

ABSTRACT

Spatial Trends in Surface-based Carbonaceous Aerosol Measurements during DISCOVER-AQ in Houston, TX

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Carbonaceous aerosol (both fine particulate matter ($PM_{2.5}$) and total suspended particulate (TSP)) were collected during NASA's DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) in Houston, TX during September 2013. Four ground-based sampling sites were chosen to represent the Houston metropolitan area: primary sites Moody Tower (downtown; urban) and Manvel Croix (southern; suburb) and supplementary sites Conroe (northern; suburb) and La Porte (east; near Houston Ship Channel). Samples were analyzed for organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) ambient concentrations. On average, peak concentrations of OC, EC and WSOC occurred during the last week of the campaign, which coincided with peak ozone on September 25, 2013. Determining carbonaceous aerosol concentrations is fundamental in understanding urban air quality. Tracking spatial distributions of EC and WSOC is relevant to understand exposure and potential health impacts of $PM_{2.5}$ to Houston.

Spatial Trends in Surface-based Carbonaceous Aerosol Measurements during DISCOVER-AQ in
Houston, TX

by

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ACRONYMS AND ABBREVIATIONS

A	Afternoon sample; 10:00- 20:00 (10 h)
B	Blank Sample
BT	Back Trajectory
C	Conroe Sampling Site
D	Day sample; 06:30- 20:00 (13.5 h)
DDT	Dithiothreitol
DISCOVER-AQ	Deriving Information on Surface conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality
EC	Elemental carbon
EC/OC	Elemental carbon to organic carbon ratio
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
HV	High volume
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory
IDW	Inverse Distance Weight
LP	La Porte Sampling Site
M	Morning sample; 06:30- 10:00 (3.5 h)
MC	Manvel Croix Sampling Site
MV	Medium volume
MT	Moody Tower Sampling Site
N	Night sample; 20:00- 06:30 (10.5 h)
NCAR	National Center for Atmospheric Research
OC	Organic carbon
PM	Particulate matter
PM _{2.5}	Fine particulate matter
POA	Primary organic aerosol
QFF	Quartz fiber filter

ROS	Reactive oxidative species
SOA	Secondary organic aerosol
TCEQ	Texas Commission of Environmental Quality
TOT	Thermal-optical transmission
TC	Total carbon (does not include inorganic carbon)
TSP	Total suspended particulate
VOC	Volatile organic compound
WSOC	Water-soluble organic carbon
WSOC/OC	Water-soluble organic carbon to organic carbon ratio
UT	University of Texas at Austin

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DEDICATION

To the one who sparked my passion for the environment through completing multiple science fair projects, camping trips across Texas and evenings looking at the moon through the telescope together. Thank you Dad, for always letting me take home the clams from the beach and rollie pollies from the backyard. Most importantly, thank you for teaching me to reach for the stars. I think I might be one step closer.

CHAPTER ONE

Introduction

Understanding the emissions, interactions and effects of atmospheric pollutants in urban areas is a global concern, as over 1 billion people are exposed to outdoor air pollutants every year (http://www.unep.org/urban_environment/Issues/urban_air.asp). The increase in urbanization across the world has raised awareness into the exposure of atmospheric pollutants and risk to human health (Lin, et al. 2001; Tayanc, Karaca, and Yenigun 1997; Moore, Gould, and Keary 2003). Particulate matter (PM) is emitted into the atmosphere through a collection of sources, both biogenic and anthropogenic. One of the main sources of PM is from urban areas. Within an urban area, spatial and temporal heterogeneity of PM is due to various activity in the area, including traffic emissions and industry within and around the area. Temporally, PM concentrations differ due to meteorology and seasonal trends. PM sources include emissions from automobiles (including road abrasion and break and tire wear), industry, biomass combustion, cooking emissions, diesel and gasoline vehicle exhaust and road dust (Schauer, et al. 1996; Fraser, Yue, and Buzcu 2003; Buzcu, et al. 2006; Thorpe and Harrison 2008). One major pollutant of concern to human, especially living in major urban areas is particulate matter (PM), which is a primary focus for current air quality studies and the focus of this thesis.

PM is an important component of atmospheric pollution. PM is a non-water substance that is of microscopic size that exists as a solid or liquid in the atmosphere (Seinfeld and Pandis 2006). PM is composed of a combination of small particles and

liquid droplets that are found in the atmosphere that is directly emitted or that condenses by gas-phase chemical reactions in the atmosphere (Fraser, et al. 2002). Various components of PM include carbonaceous components (organic and elemental carbon), inorganic components (ie. sulfate, nitrate, ammonium, potassium, etc.) and metals (i.e. aluminum, silica, iron, vanadium, etc.). PM has the ability to travel long distances and impact regional or surrounding areas. The ability for PM to undergo long-range atmospheric transport depends on many factors including size fraction and chemical composition (Allen and Turner 2008; Seinfeld and Pandis 2006). The characteristics of PM has the potential to influence climate forcing and human health, making it important in atmospheric research.

Atmospheric PM can participate in climate forcing as a cloud condensing nuclei (CCN), which is important in cloud formation (Chalbota, et al. 2016). Since atmospheric PM can act as CCN, equal amounts of cloud liquid water is distributed among increased CCN in the clouds (Twomey 1977). This reduces the overall cloud droplet size, causing higher albedo and indirect climatic effects. Processes similar to increased CCN, as a result of increased PM suggests major climate forcing to occur in the atmosphere (Charlson, et al. 2001). The atmospheric lifetime of PM (average 7-14 days) is much shorter than long-lived greenhouse gases, including CO₂ (average 30-35 kyr)(Archer, et al. 2009). PM duration in the atmosphere also contributes to poor air quality, particularly in urban areas with dense populations and increased emission sources (Lin, et al. 2001; Tayanc, Karaca, and Yenigun 1997; Moore, Gould, and Keary 2003). Within urban areas, PM_{2.5} concentrations have shown to display homogeneity within sub-regions

(southeast United States) and heterogeneity between urban regions, due to emissions sources and regional location (Pinto, Lefohn, and Shadwick 2004).

PM can be categorized by size into two main types: fine PM (aerodynamic diameter less than $2.5\mu\text{m}$, $\text{PM}_{2.5}$) and coarse PM (PM_{10} , diameter less than $10\mu\text{m}$, minus $\text{PM}_{2.5}$) and both of which are shown to impact susceptible populations, including children, elderly and those with pulmonary health concerns and the general public. Exposure to $\text{PM}_{2.5}$ has become a major public health concern worldwide. $\text{PM}_{2.5}$ exposure has been linked to the progression of cardiovascular disease, asthma, respiratory allergies, diabetes, and genetic and epigenetic molecular abnormalities in susceptible populations (O'Neill, et al. 2012; Parker, Akinbami, and Woodruff 2009). Long-term exposure to $\text{PM}_{2.5}$ showed positive correlations to first hospital admissions for dementia, Parkinson's disease, and Alzheimer's disease in a multi-city cohort study of 9.8 million elderly patients from 1999-2010 (Kioumourtoglou, et al. 2016). Specifically, diesel engine exhaust from roadways is a major source of black carbon fractions of PM emissions and exposures in developed countries, including the United States (McDonald, Goldstein, and Harley 2015; Miguel, et al. 1998) (Fruin, Winer, and Rodes 2004). However, in developing countries, public health concerns arise from exposures to coal- and biomass-burning emissions from cooking and heating (Sheesley, et al. 2003; Robinson, et al. 2006a; Robinson, et al. 2006b). Exposures to these emission sources create a global concern from poor air quality and air emissions (Eklund, et al. 2014). Continuous efforts to characterize $\text{PM}_{2.5}$ sources and compositions can aid in mitigating potential detrimental health conditions in our communities.

Characterization of Atmospheric Particulate Matter

Within PM carbonaceous components, organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) are of interest in understanding the bulk source of PM. OC is the second most abundant constituent in PM, after sulfates (Heintzenberg 1989). EC is the non-refractory fraction of particulate carbon. OC and EC are emitted into the atmosphere from traffic, industry and biomass burning emissions, contributing to the major sources of OC and EC during the summer (Xuesong Sun 2012). WSOC is a tracer for secondary organic aerosol (SOA) formation in the absence of biomass burning and contributes 20-80% of total organic carbon (Poschl 2005; Duong, et al. 2011; Du, et al. 2014). WSOC can contribute to the hygroscopicity of aerosols, changing CCN abilities of particles residing within clouds, in turn affecting cloud formation and function (Charlson, et al. 2001; Svenningsson, et al. 2006; Asa-Awuku, et al. 2008; Mochida, et al. 2006). WSOC also demonstrates light absorbing properties, which can contribute to the climate forcing potential of atmospheric PM (Kirillova, et al. 2014; Jacobson 2012; Jacobson, et al. 2000; Asa-Awuku, et al. 2008). Although the potential significance of WSOC for cloud formation and for direct climate forcing has been described, its sources and detailed chemical composition are still being investigated (Chalbota, et al. 2016).

Atmospheric particulate matter can be emitted into the atmosphere as primary (POA) and secondary organic aerosol (SOA). POA is produced by biomass and fossil fuel combustion, contributing to OC and EC sources (Seinfeld and Pandis 2006; Duan, et al. 2004). Specifically, OC is produced from biogenic and biomass-burning sources while EC is generated only as a primary source from fossil emissions. VOC (volatile organic

compounds) are emitted into the atmosphere and undergo oxidation processes. After oxidation, the product condenses into an aerosol phase to form SOA (Seinfeld and Pandis 2006). OC and WSOC can be formed through SOA processes (Seinfeld and Pandis 2006; Du, et al. 2014). WSOC specifically is emitted as an SOA through atmospheric oxidation and processing of biogenic and fossil volatile organic compound precursors (Jacobson, et al. 2000).

In general, air pollution concentrations are determined by three main factors: meteorology (which determines distribution), chemical reactions (which form PM), and source emissions into the atmosphere (Banta, et al. 2005). Weather patterns aid in determining particulate deposition and dispersal. Chemical reactions influence production of secondary organic aerosols (SOA). Lastly, source apportionment can help identify the origin of the pollutants.

This thesis looks at the spatial trends of carbonaceous aerosols in Houston, TX from four selected areas that encompass the Houston metropolitan area. Trends from Sept 2013 DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) campaign provide the foundation towards understanding the impact of meteorology, chemical reactions and source emissions on carbonaceous aerosol concentrations in that urban area. In this thesis, precipitation patterns, back trajectories (BTs) and chemical coupling of PM and ozone aid in the explanation of the spatial trends in Houston. With high concentrations of EC and WSOC during a high ozone event in Houston, this raises awareness in the potential exposure to the people of Houston and the potential health effects they are at risk of obtaining.

Texas Air Quality Studies

Previous air quality studies in southeast Texas focused on tropospheric ozone (O_3) concentrations (<http://esrl.noaa.gov/csd/projects/texaqs2k/>). O_3 is a greenhouse gas that is created as a secondary organic aerosol from the formation of VOC and sunlight (Liu, et al. 1987; Meng, Dabdub, and Seinfeld 1997). O_3 is known to cause adverse health effects including lung irritation, reduced lung function, premature morbidity and increased asthma (Bromberg and Koren 1995; Koren, et al. 1989; Lippmann 1991; Tilton 1989). In southeast Texas, historical observations of O_3 concentrations occur during the late summer season, specifically in Houston, TX (Ying and Krishnan 2010; Lin, et al. 2005; Ryerson, et al. 2003). The combination of high chemical emissions from the Houston metropolitan area and surrounding industry and air mass transport create peak concentrations of O_3 in Houston, creating a public health concern for the city of Houston.

To investigate high levels of O_3 , two main air quality studies have been conducted in the gulf coast region of Texas: TexAQS 2000 and TexAQS 2006. The TexAQS 2000 air quality study was a month-long sampling campaign that occurred from August 15 - Sept 15, 2000 to investigate high O_3 concentrations exceeding the National Ambient Air Quality Standard (NAAQS) of 120 ppbv in one hour (Daum, et al. 2004). Spatial trend results from this air quality study had high concentrations of secondary organic aerosol emissions (specifically NO_x and hydrocarbons) from petrochemical facilities near the Houston Ship Channel, contributing to the photochemical production of O_3 in the gulf coast (Kleinman, et al. 2002). The Houston Ship Channel is the location of 25% of the United States' petrochemical facilities, contributing to high concentrations of O_3

throughout the Houston metropolitan area. O₃ concentrations observed during the TexAQS 2000 study exceeded the NAAQS, with a concentration exceeding 150 ppbv.

The second air quality project, TexAQS 2006, was a follow-up project to TexAQS 2000. The transport and formation of various air pollutants were investigated in the Gulf of Mexico and Houston-Galveston regions, with some studies focusing on commercial marine shipping emissions (Williams, et al. 2009). Results from this specific study showed that NO_x emissions from tanker ships, commercial ships, passenger ships and freight carriers emitted the highest amount of NO_x, a key contributor to ozone.

Overall, both studies portray the potential for outflow of urban aerosol concentrations from the Houston Metropolitan area to regional areas of Texas. They also highlight the emissions of urban aerosols contributing to tropospheric ozone in Houston, causing concern for Houstonians. Understanding trends in O₃ from previous studies provides trends in potential atmospheric aerosol concentrations in Houston in current studies. PM and O₃ are chemically coupled in the atmosphere and can provide potential PM aerosol trends in Houston from the DISCOVER-AQ sampling campaign (Meng, Dabdub, and Seinfeld 1997).

