RICE UNIVERSITY

Characterization of Ambient Aerosols and Evolution of Organic Aerosol in Fort Worth, Houston and Centreville Alabama

by

Basak Karakurt Cevik

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE

Robert J. Griffin, Chair,
Professor and Department Chair of Civil and Environmental Engineering

Caroline A. Masiello
Associate Professor of Earth Science and Chemistry

Philip B. Bedient
Herman Brown Professor of Engineering,
Civil and Environmental Engineering

HOUSTON, TEXAS
May 2016
ABSTRACT

Characterization of Ambient Aerosols and Evolution of Organic Aerosol in Fort Worth, Houston and Centreville Alabama

by

Basak Karakurt Cevik

The composition and concentration of submicron particulate matter (PM$_1$) were measured by an Aerodyne high-resolution time-of-flight aerosol mass spectrometer at three locations: Dallas-Fort Worth (DFW), TX (June, 2011) Centreville, Al (June 1$^{st}$ – July 15$^{th}$, 2013) and Houston, TX (May 12$^{th}$ -29$^{th}$, 2015) to improve the understanding of the sources and transformation processes of PM$_1$ components with an emphasis on Organic aerosol (OA) and relationships between secondary OA concentrations and various aging metrics in these three US cities.

OA and sulfate aerosol were the most dominant PM$_1$ components in all three sites. The DFW site was the cleanest with respect to PM pollution. The lowest concentrations of OA, sulfate, and total PM$_1$ were observed at this site. Centreville, the most rural site, was characterized with the highest average concentrations of OA and total PM$_1$. This indicates significant transport of material from urban locations and the influence of local biogenic VOC emissions. Houston site was characterized with frequent high peak events of organics and sulfate resulting from point source emissions. High OA events were mostly driven by emissions from Houston Ship Channel.
OA in both DFW and Houston was apportioned into three OA factors including hydrocarbon-like OA, semi-volatile oxygenated organic aerosol (OOA) and low-volatility OOA. OA in Centreville was apportioned into four factors including isoprene-derived OA (IEPOX OA), biomass burning organic aerosol (BBOA), SVOOA, and LVOOA.

This study uses a variety of aging metrics and their relations to OA/ΔCO and OA/ΔCO factor to characterize SOA. In DFW, LVOOA/ΔCO shows a positive correlation with sulfate aging metric and SVOOA/ΔCO shows an overall increase with nitrogen aging metric, indicating the different origin of the two OA factors, regional and local, respectively. In Centreville, a significant positive correlation is observed between LVOOA/ΔCO and the nitrogen aging metrics, which signifies the local characteristic of LVOOA at this site.
Acknowledgments

First and foremost, I would like to express my sincere gratitude to my advisor Prof. Robert J. Griffin for his invaluable support, guidance and patience throughout my graduate studies. His immense knowledge and supervision helped me in all the time of Ph.D work and writing of this thesis. I could not have imagined having a better advisor and a role model. He set an excellent example of how to be a great mentor and lecturer.

I would like to thank Dr. Carrie Masiello and Dr. Philip Bedient for serving on my committee and for their guidance and feedbacks through this process. I would also like to thank Andrew P. Rutter, Longwen Gong, Yu Jun Leong, Nancy Sanchez, William Wallace and all other members of Griffin Research Group whom I had a privilege to work with.

Special thanks my niece Eylul for being a source of joy to me during difficult times. I especially thank to my mother, father and sister for their unconditional love and support. They did not hesitate one second to travel overseas whenever I needed them and they put up with me when I was all irritable and depressed. Last but not the least, I find it difficult to express my appreciation for my husband Emin considering all the sacrifices he has made to join my journey in US. I cannot thank him enough for his continued love and support and for being there during my good and bad times. I find myself very lucky to have such a great family so it only seems right that I dedicate this thesis to my family and my husband. I love them all dearly.
# Contents

ABSTRACT.................................................................................................................................................. ii  
Acknowledgments .................................................................................................................................... iv  
Contents ................................................................................................................................................... v  
List of Figures......................................................................................................................................... viii  
List of Tables .......................................................................................................................................... xii  
Introduction ........................................................................................................................................... 1  
1.1. Aerosols and their impacts ............................................................................................................... 1  
1.1.1. Health Impacts .......................................................................................................................... 2  
1.1.2. Climate Impacts ........................................................................................................................ 3  
1.1.2.1. Direct Effect ......................................................................................................................... 3  
1.1.2.2. Semi-direct Effect .............................................................................................................. 4  
1.1.2.3. Indirect Effect ...................................................................................................................... 4  
1.1.3. Environmental Impacts .......................................................................................................... 5  
1.2. Organic aerosol ............................................................................................................................... 5  
1.3. Positive matrix factorization ......................................................................................................... 10  
1.4. Evolution of organic aerosol and photochemical aging .............................................................. 12  
1.4.1. Average carbon oxidation state .............................................................................................. 12  
1.4.2. Organic aerosol enhancement with respect to ΔCO ............................................................... 13  
1.4.3. Photochemical aging metrics .................................................................................................. 14  
1.4.3.1. Photochemical age ............................................................................................................ 14  
1.4.3.2. -log(NO$_x$/NO$_y$) ....................................................................................................... 15  
1.4.3.3. Ratio of sulfate aerosol to total sulfur ............................................................................... 15  
Characterization of PM$_1$ and airmass aging metrics derived from particle and other measurements near Fort Worth ................................................................................................................... 17  
2.1. Introduction ..................................................................................................................................... 17  
2.2. Experimental .................................................................................................................................. 18  
2.2.1. Sampling site and meteorology ............................................................................................... 18  
2.2.2. Instrumentation ....................................................................................................................... 20
2.3. Results and Discussion

