025 to 60 ng/m3. In addition four current-use pesticides, malathion, bifenthrin, λ-cyhalothrin, and chlorothalonil were frequently detected at all four sites. Organophosphate ester (OPEs), an emerging contaminant, were detected at all four sites. ΣOPEs atmospheric concentrations (HV PM$_{2.5}$ and TSP) ranged from 160 pg/m3 to 3400 pg/m3. The four sites exhibited different OPE profiles of chlorinated and non-chlorinated.

The source apportionment efforts, which were the culmination of many of the chemical analyses in the current project (OC, EC, organic tracers, ^{14}C) and were strengthened by the remaining analyses (WSOC, inorganic ions and elemental tracers), resulted in the spatial characterization of organic aerosol in the greater Houston area. The radiocarbon apportionment effectively constrained the CMB results to provide estimation of both primary and secondary contributions to TOC. The end results indicated that Moody Tower (a site indicative of urban Houston) had a consistent primary motor vehicle exhaust contribution (18-27%) and a fossil SOA contribution that varied from 5-33% depending on atmospheric condition. Conroe (a site indicative of aged urban aerosol combined with biogenics) had a lower contribution of motor vehicle exhaust (5-10%) and a similarly variable fraction of fossil SOA (4-25%). Manvel Croix (a site indicative of residential Houston area) had an interim motor vehicle contribution (9-15%) with a variable fossil SOA (5-30%). For contemporary OC, there was minimal wood smoke contribution during the examined week (0-9% at all sites) except one La Porte TSP sample which delivered a maximum of 16% wood smoke contribution. This confirms that wood smoke is an event-based contribution for summer in Houston at the urban sites. However, the biogenic SOA was a large contributor at all sites; this ranged from 40-75% at Moody Tower, 56-81% at Manvel Croix and 60-79% at Conroe. In summary, the motor vehicle contribution was consistent at each site during the analysis week, the biogenic SOA was consistently high, while the fossil SOA showed the most variability.

Future Work

Based on the results from the current project, conversations with TCEQ and discussion with other AQRP PI, the PIs have identified four projects which are recommended for future study.

- Investigation of sources of semi-volatile OC using radiocarbon

  Rationale: As demonstrated in the current combined CMB + ^{14}C radiocarbon source apportionment and discussed in the AQRP final project meeting, sources and production of SOA are of high interest in understanding the organic carbon fraction of $PM_{2.5}$. While mechanistic and modeling studies can provide clues about the production of SOA in the atmosphere, it is important to understand the bulk source contribution of the atmospherically labile fraction of OC. Radiocarbon source apportionment has been demonstrated to provide clear demarcation between fossil and contemporary (i.e. biogenic) sources of OC. New instrumentation and methodology residing in the Baylor PI labs enables selective collection of semi-volatile OC for radiocarbon analysis.

- Extend detailed source analysis during DISCOVER-AQ

  Rationale: In the current study, detailed analysis and source apportionment was applied to characterize the final week in September, which had been identified as a high ozone event with the potential for high contributions of SOA. The bulk and elemental characterization of the remaining samples in September revealed peak OC, EC and trace elements in the week of 9/9 to 9/17. This week has indications of higher contributions of primary sources which may include industrial emission, ship emissions events, crustal material and other combustion sources. Additional detailed organic tracer characterization, analysis of wind fields and back trajectories would enable determination of additional source contributions to primary $PM_{2.5}$ events.

- Examine processing of particle phase organics with ozone

- Rationale: In this current round of AQRP projects, there was significant discussion and questions related how organics associated with particulate matter impact known ozone chemistry, and therefore ozone concentrations. This discussion was extremely timely with the consideration of changes to federal ground-level ozone standards. Organics associated with the particle phase have the ability to directly and indirectly (i.e. through NOx chemistry) effect ground-level ozone concentrations. PIs suggest examining the atmospheric processing of particle-phase organic as it relates to ozone chemistry (via direct and indirect

ozone chemistry) through the characterization of PM on high NOx and ozone event. This line of research would utilize existing TCEQ air monitoring efforts, while expanding PM characterization.

- Seasonal variability of primary vs secondary organic aerosol

  Rationale: The current project focused on a high photochemical, which would provide information for summer source apportionment under similar conditions in Houston, but more work is needed to understand low photochemical activity periods in summer and wintertime primary source contributions. The PIs recommend exploiting the DISCOVER-AQ filter set already collected by Baylor for additional CMB and ^{14}C source apportionment in the first half of the month dominated by primary emissions. In addition, the PIs recommend an additional, limited field campaign at Moody Tower and one additional TCEQ site (Manvel Croix or Clinton Ave) to collect samples during wintertime for source apportionment. Baylor has recently developed a Mobile Sampling Trailer: outfitted with PM (TSP and 2.5) NOx, Ozone, Aethalometer, and PTR-MS (VOCs) and filter samplers which would allow rigorous sampling for a wintertime campaign.

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