General Summary of DISCOVER-AQ

NASA's DISCOVER-AQ was the next large, multi-institution field campaign studying ground-based atmospheric pollutants across various metropolitan areas of the United States. This field campaign aimed to overall improve air quality monitoring satellites to better understand world-wide ground level air quality patterns and conditions for efforts in improving public health and protecting the environment (Crawford 2014). This four-year sampling campaign focused its initial efforts in ground-based sampling,

collaborating with scientists from various government agencies (e.g. NASA, NOAA, EPA, NCAR, etc.), industry (TCEQ, Aerodyne) and 15 universities, including Baylor University (<http://discover-aq.larc.nasa.gov/participants.php>). The campaign delineated three main goals to towards improving space air quality monitoring satellites: the ability to forecast air quality trends, further understand source apportionment of air pollutants and determine emission level fluctuations. The campaign engaged NASA aircraft to make flight-based measurements for particulate and gaseous pollution. Coupled with ground-based measurements, a collection of data is available to initiate air pollution mitigation efforts across the United States.

Through AQRP (Air Quality Research Program) grants, TCEQ funding, and collaborations with NASA's DISCOVER-AQ investigators, PI's Rebecca Sheesley and Sascha Usenko and graduate students of both labs sampled TSP and PM_{2.5} at four representative Houston sites during the month of Sept 2013. Post-collection of the sampled air filters has Baylor University to process the PM collected on the filters for organic contaminants, metals, radiocarbon and molecular tracers on select days and carbonaceous aerosols concentrations during the whole month. This thesis will focus on spatial and temporal trends in the concentrations of OC, EC and WSOC for the month of Sept across all four Houston sites. Continuous efforts to understand the atmospheric composition and sources in Houston, TX will allow research to move towards spatially and temporally characterizing PM exposure in the Houston metropolitan area.

Description of Laboratory Methods

OC and EC concentrations were quantified for PM collected on quartz fiber filters (QFF) using a thermal-optical method (NIOSH-5040) on a thermo-optical transmission (TOT) analyzer (Sunset Laboratories, Tigard, OR), as seen in Figure 1.1 (Birch and Cary 1996).

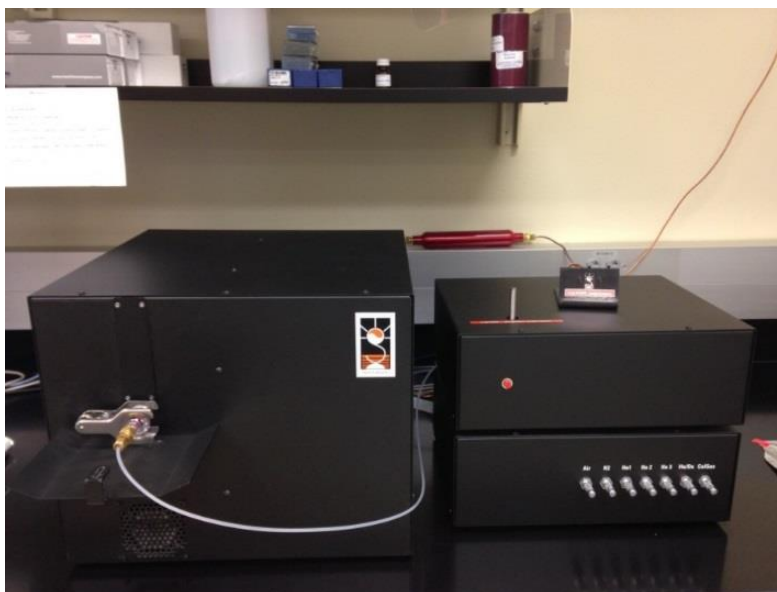


Figure 1.1. Thermo-optical transmission (TOT) analyzer (Sunset Laboratories, Tigard, OR)

This method controls the temperature and gases flowing through the instrument while continuously monitoring light transmission through the filter with a He-Ne laser at 678 nm. To achieve this, a portion of the QFF (1.5 cm^2) is placed into the Sunset OC-EC analyzer, where OC and EC are determined by two separate steps (Figure 1.2). The first step includes the volatilization of OC from the sample in 100% He gas, with the increase of the oven temperature to 820°C . The OC is further oxidized to CO_2 gas by the addition of MnO_2 , then reduced into CH_4 in a methanator oven. An FID (Flame Ionization

Detector) detects and quantifies the reduced CH_4 . The temperature of the oven is then reduced to 525 °C. During the second step, correction of pyrolytic carbon and EC concentrations are determined. Upon the introduction of 10% oxygen/helium gas mixture into the system, the temperature is increased to 850 °C. During this phase, additional EC is created through a process called “charring.” This “char” will cause the transmission to

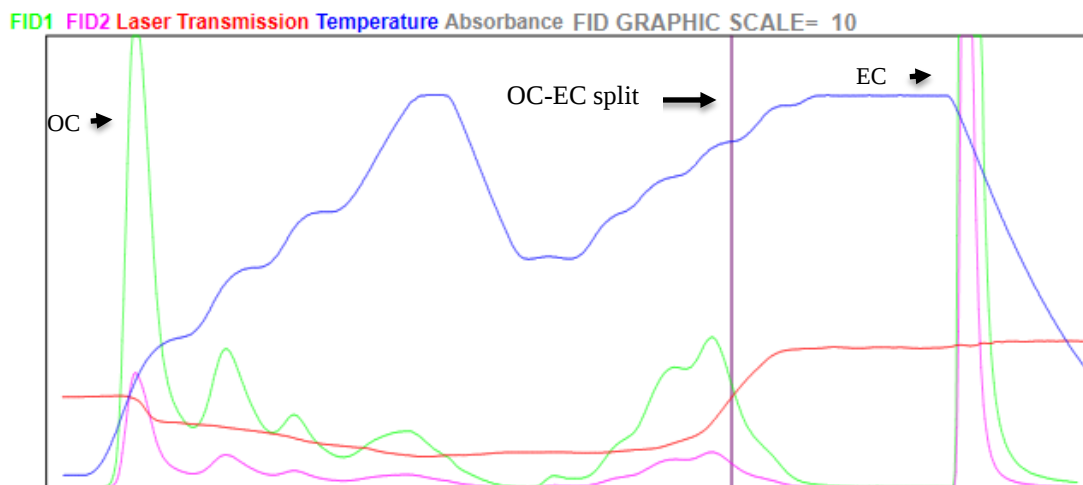


Figure 1.2. Example thermo-optical transmission (TOT) analyzer Thermogram for a $\text{PM}_{2.5}$ sample

decrease. The char is burned off by the instrument once oxygen is added into the system. This artificially created EC is volatilized by the addition of oxygen, and the FID reading is returned to its original value. This process is called the “split” point between OC and EC. Any carbon measured before the split is considered OC, while carbon created after the split is true, atmospheric EC. An instrument blank and sucrose check standard are run on each sample prior to analysis. A triplicate sample is also run every tenth sample.

Water soluble organic carbon concentrations were analyzed using the following procedure (Figure 1.2). All materials used were triple rinsed with de-ionized water prior

to analysis. Concentrations of OC from each filter were used to determine a filter area required to receive 60 µg of OC for WSOC analysis. Each subsample of filter was placed in 30 mL of DI water in 50 mL centrifuge tubes (BioLink Scientific, Wimberly, TX). Samples were sonicated for 15 minutes and centrifuged for 10 minutes. Extracts were decanted into a Millex GV Durapore PVDF Membrane disposable syringe filter (0.22 µm; Merck Millipore, Ltd.) to remove filter and particles from sonication. Finally, 60 µL of 6N hydrochloric acid was added to each sample to remove inorganic carbon from the

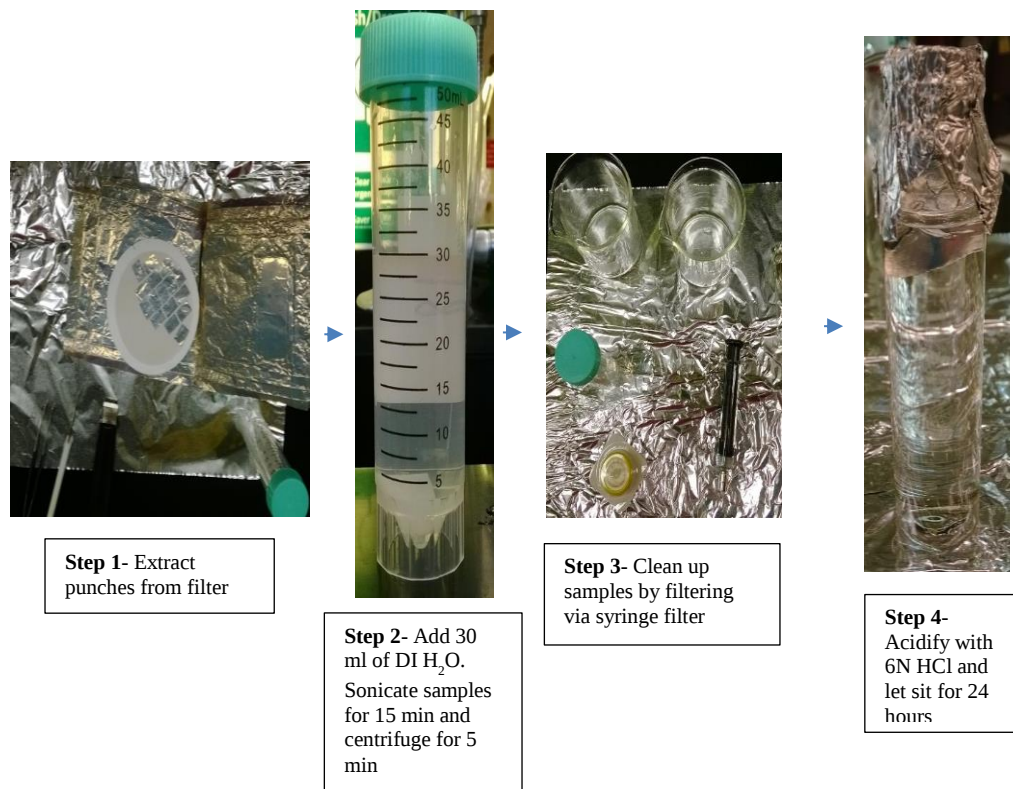


Figure 1.3. Schematic of water-soluble organic carbon (WSOC) extraction

solution. A Shimadzu Total Organic Carbon Analyzer (Model TOC-5000A, Kyoto, Japan) was used to measure dissolved organic carbon. Water blanks averaged 0.06 +/-

0.05 mg/L. Each sample includes a blank correction, calculated as a site specific blank average. Filter blank fraction contributions to filter concentrations of the filter sample concentration 20.4% for HV_{2.5} and 13.4% for TSP. Sucrose spike recovery had an average recovery rate of 101%.

CHAPTER TWO

Spatial Trends in PM_{2.5} Surface-based Carbonaceous Aerosol Measurements during DISCOVER-AQ in Houston, TX

Abstract

Carbonaceous aerosols emitted into the atmosphere through biogenic and anthropogenic emissions greatly influence urban air quality. In order to understand vertical and spatial gradients in urban air quality, NASA's DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) campaign conducted a field experiment in Houston, TX in Sept 2013. As a part of this project, organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) were measured from PM_{2.5} and TSP filters collected at four ground-based sampling sites representing the Houston metropolitan area: primary sites Moody Tower (downtown; urban) and Manvel Croix (southern; suburb) and supplementary sites Conroe (northern; suburb) and La Porte (eastern; near Houston Ship Channel). The DISCOVER-AQ sampling campaign captured different conditions in Houston, including a high ozone event on Sept 25th which influenced OC, EC and WSOC ambient concentrations. This paper describes the spatial and temporal trends for ground-based carbonaceous aerosol in Houston during Sept 2013. Future efforts for this field experiment will include detailed characterization of organic contaminants and source apportionment of organic and elemental carbon from DISCOVER-AQ.

1. Introduction

Fine particulate matter (aerodynamic diameter less than $2.5\mu\text{m}$, $\text{PM}_{2.5}$) is a critical concern in metropolitan areas, due to its impact on human health and ability to act as a short-lived climate forcer. Carbonaceous aerosol is a bulk fraction of $\text{PM}_{2.5}$. Within $\text{PM}_{2.5}$, organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) are commonly measured to understand potential human health exposure of carbonaceous aerosols. EC represents pure combustion sources while OC would include a complex mixture of combustion, secondary organic aerosol (SOA), and primary biogenic sources. WSOC is tracer SOA formation in the absence of biomass burning (Weber, et al. 2007). Exposure to $\text{PM}_{2.5}$ has been linked to cardiovascular disease, pulmonary aggravation causing asthma, diabetes and genetic and epigenetic molecular abnormalities in susceptible populations (O'Neill, et al. 2012; Dockery, et al. 1993). Linear regressions between aerosol chemical components and dithiothreitol (DTT) activity have reported strong associations between the reactive oxidative species (ROS) generation potential of PM and water-soluble organic carbon in the summer (Verma, et al. 2014). This relationship between the ROS generation potential of PM and water-soluble organic carbon concentrations are of interest due to potential human health impacts. EC emissions in urban areas have been attributed to traffic emissions, with higher concentrations found on weekdays than weekends (Maciejczyk, et al. 2004). This is shown to contribute to human exposures, including children with asthma residing in communities with high volumes of traffic (Maciejczyk, et al. 2004; Spira-Cohen, et al. 2010). Efforts to characterize $\text{PM}_{2.5}$ sources and compositions are necessary to

effectively understand spatial and temporal differences in potential human health exposure and control urban PM levels.