2.3.1. PM$_1$ overview ................................................................. 23
2.3.2. OA Characterization .......................................................... 27
2.3.3. OA/ΔCO Analysis .............................................................. 30
2.3.4. Airmass Aging Metrics ....................................................... 33
   2.3.4.1. Uncertainty Analysis .................................................. 34
   Sulfur ................................................................................. 35
   NO$_x$/NO$_y$ ....................................................................... 37
   Photochemical Age ............................................................. 41

Characterization of Ambient Aerosols and Evolution of Organic Aerosol during the Southern Oxidant and Aerosol Study (SOAS) ................................................. 45

3.1. Introduction ................................................................. 45
   3.1.1. Air Quality in Southeast US ............................................ 47
3.2. Experimental ................................................................. 49
   3.2.1. Sampling Site and Meteorology ...................................... 49
   3.2.2. Instrumentation ............................................................ 50
3.3. Results and Discussions .................................................. 50
   3.3.1. PM$_1$ Overview ............................................................. 50
   3.3.2. OA Characterization ....................................................... 54
   3.3.3. PMF RESULTS ............................................................... 56
   3.3.4. OOA-Aging Relationships.............................................. 58
      3.3.4.1. Sulfur .................................................................. 58
      3.3.4.2. NO$_x$/NO$_y$ .......................................................... 60
3.4. Conclusions ................................................................. 65

Characterization of Ambient Aerosols and Evolution of Organic Aerosol in Houston ......................................................................................................................... 67

4.1. Introduction ................................................................. 67
4.2. Experimental ................................................................. 67
   4.2.1. Sampling site and Instrumentation .................................. 67
4.3. Results and Discussions .................................................. 69
   4.3.1. PM$_1$ Overview ............................................................. 69
   4.3.2. OA Characterization ....................................................... 72
   4.3.3. PMF Results ................................................................. 74
   4.3.4. OOA-Aging Relationships.............................................. 77
List of Figures

Figure 1-1 Interaction between biogenic emissions and anthropogenic pollution can affect atmospheric photooxidation chemistry (SOAS White Paper). ........................................... 8

Figure 1-2 Possible combinations of average carbon oxidation state ($\text{O}_C$) and number of carbon atoms (nC) for stable organic molecules of atmospheric significance (Kroll et al., 2011). ................................................................................................................................ 13

Figure 2-1 a) Map indicating the location of the EML site (black arrow) relative to the DFW metropolitan areas (map credit: TCEQ). b) Photograph of the sampling site at EML. Instrument trailers are shown to the left. Two previously existing TCEQ trailers are shown to the right.............................................. 19

Figure 2-2 24-h backward trajectories calculated using the HYSPLIT model. The trajectories were calculated every 24 hours from June 17 12:00 – June 30 00:00 with a starting height of 250m. ................................................................. 20

Figure 2-3 Time series of organic matter (green), sulfate (red), ammonium (orange), and nitrate (blue) mass concentrations (µg m⁻³). Chloride is not included due to its very small concentrations. .................................................................................................................. 23

Figure 2-4 Time series of SO₂ mixing ratios (gray, ppbv) and SO₄²⁻ mass concentrations (red, µg m⁻³). ..................................................................................................................... 24

Figure 2-5 Scatter plot of 2* [SO₄²⁻] (µmol m⁻³) versus [NH₄⁺] (µmol m⁻³) color coded by NH₃ (ppb). ......................................................................................................................... 25

Figure 2-6 Diurnal profile plots of OA (µg m⁻³), CO (ppbv), and OA/∆CO (µg m⁻³ ppmv⁻¹). The points in the middle show the mean (solid) and median, and the bottom and the top of the whiskers represent the 25th and 75th percentiles, respectively.................. 26

Figure 2-7 a.) pSOA mass concentration (µg m⁻³) versus mixing ratio of Oₓ (ppb). b.) Time series of pSOA mass concentration (black, µg m⁻³), mixing ratio of Oₓ (dashed, ppbv), and mixing ratio of O₃ (gray, ppbv). ................................................................. 28

Figure 2-8 Van Krevelen diagram of elemental ratios (O:C vs. H:C) estimated from HR-ToF-AMS measurements of OA ................................................................. 29
Figure 2-9 Diurnal profile of OSc, with formatting as described in Figure 2-6.

Figure 2-10 Time series of OA/ΔCO (gray, µg m⁻³ ppmv⁻¹), mass concentrations of OA (black, µg m⁻³), and the mixing ratio of CO (ppbv).

Figure 2-11 a.) OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻) 
b.) OA/ΔCO (µg m⁻³ ppmv⁻¹) vs. (SO₄²⁻ / (SO₂ + SO₄²⁻)). The OA/ΔCO ratios are averaged into ten bins according to SO₄²⁻ / (SO₂ + SO₄²⁻). The lack of data points that approach zero for the x-axis indicates consistently aged air with respect to sulfur. Error bars show the range of data.

Figure 2-12 OA factors /ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻)

Figure 2-13 Time series of NOₓ (gray) and NOᵧ (black) mixing ratios (ppbv).

Figure 2-14 OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by –log(NOₓ/NOᵧ) 
b.) OA/ΔCO (µg m⁻³ ppmv⁻¹) vs. –log(NOₓ/NOᵧ). The measured ratios OA/ΔCO are averaged into ten bins according to –log(NOₓ/NOᵧ). Error bars show the range of data.

Figure 2-15 OA factors /ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by –log(NOₓ/NOᵧ).

Figure 2-16 Time series of toluene (gray) and benzene (black) mixing ratios (ppbv).

Figure 2-17 OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by photochemical age (hr).

Figure 3-1 The location of Centreville field site and photo of SOAS field site.

Figure 3-2 Time series of organic matter (green), sulfate(red), ammonium (orange), and nitrate (blue) mass concentrations (µg m⁻³).

Figure 3-3 Diurnal profiles of PM₁ components: organics (top left), nitrate (top right), sulfate (bottom left) and ammonium (bottom left). Error bars on the data represent standard deviation of the data during the corresponding hour.

Figure 3-4 The molar equivalents of major cations vs. anions ([NH₄⁺] and [NO₃⁻] + 2[SO₄²⁻]).

Figure 3-5 Van Krevelen diagram of elemental ratios (O:C vs. H:C) estimated from HR-ToF-AMS measurements of OA.

Figure 3-6 Diurnal profile of elemental ratios of OA with formatting as described in Figure 3-3.
Figure 3-7 Mass spectra profiles show the fraction of each m/z in total OA factor mass. b) Mass spectra for the four OA factors identified using PMF analysis and time series of the corresponding factors.  

Figure 3-8 Diurnal profiles of the OA factors with formatting as described in Figure 3-3.  

Figure 3-9 OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻).  

Figure 3-10 OA factors/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻).  

Figure 3-11 Diurnal profile of -log(NOₓ/NOᵧ) with formatting as described in Figure 3-3.  

Figure 3-12 OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by -log(NOₓ/NOᵧ).  

Figure 3-13 OA/ΔCO (µg m⁻³ ppmv⁻¹) vs – log(NOₓ/NOᵧ). The measured ratios OA/ΔCO are averaged into 10 bins according to – log(NOₓ/NOᵧ). Error bars show the error of the mean.  

Figure 3-14 OA factors/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by –log(NOₓ/NOᵧ).  

Figure 3-15 LVOOA/ΔCO, SVOOA/ΔCO and IEPOX OA/ΔCO ratios averaged into 10 bins according to –log(NOₓ/NOᵧ). Error bars show the error of the mean.  

Figure 4-1 The location (red pin) and a photograph of the Clinton Drive TCEQ field site  

Figure 4-2 Time series of mass concentrations of organic matter, sulfate, ammonium, nitrate, and chloride at Clinton Drive (µg m⁻³).  

Figure 4-3 HYSPLIT 24-hour backward trajectories for the days with high OA concentration events.  

Figure 4-4 Diurnal profiles of OA, sulfate, ammonium, and nitrate during the Clinton Drive sampling campaign. Mean values are plotted with solid lines; median values are plotted with squares and bars showing the standard deviation.  

Figure 4-5 HYSPLIT 24-hour backward trajectories for the days with high sulfate concentration events.  

Figure 4-6 Diurnal profiles of elemental ratios OM:OC, O:C, and H:C of OA during the Clinton Drive sampling campaign.
Figure 4-7 Van Krevelen diagram of elemental ratios (O:C vs. H:C) estimated from HR-ToF-AMS measurements of OA at Clinton Dr. ................................................................. 74

Figure 4-8 Mass spectra for the three components identified in the PMF analysis for OA during the Clinton Drive sampling period. Each color in the plot represents a certain type of OA factor that contributes to total OA. ............................................................................................. 75

Figure 4-9 Time series of the three organic aerosol components. ............................. 76

Figure 4-10 Diurnal profiles of the three organic aerosol components. ................. 77

Figure 4-11 OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻) ...... 79

Figure 4-12 OA factors/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻) ................................................................................................................................. 79

Figure 4-13 OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻) ...... 80

Figure 5-1 Comparison plot of average concentrations of total PM1 and PM1 components at the three field sites investigated in this work. ................................................................. 90

Figure 5-2 Average fractions of OA components over the campaigns at the three sites investigated in this work. ......................................................................................................... 91

Figure 5-3. Comparisons of mass spectra of OA factors at the three sites investigated in this work......................................................................................................................... 95
List of Tables

Table 2-1 Statistics of OA/ΔCO and other aging metrics.................................................. 33

Table 2-2 Analytical uncertainties in relevant measurements and estimated uncertainties
in OA/ΔCO, SO$_4$$_2^{-}$/ (SO$_4$$_2^{-}$+SO$_2$), -log (NO$_x$/NO$_y$) and photochemical age. .................... 34

Table 3-1 Statistics of PM$_1$ components ........................................................................... 51

Table 3-2 Statistics of aging metrics................................................................................... 59

Table 4-1 Statistics of aging metrics................................................................................... 78
CHAPTER 1

Introduction

1.1. Aerosols and their impacts

An aerosol, a term often used interchangeably with particulate matter (PM), is defined as a suspension of solid or liquid particles in a gas, in this case air. The particles generally are assumed to be spherical, and their size ranges from approximately one nanometer (nm) to approximately ten micrometers (μm) in diameter. The size of the particle is an important factor that determines its removal mechanism, transformation, optical properties, and health effects.