Houston, the fourth largest metropolitan area in the United States, is a model “field laboratory”, due to its high anthropogenic activity combined with high potential for biogenic contributions due to its proximity to forested regions. Specifically, Houston is subject to a wide range of potential local and regional sources of primary and secondary carbonaceous aerosol. For example, Houston is home to one of the world’s largest petrochemical complexes, housing approximately 25% of the United States’ refining capacity (Bozlaker, et al. 2013). The industrial activities, heavy duty motor vehicle traffic and shipping traffic in and around the Houston Ship Channel impact $PM_{2.5}$ concentrations in the Houston metropolitan area (Fraser, Yue, and Buzcu 2003). This includes road dust emissions from unpaved roads located within the Houston Ship Channel’s industry which have been shown to contribute to fine particulate matter concentrations in local areas, with concentrations decreasing since 2006 (Sullivan, et al. 2013). Previously published literature also has demonstrated a correlation between peak ozone and peak secondary organic carbon in Houston, however additional characterization is still needed (Russell and Allen 2004). Houston has also shown to impact carbonaceous aerosol components of $PM_{2.5}$ in other areas, including Central Texas, creating regional air quality concerns (Barrett and Sheesley 2014).

The meteorological conditions in Houston can also affect atmospheric lifetimes and concentration of carbonaceous aerosol (Anderson, et al. 2008; Darby 2005; Banta, et al. 2005). Back trajectories (BTs) provide insight into the travel of wind masses to sampling sites. BTs provide insight into wind masses that influence spatial and temporal

aerosol concentrations. Precipitation distributions can also demonstrate the differential effects of precipitation washout on WSOC and OC vs EC.

Previous sampling campaigns in Houston and Central Texas have investigated aerosol composition, formation and sources, but significant work is still needed to understand long-term trends and to characterize aerosols during peak events in this region (Barrett and Sheesley 2014; Buzcu, et al. 2006; Wright, et al. 2010; Brock, et al. 2003). This study provides the distribution of carbonaceous aerosol concentrations for Southeast Texas, with a focus on Houston, TX, during the month-long DISCOVER-AQ campaign in Sept 2013. The overall goals of the current manuscript is to understand spatial and temporal variability in carbonaceous aerosols across Houston, with respect to bulk carbon fractions. Special emphasis is placed on the last week of the campaign and discussion of aerosol and back trajectory characterization during a peak ozone period (Sept 25-26, 2013), which has been previously documented (Baier, et al. 2015). 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 (northern; suburb) and La Porte (eastern; near Houston Ship Channel). The chemical characterization included OC, EC and WSOC. These are discussed within the context of BTs, precipitation rates during DISCOVER-AQ, along with fine particulate matter and ozone concentrations from Texas Commission of Environmental Quality (TCEQ) air monitoring sites located in and around Houston.

2. Materials and Methods

2.1 Sampling Site

PM_{2.5} and TSP samples were taken in conjunction with NASA's DISCOVER-AQ (<http://discover-aq.larc.nasa.gov/>) at four sites around the Houston Metropolitan area, as (Crawford 2014). These sampling sites (Figure 2.1) were chosen to allow for improved spatial and temporal resolution of carbonaceous aerosols in Houston: Moody Tower (MT; 29.7197, -95.3432; ~4 km from downtown Houston), Manvel Croix (MC; 29.5205, -95.3925; a suburb of Houston, ~27 km south of MT), La Porte (LP; 29.6692, -95.0642; near the Houston Ship Channel, ~25 km east of MT), and Conroe (30.3525, -95.4144; a suburb of Houston ~74 km north of MT).

In addition to filter collections above, measurements from TCEQ on-going monitoring sites in Houston were also utilized including daily ozone maximum concentrations and daily average PM_{2.5} concentrations from TCEQ air monitoring sites: Park Place (AQS 482010416), Galveston (AQS 481671034), Seabrook (AQS 482011050), Deer Park (AQS 482011039), Houston East (AQS 482011034), Clinton (AQS 482011035), and Conroe (AQS 483390078). Daily ozone maximum concentrations (Sept 1st – 29th 2013) were retrieved from the Texas Air Monitoring Information System (TAMIS) web interface (<http://www17.tceq.texas.gov/tamis/index.cfm?fuseaction=home.welcome>). Daily average PM_{2.5} concentrations (Sept 1st – 29th 2013) were measured using a tapered element oscillating microbalance and were retrieved from TCEQ upon request (personal communication with Jim Price).

2.2 Sample Collection

PM_{2.5} was collected on two types of quartz fiber filters (QFF; 90 and 102 mm diameter; Pall Corporation, Port Washington, NY, USA) using a medium volume (90 L/min; URG Corporation, Chapel Hill, North Carolina, USA) and high volume sampler (Tisch Environmental, Cleves, OH, USA), respectively. For the high volume samplers,

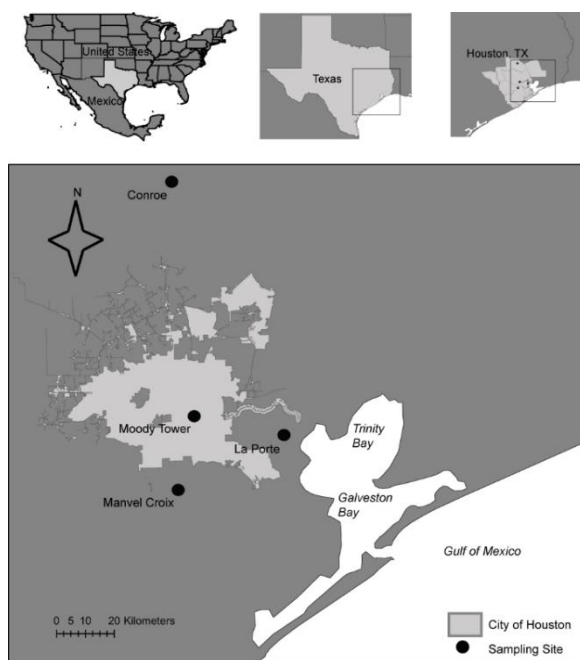


Figure 2.1. Baylor University four ground-based sampling sites

the flow rate was 200 L/min at MT and 225 L/min at both MC and Conroe. TSP was collected on QFF (20x25 cm; Pall Corporation, Port Washington, NY, USA) using a high volume sampler (Tisch Environmental, Cleves, OH, USA). Flow rate was 1170 and 1130 L/min at MT (day and night, respectively), 1700 L/min at MC, and 1000 L/min at LP. All samplers were calibrated prior to field deployment; differences in flow rate were due to small differences in sampler design. QFF were baked at 550 °C for 12 h in

individual foil packets. Filters were stored in -10 °C freezers pre- and post-sampling. Field blanks were collected during the campaign for each type of sampler. Blanks were handled in the same manner as ambient samples.

At MT and MC, both PM_{2.5} and TSP samples were analyzed. PM_{2.5} samples were taken at MT and MC from 06:00 to 20:00 (day), while TSP samples at MT were taken diurnally (day: 06:00 to 20:00; night: 20:00 to 06:00), with a few morning (06:30 to 10:00) and afternoon (10:00 to 20:00) samples. Conroe PM_{2.5}, LP TSP and a few MT TSP and MC TSP were 24 h samples (06:00 to 05:30).

3. Sample Analysis

3.1 Organic and Elemental Carbon

Filters from the campaign were analyzed for OC and EC by thermal optical transmission using the NIOSH 5040 method (Sunset Lab Carbon Analyzer), detailed in previous studies (Schauer, et al. 2003; Birch and Cary 1996; Barrett and Sheesley 2014). This method controls the temperature and gasses flowing through the instrument while continuously monitoring light transmission through a 1.5 cm² aliquot of the filter with a He-Ne laser at 678 nm. Triplicate analysis was completed every tenth sample with an average standard deviation of 0.28 µg/cm². Samples were blank corrected with site- and sampler-specific filter blanks. Blank filter concentrations for HV PM_{2.5} filters for OC averaged 0.68 µg/cm², contributing to an average of 8.53% of OC final ambient concentrations. TSP blank filters averaged 0.49 for OC µg/cm², with OC fraction contributions averaging 3.24%. HV PM_{2.5} and TSP filters had no blank EC fraction contributions. MV PM_{2.5} blank filter concentrations for OC and EC averaged 1.47 and 0.06 µg/cm², respectively, contributing to an average blank fraction 25.3% of for OC and

9.76% for EC. This process produced results in $\mu\text{g C /cm}^2$ which were manually converted to $\mu\text{g C /m}^3$ based on air volume sampled through the filter.

Day and nighttime calculations were performed to understand diurnal concentration patterns during DISCOVER-AQ Houston. Daytime concentrations were calculated by adding a morning time concentration (06:30 -10:00) and an afternoon concentration (10:00 - 20:00) and volume normalizing to the runtime duration of the samples. Nighttime concentrations were calculated by subtracting a daytime concentration (06:30 -20:00) from a 24 h concentration (06:30 - 06:00) volume normalizing to the runtime duration of the samples.

3.2 Water-Soluble Organic Carbon

The WSOC analysis protocol has been described previously (Barrett and Sheesley 2014). All materials used were triple rinsed with de-ionized water prior to analysis. Concentrations of OC from each filter were used to determine a filter area required to receive 60 μg of OC for WSOC analysis. Each subsample of filter was placed in 30 mL of DI water in 50 mL centrifuge tubes (BioLink Scientific, Wimberly, TX). Samples were sonicated for 15 min and centrifuged for 10 min. Extracts were decanted into a Millex GV Durpapore PVDF Membrane disposable syringe filter (0.22 μm ; Merck Millipore, Ltd.) to remove filter and particles from sonication. Finally, 60 μL of 6N hydrochloric acid was added to each sample to remove inorganic carbon from the solution. Sucrose spike recovery had an average recovery rate of 102%. A Shimadzu Total Organic Carbon Analyzer (Model TOC-5000A, Kyoto, Japan) was used to measure dissolved organic carbon. Laboratory water blanks averaged 0.06 +/- 0.05 mg/L. Each sample includes a blank correction, calculated as a site specific blank average. Filter blank fraction

contributions to filter concentrations of the filter sample concentration 20.4% for HV_{2.5} and 13.4% for TSP.

3.3 HYSPLIT Back Trajectory Analysis

BTs were calculated and produced every hour for 24 h from Sept 4-28th, reproducing wind patterns during the DISCOVER-AQ Houston campaign. Back trajectory calculations were performed for the four ground-based sampling sites using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model, version 4, May 2012 release (Draxler 2010). Individual BTs were run with an initial height of 0 m above ground level for MC, C and LP and 80 m above ground level for MT using GDAS data vertical velocity fields. To understand the major air masses traveling to the site during Sept, resulting back trajectories were clustered by site using the clustering function in the HYSPLIT model. Final back trajectories were plotted using ESRI's ArcGIS 10.1 mapping software. To model potential uncertainty in the HYSPLIT model BTs during DISCOVER-AQ, a sensitivity study was performed for MT, C and LP at 10 km North and South of each site. LP and C were plotted at 0, 50 and 100 m above ground level. MT included 0, 80 and 100 m above ground level. The sensitivity study results show that the HYSPLIT model is robust and reproducible at various locations and heights from the initial sampling site.

3.4 Precipitation Pattern Analysis

Archived precipitation data from the National Weather Service was utilized to create an Inverse Distance Weight (IDW) Interpolation through ArcMap GIS. Observed Weather Reports from the National Weather Service provided Daily Climate Reports

with precipitation data. IDW provided a non-statistical distribution of precipitation patterns throughout the four DISCOVER-AQ sampling sites. Data displayed on the ArcMap provides the ability to understand temporal and spatial distributions of precipitation during the highest precipitation event of the campaign: Sept 19-21st.

4. Results and Discussion

OC, EC and WSOC measurements are discussed by aerosol size (PM_{2.5} and TSP). Data analyzed for this study have been measured or calculated to represent Day (06:00-20:00 CST) and Night (20:00-06:00 CST). PM_{2.5} and TSP ambient concentrations are reported for primary sites MT and MC. Secondary-sites C and LP are discussed as 24 h samples (06:00-06:30 CST) for PM_{2.5} and TSP, respectively. Results from the Baylor ground-based sampling sites will be placed in context with PM_{2.5} and ozone trends at selected TCEQ sites in Houston.

4.1 Back Trajectories

BTs were clustered by site for the month of Sept 2013 and the resulting cluster means are presented in Figure 2.2 with daily cluster averages in Table 2.1. All four sites show contribution from east-southeasterly air masses (ESE, 57-68%) and north-northeasterly air masses (NNE, 15-26%); the ESE air masses dominated until Sept 21, when the BT analysis indicated a shift to air masses from the NNE. MC, C and LP have a small contribution from southerly air masses (S, 11-13%), while MT and LP have an 11% and 28% contribution from southeasterly (SE) air masses, respectively. However, because the sites are distributed around the Houston metropolitan area, these directional impacts have different implications for each site. In addition, MT was the only elevated

site, at 70 meters above ground level. Since MT is closer to central Houston, all directions would contribute an urban emissions signal to the site (i.e. mixed motor vehicle, potential residential wood smoke and commercial/residential food cooking). For MC, the S and ESE BTs will represent conditions of limited impact from downtown Houston. In contrast, for C, it is the NNE BT cluster which will be regional background, not urban. For all sites there are clustered BTs originating in the Gulf of Mexico. MT has a significant fraction of BTs (ESE cluster means) which pass over the Houston Ship Channel, which is an area of dense industry, heavy duty diesel traffic and shipping emissions.