Particulate matter, which refers only to the solid or liquid material, is divided into two main modes based on size: fine particles with a diameter less than or equal to 2.5 μm (PM$_{2.5}$) and coarse particles with a diameter larger than 2.5 μm. Fine particles consist of two sub-modes: nucleation and accumulation. Nucleation mode particles have a diameter up to 100 nm, and they dominate the total aerosol number concentration. These particles are formed by homogenous nucleation or condensation of hot vapors during combustion processes. They form larger particles by coagulation. The accumulation range includes particles with a diameter between 0.1 and 2.5 μm and dominates the total aerosol surface area. The particles in this range are formed by coagulation of nucleation particles or condensation of vapor onto existing aerosol. Accumulation mode particles have relatively
long lifetimes because the dry deposition rate for this mode is the small. Coarse particles typically are generated mechanically and removed from the atmosphere easily by sedimentation because of their relatively large size.

Atmospheric aerosol results from a wide variety of natural and anthropogenic sources. The natural types of aerosols include wind-driven soil dust, material from volcanic eruptions, sea salt, biological debris, and extraterrestrial dust, whereas biomass burning, fossil fuel combustion, industrial processes, and construction works are examples of anthropogenic sources. In addition to those particles that are emitted directly into the atmosphere (primary aerosols), particles that are formed in the atmosphere through the oxidation of precursor gases, such as sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$ = nitric oxide (NO) plus nitrogen dioxide (NO$_2$)), and volatile organic compounds (VOCs), are referred to as secondary aerosol, the formation of which is driven by a combination of complex factors that include meteorology and chemistry.

### 1.1.1. Health Impacts

The concentrations of aerosols in the troposphere play an important role in human health, as increased levels of PM have been correlated strongly to increased rates of human respiratory and allergic illnesses and death (Pope et al., 2002). Exposure to PM$_{2.5}$ is associated with cardiovascular disease and premature mortality and morbidity (Brook et al., 2010). Ultrafine particles (diameter smaller than 100 nm) are speculated to have adverse effects on human health because they are small enough to penetrate deeper into lungs, cross tissue boundaries, enter the blood stream, and be transported to the nerves in the brain (Oberdorster et al., 2005). Moreover, toxicological studies show that ultrafine
particles have considerably elevated toxicity (Nel, 2005). For ultrafine, fine, and coarse aerosols, physical and chemical characteristics determine their adverse health effects (Poschl, 2005).

1.1.2. Climate Impacts

1.1.2.1. Direct Effect

The global energy budget of the Earth is balanced by absorbed incoming solar energy and net radiation of long-wave energy out of the atmosphere. The concept of radiative forcing (RF) comes into play when there is an anthropogenic perturbation from this balance of radiative energy. This perturbation can occur due to the emissions of greenhouse gases like carbon dioxide and methane (CH$_4$) into the atmosphere due to human activities. In the context of this study, the RF is the perturbation caused by the presence of human-induced aerosols in the atmosphere. This RF is calculated using a deviation of aerosol concentrations from an initial reference state, which could be the state with complete absence of aerosols, pre-industrial aerosol concentrations, or current natural aerosol loading (Chin et al., 2009). Estimated RF values differ depending upon which initial state they are based, as well as for which atmospheric compartment they are calculated (troposphere, stratosphere or ground level). Current aerosol models usually predict RF values with respect to pre-industrial periods.

Aerosols affect Earth’s climate in this way by scattering or absorbing radiation. The resulting forcing is defined as the direct effect of aerosols on global climate and depends strongly on the size and chemical composition of aerosol. Scattering aerosols
like sulfate, nitrate and most types of organic carbon mostly have a cooling effect while black carbon (BC, so-called soot) and brown carbon (BrC) warm the atmosphere.

### 1.1.2.2. Semi-direct Effect

Light-absorbing material like BC that is present in cloud droplets or near clouds can warm the portion of the atmosphere in which clouds form. The ‘burning-out’ of clouds due to this absorbing PM is referred to as the semi-direct effect (Isaksen et al., 2009). Due to the indirect and semi-direct effects, it can be inferred that the location of each aerosol particle with respect to clouds is an important parameter when considering aerosol RF.

### 1.1.2.3. Indirect Effect

Particles also serve as cloud condensation nuclei (CCN) for cloud droplet formation. Increased concentrations of aerosols that act as CCN increase the total droplet concentration and decrease the size of the water droplets in the clouds, resulting in increased optical thickness and cloud reflectivity (Twomey, 1991). The decrease in the droplet size also increases cloud lifetime, which inhibits precipitation. Certain types of aerosols also trigger ice formation and activate cold cloud formation in higher portions of the atmosphere (Lohmann, 2002). These effects of aerosols on clouds are considered as an indirect climate effect because of the change in planetary albedo. Although aerosols have key roles in climate forcing, there are uncertainties on net climate impact of aerosols due to the gaps in the knowledge of their sources, properties, and formation mechanisms (IPCC, 2007).
1.1.3. Environmental Impacts

The impact of aerosols on visibility is caused mainly by the scattering of visible light by particles with diameters between 0.1 and 1.5 μm. Essentially, such particles prevent light reflected by objects from reaching the eye of the viewer. Visibility degradation due to particulate pollution is an issue in both urban and rural areas.

The deposition of acidic aerosols to lakes and streams can decrease the pH of these systems, which can cause reduction in fish population, elimination of certain fish species that are very sensitive to acidic conditions, and reduction of biodiversity. The deposition of nitrogen-containing aerosols is also an important factor that can result in eutrophication of water bodies. Eutrophication, which refers to enhanced production of algae in the water system, also may cause oxygen depletion in waters. Acidic aerosols affect the nutrients levels of soil by increasing the solubility of nutrients and minerals, which are then washed away. This affects the availability of nutrition for plants; acidic particles also can damage leaves. In addition, aerosols may clog the stomata of the leaves, reducing photosynthetic capabilities in plants. Deposition of acidic particles on to buildings, bridges, or cultural objects may contribute to the deterioration of paint and materials such as marble and limestone.

1.2. Organic aerosol

Atmospheric aerosols consist of sulfate, ammonium, nitrate, sodium, chloride, trace metals, crustal elements, water, and organic matter. However, organic aerosol (OA) comprises a significant fraction (20-90%) of fine PM, and secondary OA (SOA) is
estimated to account for a large fraction of total OA (Kanakidou et al., 2005, Zhang et al., 2007, Jimenez et al., 2009b). Despite the significant contribution of SOA to total mass concentration of aerosols, models historically have underestimated SOA formation considerably (de Gouw et al., 2005, Volkamer et al., 2006). This underestimation is a result of the complexity in the sources of the precursor gases, unknown formation processes, and a large number of participating oxidation species and products, some of which are difficult to measure. Thus, a better understanding of formation, properties, and transformation of SOA is essential to improve models and air quality.

Secondary OA is formed by the oxidation of VOCs by species such as the hydroxyl radical (OH), ozone (O₃), and the nitrate radical (NO₃) in the atmosphere. Adding oxygen or nitrogen atoms to organic molecules can result in the formation of oxidation products with lower volatility and higher polarity/solubility relative to the parent compound due to functional groups such as aldehydes (−C(=O)H), ketones (−C(=O)−), alcohols (−OH), nitrates (−ONO₂), peroxyacyl nitrates (−C(=O)OONO₂), carboxylic acids (−C(=O)OH), hydroperoxides (−OOH), and percarboxylic acids (−C(=O)OOH) (Seinfeld and Pandis, 1998). These semi-volatile organic compounds (SVOCs) can follow different mechanisms to form SOA. They can participate in a nucleation process and form new particles, or they can sorb onto/into pre-existing aerosol. This SOA also can form through cloud processing or through heterogeneous reactions of VOCs at particle surfaces.

On a global basis, 90% of the total VOC emissions are constituted by biogenic VOCs (BVOCs) such as isoprene and monoterpenes (Kanakidou et al., 2005). With
regard to BVOC-SOA, monoterpenes previously were believed to be the major contributor to SOA formation (Chung and Seinfeld, 2002).

However, isoprene ($C_5H_8$) is the most abundant non-methane hydrocarbon in the atmosphere, with an estimated emission rate of 500 to 800 Tg yr$^{-1}$. Historically, it was not included in traditional air quality models for prediction of SOA (Guenther et al., 2006) based on the assumption that isoprene would not contribute to atmospheric SOA due to the high volatility of its oxidation products (Pandis et al., 1991). However, Claeys et al. (2004a) reported the identification of two previously unfound compounds (2-methylthreitol and 2-methylerythritol) in filter samples. Based on their carbon backbone structure, these compounds were explained by OH-initiated photooxidation of isoprene (Claeys et al., 2004a). The presence of these compounds has been verified by other field observations (Claeys et al., 2004b, Edney et al., 2005, Ion et al., 2005). Several laboratory studies re-examined SOA formation by isoprene oxidation under different conditions and observed SOA formation (Kleindienst et al., 2006, Kroll et al., 2006, Surratt et al., 2007a). More recent studies that incorporated these findings into atmospheric models estimated a significant contribution of isoprene to total SOA ranging from 38% to up to 58% globally (Henze and Seinfeld, 2006, Kroll et al., 2006, Liao et al., 2007).

It is clear that BVOCs lead to significant amounts of SOA. However, it also has been demonstrated that anthropogenic pollutants such as NO$_x$ and SO$_2$ affect the oxidation process of BVOCs and ultimately the yield of SOA formation (Figure 1-1) (Edney et al., 2005, Kroll et al., 2005, Ng et al., 2007, Surratt et al., 2007b). This occurs both directly by participating in reactions and indirectly by influencing the level of
oxidants such as OH and O₃. It is critical to understand the mechanisms and importance of anthropogenic influence on SOA to develop effective PM₂.₅ control strategies for protection of public health and to assess the impact on the climate system. In fact, Carlton et al. (2010) suggested that a large fraction (~50%) of biogenic SOA in the Southeastern United States (U.S.) theoretically could be controlled.

Figure 1-1 Interaction between biogenic emissions and anthropogenic pollution can affect atmospheric photooxidation chemistry (SOAS White Paper).

Laboratory studies show that BVOCs such as isoprene and α-pinene (C₁₀H₁₆) have the highest aerosol yield under low-NOₓ conditions. This phenomenon is explained by organic peroxy radical (RO₂) + hydroperoxy radical reactions forming less volatile products such as hydroperoxides when compared to the RO₂ + NO reaction, which forms
more volatile organic products (Hatakeyama et al., 1991, Presto et al., 2005, Kroll et al., 2006). These studies are not enough to understand the overall NO$_x$ effect on SOA yield. For example, Chan et al. (2010) studied the effect of the NO$_2$ to NO ratio (NO$_2$/NO) on the SOA yield and observed an increase of SOA yield from methacrolein and two related $\alpha,\beta$-unsaturated aldehydes (acrolein and crotonaldehyde) with an increase in NO$_2$/NO. Under atmospherically relevant NO$_2$/NO conditions, the SOA yield from methacrolein (a major oxidation product of isoprene) was even higher than the low-NO$_x$ conditions. This is explained by the RO$_2$ + NO$_2$ reaction competing with the RO$_2$ + NO reaction (Chan et al., 2010). Clearly, both NO$_x$ level and speciation impact SOA yield.