As mentioned previously, the final week of the campaign was dominated by NNE air masses. However, starting on night of Sept 24 and continuing across the metropolitan area until Sept 26, there were high ozone concentrations in Houston corresponding to recirculation within downtown Houston and then transport to downwind sites (Baier, et al. 2015). BT analysis indicates that MT and LP sites have changing ESE, NNE and S BTs over this two day period, while C and MC more smoothly transition from NNE to S source regions. Measurement and analysis of direct ozone production rate at MT and at Smith Point (at the mouth of the Houston Ship Channel) indicated high ozone production within the area around MT with advection to Smith Point and outlying areas in Houston (Baier, et al. 2015). The recirculation pattern coupled with the high ozone production make Sept 24-26 a time of high interest.

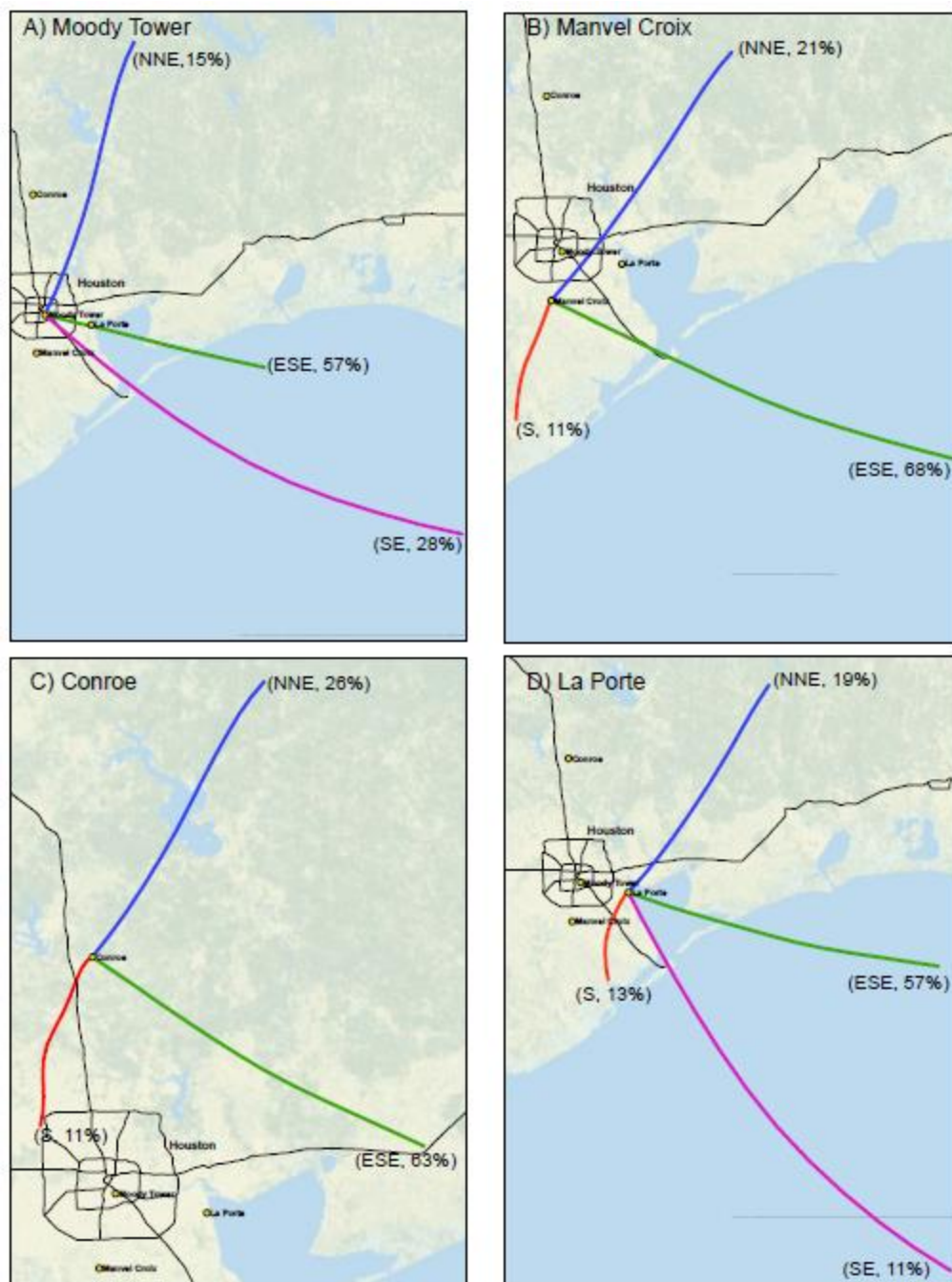


Figure 2.2. Twelve hour Back Trajectories were performed to display percentages of air masses that traveled to the sampling sites during DISCOVER-AQ: North-northeast (blue, NNE), East-southeast (green, ESE), Southeast (purple, SE) and South (red, S).

Table 2.1. Sept 2013 Daily Back Trajectory (BT) Cluster Average

	<u>Moody Tower</u>	<u>Manvel Croix</u>	<u>Conroe</u>	<u>La Porte</u>
Day	Daily Cluster Avg*	Daily Cluster Avg	Daily Cluster Avg	Daily Cluster Avg
4-Sept	ESE	S	S	S
5-Sept	ESE	ESE	SE	ESE
6-Sept	ESE	ESE	ALL-3	ALL-3
7-Sept	ESE	ESE	SE	ESE
8-Sept	ESE	ESE	SE	ESE
9-Sept	ESE	ESE	SE	ESE
10-Sept	ESE - SE	ESE	SE	ESE
11-Sept	ESE - SE	ESE	SE	ESE
12-Sept	ESE	ESE	SE	ESE
13-Sept	ALL-3	ESE	ALL-3	ALL-3
14-Sept	ESE	ESE	NNE-SE	ESE
15-Sept	ESE	ESE	SE	ESE
16-Sept	SE	ESE	SE	ESE
17-Sept	ESE - SE	ESE	SE	ESE
18-Sept	ESE	ESE	SE	ESE
19-Sept	SE	ESE	SE	ESE
20-Sept	SE	ESE	SE	SE
21-Sept	NNE	ALL-3	NNE	ALL-3
22-Sept	NNE	NNE	NNE	NNE
23-Sept	ESE	NNE	NNE	NNE
24-Sept	ESE	NNE	NNE	NNE
25-Sept	NNE	NNE-S	NNE	NE-S
26-Sept	ESE	S	S	S
27-Sept	ESE	ESE	SE	SE
28-Sept	SE	ESE	SE	SE

* Average (Avg) North-northeast (NNE), East-southeast (ESE), Southeast (SE), Northeast (NE), South (S)

4.2 Carbonaceous Aerosol Trends and Concentrations

Carbonaceous aerosol concentrations are presented here for the late summer season in Houston (Figure 2.3-2.6). Generally, warmer months in southeastern United States have higher $PM_{2.5}$ concentrations, similar to Houston PM concentrations during August 2011 (Chen, et al. 2012; Zhang, et al. 2012; Barrett and Sheesley 2014). $PM_{2.5}$ concentrations from a Houston Clinton EPA site in 2011 were higher than concentrations found in sampling sites in Central Texas during 2011 (Barrett and Sheesley 2014). $PM_{2.5}$ concentrations from DISCOVER-AQ are higher than summer concentrations found at a regional background site in Central Texas from 2011 (Barrett and Sheesley 2014). Emissions from the Houston Ship Channel have shown to impact $PM_{2.5}$ concentrations in the Houston metropolitan area, due to traffic and industrial activity residing near the ship channel (Sullivan, et al. 2013). The OC, EC and WSOC concentrations for the second and last week of the campaign (Sept 10-15 and Sept 22-25) displayed a trend of steadily building atmospheric loading. A precipitation event during the third week of the campaign (Sept 19-21) which decreased aerosol concentrations over Houston between these events. Sept 25-26 were peak ozone days in and downwind of Houston (Baier, et al. 2015). Conroe, the northern most sampling site, displayed the one day delay, Sept 26, in peak concentrations from the high ozone event during DISCOVER-AQ.

MT, the central sampling site located close to Downtown Houston along Interstate-45, is the most representative site for the ambient concentrations and potential exposure of downtown Houston. MC and C represent different types of urban outflow sites, each with different local inputs. MC is closer to Houston rush hour traffic and industrial/shipping areas which run from Houston along the ship channel, along the bay

and to the Gulf of Mexico. C is adjacent to the southern piney woods area of east Texas and receives likely receives more biogenic contribution (Bean, et al. 2016).

4.3 $PM_{2.5}$ Organic Carbon Results

Ambient concentrations of OC and WSOC across the three $PM_{2.5}$ sites trend together for most of the month; concentrations build and peak in the second and last

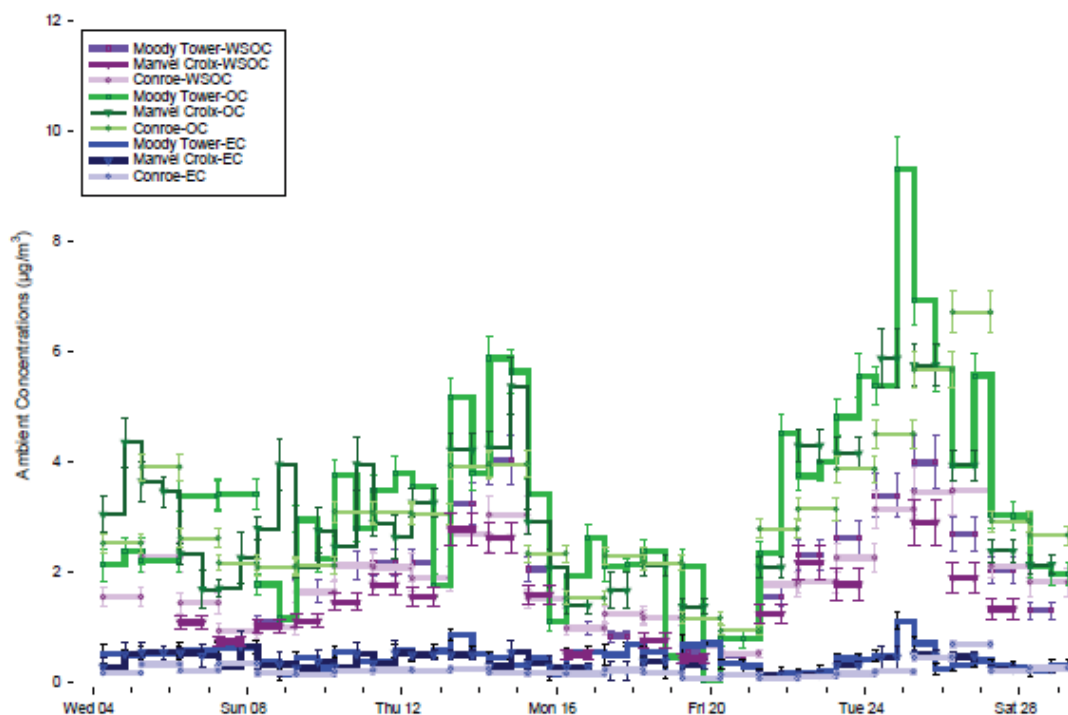


Figure 2.3. Sept 2013 $PM_{2.5}$ organic carbon (OC-green), elemental carbon (EC-blue) and water-soluble organic carbon (WSOC-purple) ambient concentrations at Moody Tower (MT-medium tones), Manvel Croix (MC-dark tones) and Conroe (C-light tones) sampling sites across Houston, TX

weeks, with the most consistent low concentrations during the intermittent rainy period in the third week (Figure 2.7). MT almost always has the highest OC and WSOC of the three sites, except for a few days in the first week of Sept when both MC and C are

higher than MT. At MT, OC PM_{2.5} concentrations built up over the final week and peaked the night before the high ozone event (Sept 24th) at 9.33 µg/m³, which was the highest concentration for OC during this campaign (Figure 2.4). The OC concentrations at MC are high for both Sept 24 and Sept 25, while 24h concentrations steadily rise for the week at C. MC, located south of MT in the suburban areas of Houston receives potential downwind emissions from MT, as seen in the results from DISCOVER-AQ.

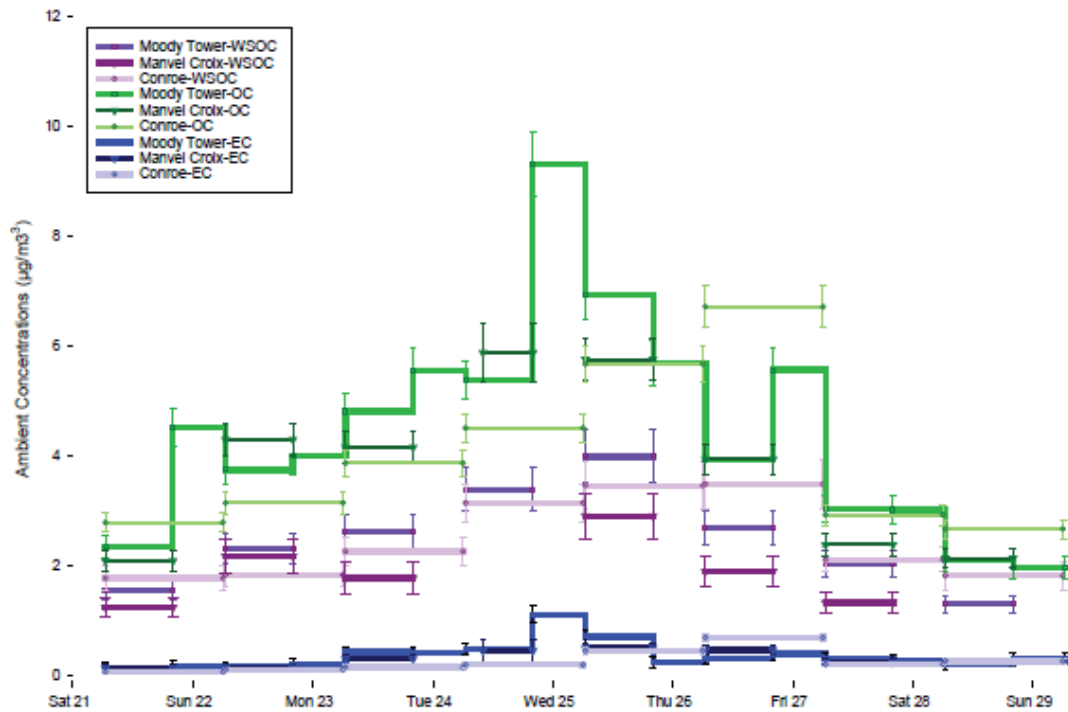


Figure 2.4. Last week of the DISCOVER-AQ sampling campaign PM_{2.5} organic carbon (OC-green), elemental carbon (EC-blue) and water-soluble organic carbon (WSOC-purple) ambient concentrations at Moody Tower (MT-medium tones), Manvel Croix (MC-dark tones) and Conroe (C-light tones) sampling sites across Houston, TX

The second week of the campaign also had a building period of OC and WSOC. The highest PM_{2.5} night concentrations at MC, were observed on Sept 14 at 5.38 µg/m³. Low

concentrations of OC occurred on Sept 6 during DISCOVER-AQ at MC, while MT and C displayed lowest concentrations of OC during the precipitation event.

PM_{2.5} results for 24 h OC concentrations for C displayed a peak OC aerosol concentration on Sept 26 at 6.72 µg/m³, the day after the high ozone event, as seen in Figure 2.3. Regional distribution of aerosol concentrations explains the delay in peak concentrations to C, the site located most north of the other three sites from DISCOVER-AQ. The results from C display the potential for sampling sites to influence measured concentrations observed at other sites during DISCOVER-AQ.

Organic carbon concentrations seen at TCEQ sites, specifically Galveston and Clinton, had OC ambient concentrations range from 0.30-3.01 µg/m³ and 1.39-5.94 µg/m³, respectively. These ambient concentrations ranges were based off of six samples taken from Galveston and five samples taken from Clinton. These TCEQ ranges, compared to the DISCOVER AQ sites, are within middle of the ranges from the TCEQ sites, with ranges from lower concentrations in Galveston to highest concentrations of OC in Clinton TCEQ sites during Sept 2013. Clinton TCEQ site is historically known to have exceeded PM_{2.5} concentrations, suggesting the concentrations seen during DISCOVER-AQ were not the highest concentrations seen during Sept 2013 (Sullivan, et al. 2013).

4.4 PM_{2.5} Water-Soluble Organic Carbon Results

As mentioned previously, WSOC concentrations at all three sites displayed overall similar trends to OC for Sept. Daytime samples were analyzed for WSOC. At MT, peak concentrations occurred on Sept 14th at 4.04 µg/m³, with minimum WSOC concentrations occurring during the precipitation event. This building period in the

second week had measured WSOC of similar magnitude to the building period in the final week, but had a higher WSOC to OC ratio. This illustrates that carbonaceous aerosol experienced two building events under different conditions within Houston: the second week had BTs from the ESE, lower ozone and higher WSOC to OC ratios while the final week had higher OC, BTs from the NNE with recirculation from Galveston Bay and high ozone (Figure 2.2). At MC, peak WSOC concentrations occurred during the high ozone event at $2.90 \mu\text{g}/\text{m}^3$, which is of similar magnitude to Sept 14-15. Minimum concentrations of daytime WSOC were very similar at both sites, at $0.48 \mu\text{g}/\text{m}^3$ and $0.42 \mu\text{g}/\text{m}^3$ at MT and MC, respectively, during the precipitation events in the third week. Similar to OC concentrations, 24 h concentrations at C displayed peak aerosol concentrations on Sept 26, the day after the high ozone event. Minimum WSOC concentrations at C also occurred during the precipitation event during DISCOVER-AQ.

As mentioned previously, WSOC has been used as a proxy for SOA in urban areas. Concentrations of WSOC indicate high contributions of SOA in all the sampling sites during the DISCOVER-AQ sampling campaign. WSOC concentrations from Houston from August to Sept 2006 averaged $1.48 \pm 2.30 \mu\text{g}/\text{m}^3$, lower than concentrations seen in $\text{PM}_{2.5}$ samples collected during DISCOVER-AQ (Anderson, et al. 2008). As mentioned in the introduction, components of water-soluble particulate matter are correlated with DTT activity in urban Georgia, suggesting the ROS (reactive oxidative species) generation potential of WSOC in urban areas (Verma, et al. 2014); this suggests that tracking spatial distributions of WSOC in Houston is relevant to understand exposure and potential health impacts of PM.

4.5 *PM_{2.5} Elemental Carbon Results*

EC concentrations displayed unique trends from OC and WSOC concentrations during the month of Sept. The EC concentrations do not always follow the same trends as the OC and WSOC, for example, EC concentrations are not as reduced during the precipitation events and do not have the same high magnitude of increase as the OC in the last week (peak ozone event).

For the primary sampling sites, MT Day EC concentrations were higher than MC (peak concentrations of 1.11 $\mu\text{g}/\text{m}^3$ and 0.65 $\mu\text{g}/\text{m}^3$, respectively). Weekday morning hours are known to provide peak concentrations in ambient EC, due to morning rush hour traffic and lower boundary heights, causing potential increases in exposure. High morning EC levels have been linked to exposure to children near highways traveling to school in the morning, leading to potential respiratory health effects including asthma (Spira-Cohen, et al. 2010; English, et al. 1999). However, from DISCOVER-AQ night time averages for MC were higher than MT during the first two weeks of the campaign. Higher EC concentrations at MC during nighttime could be spatial distribution of urban emission from Houston traveling to suburban areas of Houston during the evening.

$\text{PM}_{2.5}$ EC concentrations were lower at C than MT and MC. BT analysis displays no wind masses traveling past the other three sampling sites to C (Figure 2.2). This would suggest little direct impact from the other three sampling sites to C, although impact from the Houston metro area is likely. EC concentrations at TCEQ sites on the Gulf (Galveston) and in downtown Houston (Clinton Avenue) had ambient concentrations range from 0.00-0.19 $\mu\text{g}/\text{m}^3$ and 0.22-1.70 $\mu\text{g}/\text{m}^3$, respectively. The DISCOVER AQ sites

concentrations higher than Clinton Avenue, of C. with the exception Conroe EC concentrations were lower than Clinton but higher than Galveston.

4.6 TSP Carbonaceous Aerosol Results

TSP samples were collected at MT, MC and LP. Collecting TSP samples at these three sites provided a perspective on the potential contribution and concentrations of total carbonaceous aerosol between an urban, suburban and industrial site; TSP will include coarse PM which may have additional contributions from soil, crustal material, sea salt or other mechanically generated emissions and fine PM. Only LP had WSOC measurements for the campaign. Similar to the $PM_{2.5}$, there are two building events

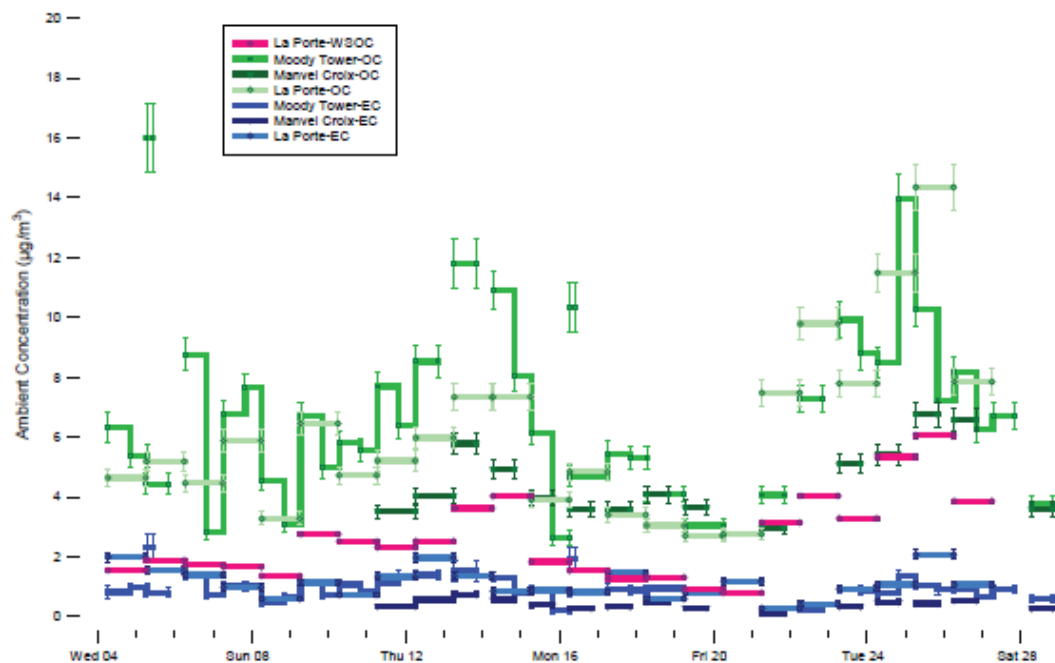


Figure 2.5. Sept 2013 TSP organic carbon (OC-green), elemental carbon (EC-blue) and water-soluble organic carbon (WSOC-pink) ambient concentrations at Moody Tower (MT-medium tones), Manvel Croix (MC-dark tones) and La Porte (LP-light tones) sampling sites across Houston, TX

during the campaign: ambient concentrations build and peak during the second and fourth week. This is particularly true at the MT site, which likely has the most consistent urban signal. The two building events peaked at similar concentrations (OC and EC) for MT and MC, despite the differences in air mass origin. However, there is a different story for OC at LP for these two building periods; for the second building event, the OC was nearly twice as high at LP on Sept 25, compared to peak concentration for Sept 13. The EC concentration at LP, MT and MC was similar for these two peak events. Additionally, for the second event, all three components (OC, EC and WSOC) peak on

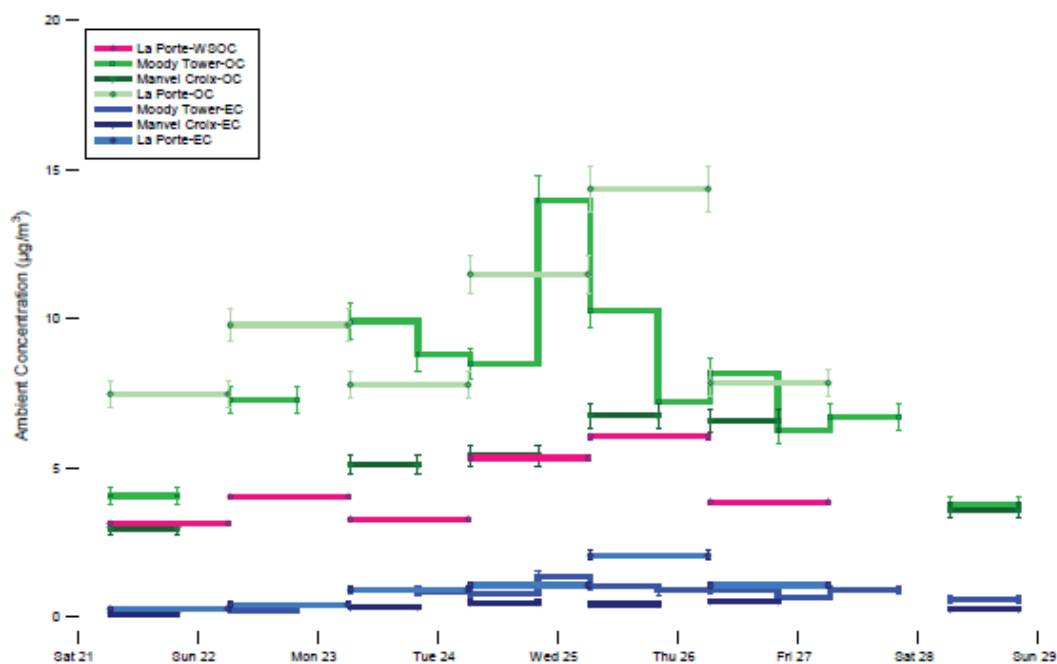


Figure 2.6. Last week of the DISCOVER-AQ sampling campaign TSP organic carbon (OC-green), elemental carbon (EC-blue) and water-soluble organic carbon (WSOC-pink) ambient concentrations at Moody Tower (MT-medium tones), Manvel Croix (MC-dark tones) and La Porte (LP-light tones) sampling sites across Houston, TX

Sept 25, while in the first event, the peak concentration for the three components diverged over Sept 12-14 (Figure 2.6). As discussed previously, the Sept 25 event included recirculation, high ozone production and BTs from the NNE, while the building event in the second week had BTs from the ESE and lower ozone (Figure 2.2 and Table 2.1). LP differs from other sites, with all of the concentrations peaking on the high ozone event. Further characterization is needed to determine whether industrial emissions contributed to the high ozone production and associated peaks in OC. Overall, lower concentrations were seen for all three sites during the week of Sept 16, which had intermittent rain events. At the LP 24 h TSP site, OC, WSOC and EC displaying lowest concentrations on Sept 19, 20, and 21, respectively.