In contrast, sesquisterpenes (C$_{15}$H$_{24}$) have the highest yield under high-NO$_x$ conditions, explained by production of highly nonvolatile organic nitrates (Ng et al., 2007). High yields also have been observed for large alkanes (>C$_{12}$) in the presence of high NO$_x$ concentrations (Lim and Ziemann, 2005).

Another mechanism through which NO$_x$ can alter SOA yields is by formation of NO$_3$ through the NO$_2$ + O$_3$ reaction, particularly at night. Chamber studies show that NO$_3$ oxidation of isoprene and monoterpenes creates SOA in large yields and is an important source of OA on the global scale (Ng et al., 2008, Fry et al., 2009). High NO$_x$ concentrations and low-light conditions favor NO$_3$ formation and subsequently SOA production at night (Hoyle et al., 2011).

Lastly, SO$_2$ and NO$_x$ emissions, which result in sulfuric and nitric acid, respectively, can lead to particle-phase acidity. Laboratory studies show that particle acidity enhances SOA formation (Jang et al., 2002, Gao et al., 2004, Inuma et al., 2004,
Kleindienst et al., 2006, Surratt et al., 2007b). Surratt et al. (2007a) demonstrated that aerosol mass concentrations for the 2-methyltetrols and sulfate esters that serve as organic tracers for isoprene SOA increased significantly with enhanced aerosol acidity, which was explained by particle-phase acid-catalyzed reactions. Surratt et al. (2008) also observed organosulfate formation from the oxidation of monoterpenes only in the presence of acidic aerosol.

Field studies also have observed an increase of OA mass with aerosol acidity (Takahama et al., 2006, Zhang et al., 2007). However, Tanner et al. (2009) reported that aerosol acidity in the SEARCH network (described subsequently) does not impact aerosol organic carbon levels significantly. Xu et al. (2015) suggested isoprene-derived SOA is altered directly by the abundance of sulfate rather than particle acidity.

1.3. Positive matrix factorization

Positive matrix factorization (PMF) is a statistical model that estimates the number of factors, the nature, and the quantitative contributions of air pollutants at a particular point. Models developed to utilize PMF do not use pollutant emissions; instead, they use observations of the air pollutants measured at a receptor site to identify and quantify the factor contributions to receptor concentrations. In the current context, the PMF technique has been used widely for the analysis of OA spectral data collected using an aerosol mass spectrometer (AMS) and has provided significant information on different OA types contributing to total OA concentrations (Cottrell et al., 2008, DeCarlo
et al., 2008, Jimenez et al., 2009a, Ulbrich et al., 2009, Zhang et al., 2011, Hayes et al., 2013).

The PMF approach uses a multivariate factor analysis technique developed by Paatero and Tapper (1994) for solving a receptor-only bilinear factor model with the assumption that source factors with consistent profiles contribute to the measured values of species in varying amounts over the time period of dataset. The model requires no a priori assumptions for mass spectra or time trends of the source profile and uses the mass balance equation shown below:

\[ x_{ij} = \sum_g g_{ip} f_{pj} + e_{ij} \]

Equation 1-1

\[ x = \sum G F + E \]

where \( x_{ij} \) is the measured values of specie \( j \) in sample \( i \), \( p \) is the number of factors, \( g_{ip} \) is the contribution of a certain factor, and \( e_{ij} \) is the residual of specie \( j \) in sample \( i \) (Lanz et al., 2007, Ulbrich et al., 2009). To solve the equation, PMF constrains the values of the profiles and contributions to be non-negative and the values of \( G \) and \( F \) are iteratively fit to the data using a weighted least-squares method. Determining the number of factors is the most subjective step of the model and is performed by examining the scaled residuals and using correlation with supplementary tracers such as carbon monoxide (CO), sulfate, and nitrate (Engel-Cox and Weber, 2007).

The PMF model is a powerful method that can handle non-representative data such as below detection limit, missing data and outliers. It analyzes the entire dataset in one run; however, it has limitations. Determining the number of factors is a subjective
step that requires user interpretation. Multiple possible solutions of the source profiles and contributions make it challenging to select the most relevant solution.

1.4. Evolution of organic aerosol and photochemical aging

1.4.1. Average carbon oxidation state

The H:C and O:C elemental ratios of ambient OA can be estimated by summation of the contribution of each element within each ion from a mass spectrum (Aiken et al., 2008). Carbon oxidation state ($\overline{OS}_c = 2*O:C - H:C$) describes the extent of OA processing and usually ranges between -2 to +1 for observed OA (Kroll et al., 2011).

Figure 1-2 shows the locations of organic molecules significant in the atmosphere in a $\overline{OS}_c$ versus number of carbon atoms space. As oxidation continues, organics follow the blue arrows that eventually reach the oxidation end product CO$_2$. Lower $\overline{OS}_c$ represents (HOA) (between -1.7 to -1.6), while oxygenated organic aerosol (OOA) typically has an $\overline{OS}_c$ between -0.5 to +0.9 (Kroll et al., 2011). Factors described as HOA and various types of OOA are what result from the PMF model described above.
1.4.2. Organic aerosol enhancement with respect to ΔCO