4.7 Precipitation Patterns

Precipitation occurred at the highest average of approximately 6.95 inches on Sept 20th, the heaviest rain event during the campaign. Within the week of Sept 16 there were intermittent rain events which brought the OC and WSOC concentrations down, but had less apparent effect in EC concentrations in the 24 h samples from C and LP, as seen in Figure 2.7. When EC is compared to the highest precipitation event (Sept 19-21) that occurred during DISCOVER-AQ in Houston, EC concentrations did not lower with increasing precipitation rates. Previous studies on EC removal from the atmosphere specify that EC that is hydrophobic is expected to have a residence time that is longer in the atmosphere than other fractions of carbonaceous aerosols (Ogren, Groblicki, and Charlson 1984). This longer residence time is due to less effective diffusion and nucleation scavenging to cloud droplets by EC. Another explanation for these results could be the amount of hygroscopic substances that are coated on the EC from this

sampling campaign (Ogren, Groblicki, and Charlson 1984). Higher resolution impact analysis is needed to fully understand the impacts of precipitation on aerosol concentrations.

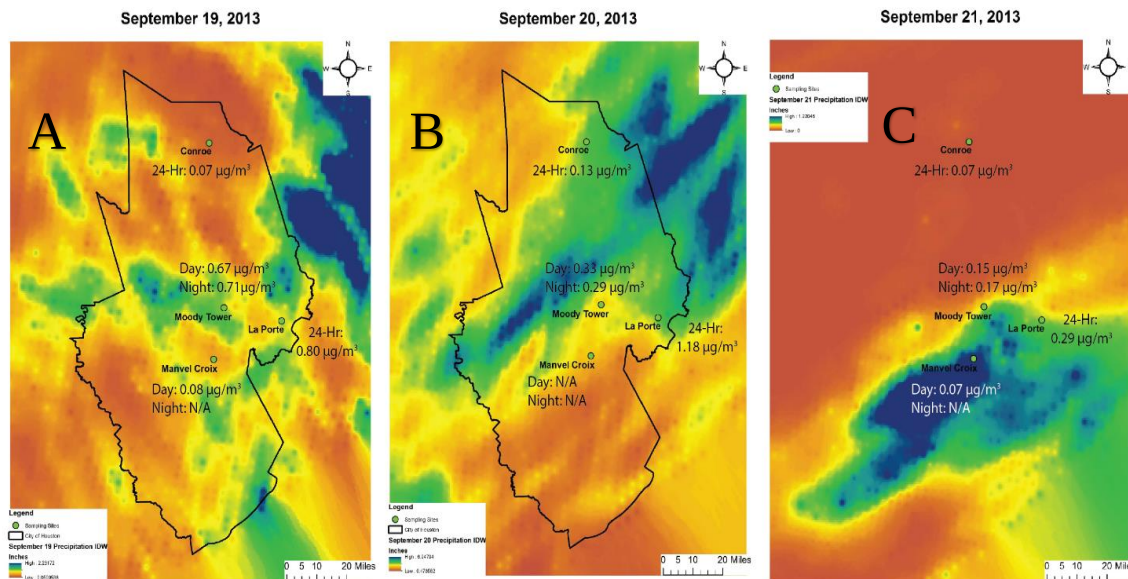


Figure 2.7. IDW Analysis of precipitation rates during the high rain event (A) Sept 19, (B) Sept 20, (C) Sept 21 in Houston. Monitoring sites are labeled for day (Moody Tower, Manvel Croix, Conroe, and La Porte) with their respective elemental carbon concentrations. The total precipitation scale is: A) dark blue: 2.23 inches, red: 0.05 inches B) dark blue: 6.95 inches, red: 0.47 inches C) dark blue: 1.22 inches, red: 0 inches

4.8 Comparison with $PM_{2.5}$ and Ozone

There is increasing evidence within the literature linking SOA formation to atmospheric oxidants, such as ozone (Zhang, et al. 2014; Liu, et al. 2011). Here we examine this relationship in the Houston metropolitan areas utilizing ozone maximums daily average $PM_{2.5}$ concentrations from long term monitoring sites in Houston: Park Place, Galveston, Seabrook, Deer Park, Houston East, Clinton, and Conroe (see Sampling Site section). A previous study determined that correlation between the daily ozone maximum and the daily average $PM_{2.5}$ yielded the highest correlation coefficients (Brown

and Jin 2013). Higher time resolution data, (e.g. hourly) for a California study, resulted in relatively weak negative correlations ($r^2 < 0.3$), potentially due to short term temporal

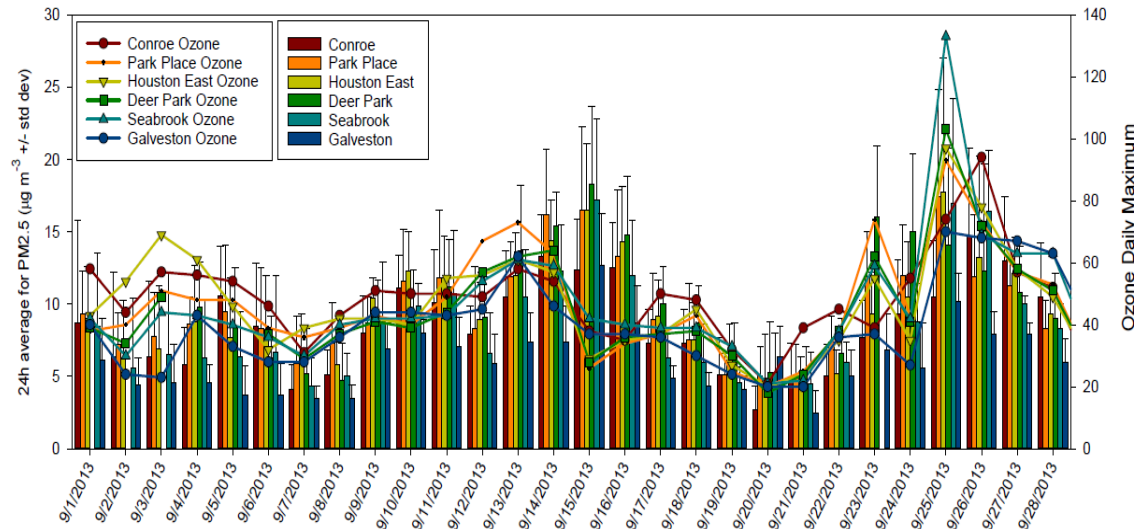


Figure 2.8. TCEQ Monitoring Sites ozone and PM_{2.5} concentrations across the southeastern regions of Texas

differences in the relationships of ozone and PM with temperature and relative humidity (Brown and Jin 2013). However, longer times scales (e.g. daily) were shown to provide relatively strong positive correlations ($r^2 > 0.5$) for the same study. For the current study, regression analysis using daily ozone maximums and daily average PM_{2.5} concentrations from the seven sites (Sept 1 – 29, 2013) yielded relative weak positive correlations with r-squared values ranging from 0.25 to 0.38, with a stronger relationship at Seabrook ($r^2=0.47$). However, daily ozone maximum concentrations and daily average PM_{2.5} concentrations generally trended together with the exception of a divergent for Sept 15 and 16 (Figure 2.8). A second round of regression analysis, excluding data from the 15th and 16th, yielded relative strong positive correlations with r-squared values ranging from

0.52 to 0.69. The removal of these two data points provided an average increase in r -squared values of 0.27. This temporal relationship between ozone and $\text{PM}_{2.5}$ parallels the previous study in California (specifically during the late summer and early fall; i.e. August and Sept) (Brown and Jin 2013). In California, this relationship is concurrent with periods of high temperatures and stagnant meteorology (Brown and Jin 2013). Similarly, in Texas summertime ozone events are driven by high temperatures and periods of stagnant meteorology (Zhou, Cohan, and Henderson 2014).

5. Conclusion

The DISCOVER-AQ campaign provided the spatial and temporal distribution of carbonaceous aerosols in the city of Houston during Sept 2013. OC, EC and WSOC concentrations were impacted two building periods for PM in the second and last weeks with a clean-out period of intermittent precipitation. The carbon fractions in both size fractions ($\text{PM}_{2.5}$ and TSP), particularly OC and WSOC, peaked during an observed ozone event on Sept 25, with a delay in peak concentrations observed in the northernmost site: Conroe. The lowest concentrations occurred during a week of intermittent precipitation, however, EC concentrations were less impacted. Possible contributions to the concentrations in Houston include motor-vehicle emissions from downtown Houston, shipping emissions from the Houston Ship Channel, and biogenic emissions from agricultural and forested areas around Conroe. This campaign highlighted potential differences in exposure to OC, EC and WSOC across Houston, which calls for further mitigation efforts in Houston and other metropolitan areas.

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CHAPTER THREE

Conclusion

The DISCOVER-AQ sampling campaign of Sept 2013 in Houston, TX provided invaluable samples for the determination of spatial and temporal carbonaceous aerosol trends. Determining trends in the city of Houston, the fourth largest city in the United States, provides a framework of aerosol concentrations and exposures to potential human health effects. Peaks in OC, EC and WSOC generally occurred during the last week of the sampling campaign, during the duration of a high ozone event in the city. This suggests the potential of precursor pollutants, including volatile organic enhancing the formation of PM_{2.5} in the city of Houston.

BTs allowed for the characterization of the origin air masses during Sept 2013. All four sites selected to represent the Houston Metropolitan area had dominant air masses from the southeastern portion of the United States, passing through the Gulf of Mexico. At the MT sampling site, dominant air masses passed through the LP sampling site, located close to the Houston Ship Channel.

Precipitation patterns that occurred during DISCOVER-AQ displayed intermittent rain events during the week of Sept 16. Low concentrations of ambient aerosol occurred during the rain event, with the exception of EC at C and LP, the two auxiliary sites chosen for this sampling campaign. Further characterization of precipitation patterns and aerosol concentrations need to be examined to understand this trend that occurred during Sept 2013.

The samples collected at DISCOVER-AQ have also been analyzed for molecular tracers and radiocarbon. These analyses will improve the characterization of carbonaceous aerosols and enable determination of their emission sources. Incorporating the results from this study, along with these other research facets will provide a better understanding of air quality in the city of Houston.

APPENDIX

Table A.1. PM_{2.5} Concentrations of OC, EC and WSOC during Sept 2013¹

Name	Start Time	End Time	OC (µg/m ³)	OC Unc (µg/m ³)	EC (µg/m ³)	EC Unc (µg/m ³)	WSOC (µg/m ³)	WSOC Unc (µg/m ³)
130904_D*_MT	9/4/2013 6:30	9/4/2013 20:00	2.13	0.29	0.52	0.18	N/A	N/A
130904_HV2.5_N_MT	9/4/2013 20:00	9/5/2013 6:30	2.38	0.24	0.47	0.12	N/A	N/A
130905_MV2.5_MT	9/5/2013 6:00	9/6/2013 5:30	2.20	0.21	0.53	0.11	N/A	N/A
130906_MV2.5_MT	9/6/2013 6:00	9/7/2013 5:30	3.38	0.27	0.59	0.11	N/A	N/A
130907_MV2.5_MT	9/7/2013 6:00	9/8/2013 5:30	3.43	0.27	0.64	0.12	N/A	N/A
130908_HV2.5_D_MT	9/8/2013 6:30	9/8/2013 20:00	1.77	0.18	0.38	0.10	1.09	0.13
130908_N*_MT	9/8/2013 20:00	9/9/2013 6:30	1.15	0.17	0.14	0.10	N/A	N/A
130909_HV2.5_D_MT	9/9/2013 6:30	9/9/2013 20:00	2.95	0.24	0.44	0.10	1.66	0.20
130909_N*_MT	9/9/2013 20:00	9/10/2013 6:30	2.24	0.22	0.26	0.10	N/A	N/A
130910_HV2.5_D_MT	9/10/2013 6:30	9/10/2013 20:00	3.77	0.28	0.56	0.11	2.12	0.25
130910_N*_MT	9/10/2013 20:00	9/11/2013 6:30	2.80	0.25	0.37	0.11	N/A	N/A
130911_HV2.5_D_MT	9/11/2013 6:30	9/11/2013 20:00	3.49	0.27	0.37	0.10	2.17	0.25
130911_N*_MT	9/11/2013 20:00	9/12/2013 6:30	3.79	0.30	0.57	0.12	N/A	N/A
130912_HV2.5_D_MT	9/12/2013 6:30	9/12/2013 20:00	3.56	0.27	0.49	0.10	2.17	0.25
130912_N*_MT	9/12/2013 20:00	9/13/2013 6:30	1.76	0.20	0.56	0.12	N/A	N/A
130913_HV2.5_D_MT	9/13/2013 6:30	9/13/2013 20:00	5.18	0.35	0.86	0.12	3.24	0.37
130913_N*_MT	9/13/2013 20:00	9/14/2013 6:30	3.78	0.30	0.52	0.12	N/A	N/A
130914_HV2.5_D_MT	9/14/2013 6:30	9/14/2013 20:00	5.88	0.39	0.44	0.10	4.04	0.45
130914_N*_MT	9/14/2013 20:00	9/15/2013 6:30	5.64	0.39	0.32	0.11	N/A	N/A
130915_HV2.5_D_MT	9/15/2013 6:30	9/15/2013 20:00	3.41	0.27	0.44	0.10	2.05	0.23
130915_N*_MT	9/15/2013 20:00	9/16/2013 6:30	1.11	0.17	0.13	0.10	N/A	N/A
130916_HV2.5_D_MT	9/16/2013 6:30	9/16/2013 20:00	1.92	0.19	0.53	0.10	0.99	0.12
130916_N*_MT	9/16/2013 20:00	9/17/2013 6:30	2.62	0.25	0.54	0.12	N/A	N/A
130917_HV2.5_D_MT	9/17/2013 6:30	9/17/2013 20:00	2.10	0.28	0.50	0.17	0.84**	0.11**
130917_N*_MT	9/17/2013 20:00	9/18/2013 6:30	2.13	0.11	0.69	0.03	N/A	N/A
130918_HV2.5_D_MT	9/18/2013 6:30	9/18/2013 20:00	2.38	0.21	0.56	0.10	N/A	N/A
130918_N*_MT	9/18/2013 20:00	9/19/2013 6:30	0.46	0.14	0.16	0.11	N/A	N/A