Analysis of the ratio of OA to ΔCO (measured CO minus background CO) has been used previously to investigate the aging and formation of SOA (Kleinman et al., 2008, DeCarlo et al., 2010, Hayes et al., 2013). Carbon monoxide is a fairly conservative pollutant with a lifetime with respect to OH oxidation on the order of two months. Therefore, any dilution effect on OA concentrations on the time scale of hours to days can be minimized by analyzing the ratio of OA to CO (Hodzic and Jimenez, 2011). Because CO and primary organic aerosol (POA) generally have similar emission sources, their concentration ratios are expected to be somewhat constant in a source region over a short timeframe (Hodzic and Jimenez, 2011). Consequently, any increases in the ratio of OA to ΔCO can be used as an indicator of SOA formation. This interpretation of OA to ΔCO ratio is based on the assumption of negligible contribution of secondary CO to total
CO concentrations. However, while CO is mainly considered as an anthropogenic pollutant, it can also be formed in the atmosphere by the photo-oxidation of CH\textsubscript{4} and BVOCs (de Gouw and Jimenez, 2009). While CH\textsubscript{4} is the major precursor for the photochemical production of CO, it is expected to contribute to the background CO levels considering its long atmospheric lifetime (approximately one decade) (DeCarlo et al., 2008).

1.4.3. Photochemical aging metrics

1.4.3.1. Photochemical age

Photochemical age, \( \Delta t \), with respect to aromatic hydrocarbons (toluene and benzene) is estimated as (Roberts et al., 1984):

\[
\Delta t = \frac{1}{[\text{OH}](k_t-k_b)} \times \left[ \ln \left( \frac{[\text{toluene}]}{[\text{benzene}]} | t = 0 \right) - \ln \left( \frac{[\text{toluene}]}{[\text{benzene}]} \right) \right]
\]

Equation 1-2

where brackets represent mixing ratios or number densities and \( k_t \) and \( k_b \) are the rate coefficients for the reaction of OH with toluene and benzene, respectively (Atkinson and Arey, 2003, de Gouw et al., 2005). Photochemical age values are zero when the toluene to benzene ratio is equal to that at the point of emission (t=0).

The changes in the concentrations of the hydrocarbons resulting from mixing between air parcels is the most important limitation to this technique and may result in misinterpretation of photochemical processing. Reactions of toluene and benzene with other oxidants such as chlorine atom also are not taken into account in the age estimation.
1.4.3.2. -\log(\text{NO}_x/\text{NO}_y)

The age of the airmass with respect to a combustion source can be approximated with the value of $-\log (\text{NO}_x/\text{NO}_y)$, where NO$_y$ is total reactive oxidized nitrogen. Nitrogen oxides, which are emitted mostly by fossil fuel combustion, are oxidized to species such as nitric acid, nitrous acid, nitrate radical, dinitrogen pentoxide, peroxynitric acid, and peroxyacetyl nitrate (and its analogs) as the air is processed photochemically. Because NO$_y$ includes both NO$_x$ and all of its oxidation products, photochemical age increases with the increase of $-\log (\text{NO}_x/\text{NO}_y)$, and smaller values represent fresh emissions (Kleinman et al., 2007, DeCarlo et al., 2008, Slowik et al., 2011).

For fresh emissions, $-\log(\text{NO}_x/\text{NO}_y) = 0$, and when NO$_x$ is 10% of NO$_y$, $-\log(\text{NO}_x/\text{NO}_y) = 1$ (Kleinman et al., 2008). This metric represents aging with respect to a combustion source. Because the calculation does not include any reaction rates, oxidant levels, or emission ratios, this metric does not give a true quantitative measure of aging. However, the changes in the metric can be used qualitatively as an indicator of airmass processing. Local sources of NO$_x$ may cause an underestimation of aging, especially for aged air because nearby sources will have the greatest impact on the ratio.

1.4.3.3. Ratio of sulfate aerosol to total sulfur

The processing of an airmass with respect to SO$_2$ can be calculated by the ratio of sulfate ($\text{SO}_4^{2-}$) to total sulfur (assuming sulfate and SO$_2$ constitute total sulfur), $\text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2)$, because emitted SO$_2$ is oxidized to sulfuric acid (Quinn, et al. 2005). The photochemical age is expected to increase with the increase in the ratio of $\text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2)$ because SO$_4^{2-}$ formation from emitted SO$_2$ requires photochemical processing.
(either gas- or aqueous-phase). Away from the ocean and gypsum dust sources, because sulfur is predominantly emitted from coal-burning power plants, this aging metric is similar to a plume age.

As stated previously, OA accounts for a large fraction of atmospheric fine particulate matter, and SOA comprises an important fraction of OA. Therefore, understanding the sources and aging processes associated with SOA is critical, especially considering the significant impacts of aerosols on public health, climate, and atmospheric processes. This work describes efforts to investigate relationships between enhanced OA concentrations and various aging metrics at three sites characterized by very different emissions and atmospheric chemistry. To our knowledge, it is the first study to include multiple aging metrics simultaneously and to compare them for various locations relevant for air quality and atmospheric chemistry.
CHAPTER 2

Characterization of PM$_1$ and airmass aging metrics derived from particle and other measurements near Fort Worth

2.1. Introduction

A temporary ground-based photochemical “supersite” was established at the Eagle Mountain Lake (EML) Texas Commission on Environmental Quality (TCEQ) monitoring site in the Dallas-Fort Worth (DFW) area during June 2011. The goal of the campaign was to investigate the influence that oil and natural gas operations in this area have on local air quality. As part of this, PM measurements were made to help differentiate locally emitted and transported POA and SOA. This specific work describes efforts to investigate relationships between enhanced OA concentrations and aging processes at the site. Organic aerosol data were analyzed in the context of OA enhancements with respect to excess CO, the ratio of which can be used to investigate the relative importance of SOA (DeCarlo et al., 2010, Hayes et al., 2013). Photochemical age estimated from toluene to benzene ratios, the ratio of SO$_4^{2-}$ to total sulfur, and the ratio of NO$_x$ to NO$_2$ also were used as airmass age indicators to help characterize processes relevant to OA at the site and to allow comparison between various metrics of age.
2.2. Experimental