¹ Code for name: Year-Month-Day_Sample Type_Run Duration_Site. Site abbreviations are Moody Tower (MT), Manvel Croix (MC) and Conroe (C). Calculated samples are denoted with _D* and _N*, with Day (D – 06:30-20:00) and Night (N – 20:00-06:00). Samples with ** refer to samples run during the afternoon (A - 10:00-20:00). MV2.5 and HV2.5 refer to air samplers Medium Volume PM_{2.5} and High Volume PM_{2.5}, respectively.

130919_HV2.5_D_MT	9/19/2013 6:30 9/19/2013	9/19/2013 20:00	2.11	0.29	0.67	0.19	0.56**	0.08**
130919_N*_MT	20:00	9/20/2013 6:30	0.05	0.00	0.71	0.03	N/A	N/A
130920_HV2.5_D_MT	9/20/2013 6:30 9/20/2013	9/20/2013 20:00	0.79	0.13	0.33	0.09	0.48	0.06
130920_N*_MT	20:00	9/21/2013 6:30	0.78	0.16	0.29	0.11	N/A	N/A
130921_HV2.5_D_MT	9/21/2013 6:30 9/21/2013	9/21/2013 20:00	2.34	0.21	0.15	0.08	1.55	0.18
130921_N*_MT	20:00	9/22/2013 6:30	4.51	0.34	0.17	0.11	N/A	N/A
130922_HV2.5_D_MT	9/22/2013 6:30 9/22/2013	9/22/2013 20:00	3.75	0.28	0.17	0.08	2.32	0.28
130922_N*_MT	20:00	9/23/2013 6:30	3.99	0.32	0.19	0.11	N/A	N/A
130923_HV2.5_D_MT	9/23/2013 6:30 9/23/2013	9/23/2013 20:00	4.81	0.33	0.43	0.10	2.62	0.32
130923_N*_MT	20:00	9/24/2013 6:30	5.57	0.40	0.42	0.12	N/A	N/A
130924_HV2.5_D_MT	9/24/2013 6:30 9/24/2013	9/24/2013 20:00	5.38	0.36	0.47	0.10	3.39	0.39
130924_N*_MT	20:00	9/25/2013 6:30	9.33	0.58	1.11	0.15	N/A	N/A
130925_HV2.5_D_MT	9/25/2013 6:30 9/25/2013	9/25/2013 20:00	6.94	0.44	0.71	0.11	3.99	0.49
130925_N*_MT	20:00	9/26/2013 6:30	5.70	0.40	0.23	0.11	N/A	N/A
130926_HV2.5_D_MT	9/26/2013 6:30 9/26/2013	9/26/2013 20:00	3.93	0.29	0.31	0.09	2.69	0.31
130926_N*_MT	20:00	9/27/2013 6:30	5.57	0.40	0.39	0.12	N/A	N/A
130927_HV2.5_D_MT	9/27/2013 6:30 9/27/2013	9/27/2013 20:00	3.03	0.24	0.31	0.09	2.03	0.24
130927_N*_MT	20:00	9/28/2013 6:30	3.02	0.27	0.27	0.11	N/A	N/A
130928_HV2.5_D_MT	9/28/2013 6:30 9/28/2013	9/28/2013 20:00	2.10	0.20	0.19	0.09	1.31	0.16
130928_N*_MT	20:00	9/29/2013 6:30	1.96	0.21	0.29	0.10	N/A	N/A
130904_D*_MC	9/4/2013 6:30	9/4/2013 20:00	3.05	0.32	0.28	0.16	N/A	N/A
130904_MV2.5_N_MC	9/4/2013 20:00	9/4/2013 6:30	4.36	0.46	0.51	0.20	N/A	N/A
130905_D*_MC	9/5/2013 6:30	9/5/2013 20:00	3.65	0.35	0.55	0.17	N/A	N/A
130905_HV2.5_N_MC	9/5/2013 20:00	9/5/2013 6:30	3.47	0.28	0.54	0.12	N/A	N/A
130906_HV2.5_D_MC	9/6/2013 6:30	9/6/2013 20:00	2.34	0.20	0.53	0.10	1.08	0.12
130906_MV2.5_N_MC	9/6/2013 20:00	9/6/2013 6:30	1.69	0.36	0.48	0.22	N/A	N/A
130907_HV2.5_D_MC	9/7/2013 6:30	9/7/2013 20:00	1.71	0.17	0.28	0.08	0.74	0.08
130907_MV2.5_N_MC	9/7/2013 20:00	9/7/2013 6:30	2.26	0.46	0.65	0.28	N/A	N/A
130908_HV2.5_D_MC	9/8/2013 6:30	9/8/2013 20:00	2.79	0.22	0.32	0.09	1.02	0.11
130908_MV2.5_N_MC	9/8/2013 20:00	9/8/2013 6:30	3.95	0.47	0.33	0.21	N/A	N/A
130909_HV2.5_D_MC	9/9/2013 6:30	9/9/2013 20:00	2.08	0.18	0.26	0.08	1.114	0.121
130909_MV2.5_N_MC	9/9/2013 20:00	9/9/2013 6:30	2.76	0.41	0.37	0.21	N/A	N/A
130910_HV2.5_D_MC	9/10/2013 6:30 9/10/2013	9/10/2013 20:00	2.46	0.20	0.28	0.08	1.45	0.16
130910_MV2.5_N_MC	20:00	9/10/2013 6:30	3.96	0.48	0.51	0.23	N/A	N/A
130911_HV2.5_D_MC	9/11/2013 6:30 9/11/2013	9/11/2013 20:00	2.90	0.22	0.35	0.09	1.77	0.19
130911_MV2.5_N_MC	20:00	9/11/2013 6:30	2.63	0.40	0.53	0.22	N/A	N/A
130912_HV2.5_D_MC	9/12/2013 6:30	9/12/2013 20:00	3.26	0.24	0.50	0.09	1.55	0.17
130913_HV2.5_D_MC	9/13/2013 6:30	9/13/2013 20:00	4.22	0.29	0.50	0.09	N/A	N/A
130914_HV2.5_D_MC	9/14/2013 6:30	9/14/2013 20:00	4.25	0.29	0.29	0.08	2.78	0.29

130914_MV2.5_N_MC	9/14/2013 20:00	9/14/2013 6:30	5.38	0.51	0.54	0.20	N/A	N/A
130915_HV2.5_D_MC	9/15/2013 6:30 9/15/2013 20:00	9/15/2013 20:00	2.91	0.23	0.34	0.09	1.59	0.17
130915_MV2.5_N_MC	9/15/2013 6:30 9/15/2013 20:00	9/15/2013 6:30	2.07	0.34	0.29	0.18	N/A	N/A
130916_HV2.5_D_MC	9/16/2013 6:30 9/17/2013 10:00	9/16/2013 20:00	1.39	0.15	0.28	0.08	0.50	0.09
130917_MV2.5_A_MC**	9/18/2013 6:30 9/18/2013 20:00	9/18/2013 20:00	1.66	0.33	0.21	0.19	N/A	N/A
130918_HV2.5_D_MC	9/19/2013 6:30 9/19/2013 20:00	9/19/2013 20:00	2.11	0.18	0.38	0.09	0.77	0.14
130919_HV2.5_D_MC	9/21/2013 6:30 9/21/2013 20:00	9/21/2013 20:00	1.38	0.15	0.33	0.08	0.42	0.09
130921_HV2.5_D_MC	9/22/2013 6:30 9/22/2013 20:00	9/22/2013 20:00	2.09	0.18	0.13	0.07	1.24	0.19
130922_HV2.5_D_MC	9/23/2013 6:30 9/23/2013 20:00	9/23/2013 20:00	4.30	0.29	0.14	0.07	2.17	0.31
130923_HV2.5_D_MC	9/24/2013 6:30 9/24/2013 10:00	9/24/2013 20:00	4.16	0.28	0.30	0.08	1.77	0.31
130924_MV2.5_A_MC**	9/25/2013 6:30 9/25/2013 20:00	9/25/2013 20:00	5.88	0.54	0.45	0.20	N/A	N/A
130925_HV2.5_D_MC	9/26/2013 6:30 9/26/2013 20:00	9/26/2013 20:00	5.76	0.37	0.50	0.09	2.90	0.42
130926_HV2.5_D_MC	9/27/2013 6:30 9/27/2013 20:00	9/27/2013 20:00	3.94	0.27	0.47	0.09	1.90	0.29
130927_HV2.5_D_MC	9/28/2013 6:30 9/28/2013 20:00	9/28/2013 20:00	2.38	0.20	0.24	0.08	1.33	0.20
130928_HV2.5_D_MC	9/28/2013 6:30 9/28/2013 20:00	9/28/2013 20:00	2.14	0.18	0.24	0.08	N/A	N/A
130904_HV2.5_C	9/4/2013 6:30 9/5/2013 6:00	9/5/2013 6:00	2.52	0.17	0.17	0.04	1.55	0.18
130905_HV2.5_C	9/5/2013 6:30 9/6/2013 6:00	9/6/2013 6:00	3.91	0.24	0.32	0.05	2.28	0.27
130906_HV2.5_C	9/6/2013 6:30 9/7/2013 6:00	9/7/2013 6:00	2.62	0.17	0.21	0.05	1.44	0.19
130907_HV2.5_C	9/7/2013 6:30 9/8/2013 6:00	9/8/2013 6:00	2.17	0.15	0.34	0.05	0.93	0.12
130908_HV2.5_C	9/8/2013 6:30 9/9/2013 6:00	9/9/2013 6:00	2.09	0.15	0.16	0.04	1.01	0.13
130909_HV2.5_C	9/9/2013 6:30 9/10/2013 6:00	9/10/2013 6:00	2.12	0.15	0.14	0.04	1.63	0.19
130910_HV2.5_C	9/10/2013 6:30 9/11/2013 6:00	9/11/2013 6:00	3.09	0.20	0.20	0.05	2.12	0.26
130911_HV2.5_C	9/11/2013 6:30 9/12/2013 6:00	9/12/2013 6:00	3.07	0.19	0.23	0.05	2.09	0.25
130912_HV2.5_C	9/12/2013 6:30 9/13/2013 6:00	9/13/2013 6:00	3.05	0.19	0.21	0.05	1.89	0.23
130913_HV2.5_C	9/13/2013 6:30 9/14/2013 6:00	9/14/2013 6:00	3.93	0.24	0.25	0.05	2.68	0.31
130914_HV2.5_C	9/14/2013 6:30 9/15/2013 6:00	9/15/2013 6:00	3.96	0.24	0.17	0.04	3.04	0.35
130915_HV2.5_C	9/15/2013 6:30 9/16/2013 6:00	9/16/2013 6:00	2.34	0.16	0.16	0.04	1.53	0.18
130916_HV2.5_C	9/16/2013 6:30 9/17/2013 6:00	9/17/2013 6:00	1.52	0.12	0.15	0.04	0.98	0.12
130917_HV2.5_C	9/17/2013 6:30 9/18/2013 6:00	9/18/2013 6:00	2.30	0.16	0.23	0.05	1.24	0.15
130918_HV2.5_C	9/18/2013 6:30 9/19/2013 6:00	9/19/2013 6:00	2.17	0.15	0.17	0.04	1.17	0.15
130919_HV2.5_C	9/19/2013 6:30 9/20/2013 6:00	9/20/2013 6:00	1.17	0.10	0.07	0.04	0.66	0.08
130920_HV2.5_C	9/20/2013 6:30 9/21/2013 6:00	9/21/2013 6:00	0.93	0.09	0.13	0.04	0.53	0.07
130921_HV2.5_C	9/21/2013 6:30 9/22/2013 6:00	9/22/2013 6:00	2.79	0.18	0.07	0.04	1.77	0.22
130922_HV2.5_C	9/22/2013 6:30 9/23/2013 6:00	9/23/2013 6:00	3.14	0.20	0.11	0.04	1.83	0.23
130923_HV2.5_C	9/23/2013 6:30 9/24/2013 6:00	9/24/2013 6:00	3.87	0.23	0.15	0.04	2.26	0.27
130924_HV2.5_C	9/24/2013 6:30 9/25/2013 6:00	9/25/2013 6:00	4.51	0.27	0.19	0.05	3.14	0.36
130925_HV2.5_C	9/25/2013 6:30 9/26/2013 6:00	9/26/2013 6:00	5.67	0.32	0.45	0.06	3.46	0.43
130926_HV2.5_C	9/26/2013 6:30 9/27/2013 6:00	9/27/2013 6:00	6.72	0.38	0.69	0.07	3.49	0.43
130927_HV2.5_C	9/27/2013 6:30 9/28/2013 6:00	9/28/2013 6:00	2.93	0.19	0.20	0.05	2.11	0.22
130928_HV2.5_C	9/28/2013 6:30 9/29/2013 6:00	9/29/2013 6:00	2.67	0.17	0.26	0.05	1.82	0.27

Table A.2. TSP Concentrations of OC, EC and WSOC during Sept 2013²

Name	Start Time	End Time	OC ($\mu\text{g}/\text{m}^3$)	OC Unc ($\mu\text{g}/\text{m}^3$)	EC ($\mu\text{g}/\text{m}^3$)	EC Unc ($\mu\text{g}/\text{m}^3$)	WSOC ($\mu\text{g}/\text{m}^3$)	WSOC Unc ($\mu\text{g}/\text{m}^3$)
130904_TSP_D*_MT	9/4/2013 6:30	9/4/2013 20:00	6.32	0.50	0.82	0.21	N/A	N/A
130904_TSP_N_MT	9/4/2013 20:00	9/5/2013 6:30	5.37	0.39	0.97	0.16	N/A	N/A
130905_TSP_M_MT	9/5/2013 6:30	9/5/2013 10:00	15.98	1.14	2.32	0.44	N/A	N/A
130905_TSP_N_MT	9/5/2013 20:00	9/5/2013 6:00	4.43	0.34	0.80	0.15	N/A	N/A
130906_TSP_D_MT	9/6/2013 6:30	9/6/2013 20:00	8.76	0.56	1.44	0.18	N/A	N/A
130906_TSP_N_MT	9/6/2013 20:00	9/7/2013 6:30	2.84	0.26	0.73	0.15	N/A	N/A
130907_TSP_D_MT	9/7/2013 6:30	9/7/2013 20:00	6.78	0.43	1.03	0.14	N/A	N/A
130907_TSP_N_MT	9/7/2013 20:00	9/8/2013 6:30	7.64	0.50	1.02	0.16	N/A	N/A
130908_TSP_D_MT	9/8/2013 6:30	9/8/2013 20:00	4.55	0.32	0.48	0.11	N/A	N/A
130908_TSP_N_MT	9/8/2013 20:00	9/9/2013 6:30	3.10	0.27	0.62	0.14	N/A	N/A
130909_TSP_D_MT	9/9/2013 6:30	9/9/2013 20:00	6.71	0.43	1.08	0.14	N/A	N/A
130909_TSP_N_MT	9/9/2013 20:00	9/10/2013 6:30	4.97	0.36	0.71	0.14	N/A	N/A
130910_TSP_D_MT	9/10/2013 6:30	9/10/2013 20:00	5.84	0.38	1.07	0.14	N/A	N/A
130910_TSP_N_MT	9/10/2013 20:00	9/11/2013 6:30	5.55	0.39	0.86	0.15	N/A	N/A
130911_TSP_D_MT	9/11/2013 6:30	9/11/2013 20:00	7.69	0.48	1.10	0.14	N/A	N/A
130911_TSP_N_MT	9/11/2013 20:00	9/12/2013 6:30	6.39	0.46	1.34	0.20	N/A	N/A
130912_TSP_D_MT	9/12/2013 6:30	9/12/2013 20:00	8.52	0.52	1.40	0.16	N/A	N/A
130913_TSP_D*_MT	9/13/2013 6:30	9/13/2013 20:00	11.80	0.85	1.52	0.32	N/A	N/A
130914_TSP_D_MT	9/14/2013 6:30	9/14/2013 20:00	10.92	0.64	1.31	0.15	N/A	N/A
130914_TSP_N_MT	9/14/2013 20:00	9/15/2013 6:30	8.06	0.53	0.80	0.16	N/A	N/A
130915_TSP_D_MT	9/15/2013 6:30	9/15/2013 20:00	6.13	0.40	0.91	0.13	N/A	N/A
130915_TSP_N_MT	9/15/2013 20:00	9/16/2013 6:30	2.62	0.25	0.22	0.12	N/A	N/A
130916_TSP_M_MT	9/16/2013 6:30	9/16/2013 10:00	10.35	0.82	1.92	0.38	N/A	N/A
130916_TSP_N_MT	9/16/2013 6:30	9/17/2013 20:00	4.68	0.35	0.81	0.15	N/A	N/A
130917_TSP_D*_MT	9/17/2013 6:30	9/17/2013 20:00	5.42	0.44	0.91	0.21	N/A	N/A
130917_TSP_N_MT	9/17/2013 20:00	9/18/2013 6:30	5.29	0.39	0.87	0.16	N/A	N/A
130918_TSP_MT**	9/18/2013 6:30	9/18/2013 6:00	4.12	0.26	0.94	0.10	N/A	N/A
130919_TSP_MT**	9/18/2013 6:30	9/18/2013 6:00	3.04	0.20	0.89	0.09	N/A	N/A
130921_TSP_D_MT	9/21/2013 6:30	9/21/2013 20:00	4.06	0.29	0.19	0.09	N/A	N/A
130922_TSP_D_MT	9/22/2013 6:30	9/22/2013 20:00	7.29	0.45	0.25	0.09	N/A	N/A
130923_TSP_D_MT	9/23/2013 6:30	9/23/2013 20:00	9.92	0.58	0.92	0.13	N/A	N/A
130923_TSP_N_MT	9/23/2013 20:00	9/24/2013 6:30	8.78	0.56	0.87	0.16	N/A	N/A

² Code for name: Year-Month-Day_Sample Type_Run Duration_Site. Site abbreviations are Moody Tower (MT), Manvel Croix (MC) and La Porte (LP). Calculated samples are denoted with _D*, with Day (D – 06:30-20:00). Night samples are N – 20:00-06:00 and morning samples are M- 06:30-10:00. Samples with ** refer to samples run for 24 hours (** - 06:30-06:00).

130924_TSP_D_MT	9/24/2013 6:30	9/24/2013 20:00	8.49	0.51	0.77	0.12	N/A	N/A
130924_TSP_N_MT	9/24/2013 20:00	9/25/2013 6:30	13.95	0.83	1.33	0.19	N/A	N/A
130925_TSP_D_MT	9/25/2013 6:30	9/25/2013 20:00	10.29	0.60	1.03	0.13	N/A	N/A
130925_TSP_N_MT	9/25/2013 20:00	9/26/2013 6:30	7.22	0.51	0.90	0.18	N/A	N/A
130926_TSP_D_MT	9/26/2013 6:30	9/26/2013 20:00	8.17	0.49	0.91	0.13	N/A	N/A
130926_TSP_N_MT	9/26/2013 20:00	9/27/2013 6:30	6.24	0.46	0.67	0.17	N/A	N/A
130927_TSP_D_MT	9/27/2013 6:30	9/27/2013 20:00	6.70	0.42	0.93	0.13	N/A	N/A
130928_TSP_D_MT	9/28/2013 6:30	9/28/2013 20:00	3.77	0.27	0.59	0.11	N/A	N/A
130911_TSP_MC	9/11/2013 6:30	9/12/2013 6:00	3.51	0.22	0.35	0.05	N/A	N/A
130912_TSP_MC	9/12/2013 6:30	9/13/2013 6:00	4.04	0.24	0.56	0.06	N/A	N/A
130913_TSP_D_MC	9/13/2013 6:30	9/13/2013 20:00	5.78	0.36	0.73	0.09	N/A	N/A
130914_TSP_D_MC	9/14/2013 6:30	9/14/2013 20:00	4.92	0.31	0.56	0.08	N/A	N/A
130915_TSP_D_MC	9/15/2013 6:30	9/15/2013 20:00	3.95	0.27	0.38	0.08	N/A	N/A
130916_TSP_D_MC	9/16/2013 6:30	9/16/2013 20:00	3.58	0.25	0.27	0.07	N/A	N/A
130917_TSP_D_MC	9/17/2013 6:30	9/17/2013 20:00	3.57	0.24	0.32	0.07	N/A	N/A
130918_TSP_D_MC	9/18/2013 6:30	9/18/2013 20:00	4.07	0.27	0.49	0.08	N/A	N/A
130919_TSP_D_MC	9/19/2013 6:30	9/19/2013 20:00	3.63	0.25	0.30	0.07	N/A	N/A
130921_TSP_D_MC	9/21/2013 6:30	9/21/2013 20:00	2.96	0.21	0.12	0.06	N/A	N/A
130923_TSP_D_MC	9/23/2013 6:30	9/23/2013 20:00	5.09	0.31	0.33	0.07	N/A	N/A
130924_TSP_D_MC	9/24/2013 6:30	9/24/2013 20:00	5.39	0.34	0.48	0.08	N/A	N/A
130925_TSP_D_MC	9/25/2013 6:30	9/25/2013 20:00	6.75	0.41	0.43	0.08	N/A	N/A
130926_TSP_D_MC	9/26/2013 6:30	9/26/2013 20:00	6.56	0.40	0.53	0.09	N/A	N/A
130928_TSP_D_MC	9/28/2013 6:30	9/28/2013 20:00	3.59	0.26	0.27	0.08	N/A	N/A
130904_TSP_LP	9/4/2013 6:30	9/5/2013 6:00	4.64	0.30	1.99	0.16	1.54	0.03
130905_TSP_LP	9/5/2013 6:30	9/6/2013 6:00	5.19	0.32	1.56	0.13	1.89	0.03
130906_TSP_LP	9/6/2013 6:30	9/7/2013 6:00	4.45	0.29	1.39	0.13	1.72	0.03
130907_TSP_LP	9/7/2013 6:30	9/8/2013 6:00	5.88	0.36	0.98	0.10	1.65	0.03
130908_TSP_LP	9/8/2013 6:30	9/9/2013 6:00	3.27	0.23	0.58	0.08	1.36	0.02
130909_TSP_LP	9/9/2013 6:30	9/10/2013 6:00	6.45	0.39	1.14	0.11	2.75	0.04
130910_TSP_LP	9/10/2013 6:30	9/11/2013 6:00	4.71	0.30	0.72	0.09	2.51	0.04
130911_TSP_LP	9/11/2013 6:30	9/12/2013 6:00	5.21	0.32	1.33	0.12	2.32	0.04
130912_TSP_LP	9/12/2013 6:30	9/13/2013 6:00	5.97	0.36	1.96	0.15	2.53	0.04
130913_TSP_LP	9/13/2013 6:30	9/14/2013 6:00	7.33	0.43	1.35	0.12	3.61	0.06
130914_TSP_LP	9/14/2013 6:30	9/15/2013 6:00	7.34	0.43	0.85	0.10	4.02	0.06
130915_TSP_LP	9/15/2013 6:30	9/16/2013 6:00	3.90	0.26	0.88	0.10	1.83	0.03
130916_TSP_LP	9/16/2013 6:30	9/17/2013 6:00	4.83	0.30	0.81	0.10	1.53	0.03
130917_TSP_LP	9/17/2013 6:30	9/18/2013 6:00	3.40	0.23	1.45	0.13	1.26	0.02
130918_TSP_LP	9/18/2013 6:30	9/19/2013 6:00	3.04	0.21	0.58	0.09	1.31	0.02
130919_TSP_LP	9/19/2013 6:30	9/20/2013 6:00	2.69	0.20	0.80	0.10	0.92	0.02
130920_TSP_LP	9/20/2013 6:30	9/21/2013 6:00	2.75	0.20	1.18	0.12	0.80	0.01
130921_TSP_LP	9/21/2013 6:30	9/22/2013 6:00	7.48	0.44	0.29	0.07	3.14	0.05
130922_TSP_LP	9/22/2013 6:30	9/23/2013 6:00	9.79	0.55	0.43	0.08	4.04	0.06
130923_TSP_LP	9/23/2013 6:30	9/24/2013 6:00	7.79	0.45	0.93	0.10	3.28	0.05

130924_TSP_LP	9/24/2013 6:30	9/25/2013 6:00	11.49	0.64	1.08	0.11	5.33	0.09
130925_TSP_LP	9/25/2013 6:30	9/26/2013 6:00	14.35	0.78	2.07	0.16	6.06	0.10
130926_TSP_LP	9/26/2013 6:30	9/27/2013 6:00	7.85	0.46	1.07	0.11	3.86	0.06

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