2.2.1. Sampling site and meteorology

Measurements were performed continuously in June 2011 at the EML TCEQ monitoring site, which is located 226 m above sea level, in Fort Worth, TX, at 32° 59’16” N, 97° 28’ 37” W. Due to increased pollution levels, only the second half of the month is considered in this study. The site is in a semi-rural area and is ~40 km northwest of downtown Fort Worth. The combined DFW area is the largest metropolitan area in Texas and the fourth largest metropolitan area in the United States, with a population of approximately 6.5 million people. The site is flat and includes various grasses and shrubs (Figure 2-1). It is located a few kilometers west of a minor state highway and near abundant natural gas and oil operations. The land on which the site sits is owned by the United States National Guard and is used as rangeland for cattle.

Meteorology is described in detail in Rutter et al. (2015); a brief overview is given here. During the campaign, the wind speed and direction were fairly stable. The average wind speed was 7.9 m s\(^{-1}\), and the wind direction was almost continuously southerly and southeasterly throughout the campaign, which placed the site downwind of the DFW metropolitan area (Figure 2-2).
Figure 2-1 a) Map indicating the location of the EML site (black arrow) relative to the DFW metropolitan areas (map credit: TCEQ). b) Photograph of the sampling site at EML. Instrument trailers are shown to the left. Two previously existing TCEQ trailers are shown to the right.

There was thunderstorm activity during the night of June 21, which was the only time during the campaign with measurable precipitation. The temperature varied from 17.7 to 39.6 °C, and the relative humidity (RH) ranged from 13.8% to 93.3% during the
sampling time. Temperature and RH each varied diurnally. Days were generally cloud-free.

Figure 2-2 24-h backward trajectories calculated using the HYSPLIT model. The trajectories were calculated every 24 hours from June 17 12:00 – June 30 00:00 with a starting height of 250m.

2.2.2. Instrumentation

Particles were sampled from a main copper tubing inlet. An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and a Brechtel Manufacturing, Inc. (BMI) particle-into-liquid sampler (PILS) connected to Dionex ion chromatographs (IC) subsampled from the main inlet, which was equipped with a 2.5-µm
cyclone. The main inlet extended approximately 5 m above ground level. Rutter et al. (2015) describe instrumentation in more detail so overviews of only the HR-ToF-AMS and PILS are given here.

The HR-ToF-AMS (DeCarlo et al., 2006) is an online measurement of size-resolved chemistry of submicron non-refractory atmospheric aerosol. Air is sampled through a critical orifice and enters an aerodynamic lens that forces particles to focus into a narrow beam that is accelerated into a vacuum chamber. The size of the particle is measured by particle time of flight (PToF) through this region. After the particles pass through the PToF region, they are vaporized after impacting on a heated surface (600 ºC); vaporized material is ionized by electron impact. The resultant ions are detected by a time-of-flight mass spectrometer and attributed to specific aerosol species (sulfate, nitrate, chloride, ammonium, and organic material) based on their mass-to-charge (m/z) ratios. Based on spectral characteristics, organic material is attributed to various types of OA including HOA (thought to be a proxy for combustion-derived POA) and various types of OOA, thought to be proxies for SOA or processed POA (Zhang et al., 2005, Jimenez et al., 2009a, Ulbrich et al., 2009, Huang et al., 2010). In this case, bboa OOA (LVOOA) (termed OOAI in some studies) represents the factor that exhibits a greater extent of oxidation, and semi-volatile OOA (SVOOA) (termed OOAII in some studies) is that which is less oxidized. As a proxy for SOA mass concentration, pSOA is calculated as the sum of LVOOA and SVOOA.

The PILS provides an online measurement of water-soluble ionic aerosol chemical composition at a resolution of 16 minutes. The PILS collects particles by growing them through exposure to a saturated steam environment and then causing their
impaction on a surface. A solution containing aerosol species for injection to the ICs (Dionex ICS 1600) is generated by washing the impaction surface with deionized water (Weber et al., 2001, Orsini et al., 2003). A BMI, Inc. Model 8003 impactor was used to remove particles with diameters larger than 1 micron. Sulfate ion concentrations measured with the PILS-ICs are used to determine the collection efficiency of the HR-ToF-AMS. All data shown have been corrected for this assumed constant efficiency of 69%.

Gas-phase species were sampled from separate inlets attached to a walk-up scaffold that reached approximately 20 m above ground level. Except for the VOC measurements, trace gases were sampled through a common ¼” stainless steel tube from which instruments subsampled. The VOC inlet required ¼” PFA tubing. A Thermo Electron Corp. (TECO) 48C Trace Level CO Analyzer (gas filter correlation), a TECO 42C Trace Level NO and NO2 Analyzer (chemiluminescence), a TECO 42C-Y NOy Analyzer (molybdenum converter), a TECO 49C O3 Analyzer (ultraviolet), a TECO 43C Trace Level SO2 Analyzer (Pulsed Fluorescence), and an IONICON Analytik Proton Transfer Reaction-Time of Flight- Mass Spectrometer (PTR-ToF-MS) were deployed to measure trace gases including CO, NO2, NO, NOy, O3, SO2, and VOCs, respectively. Meteorological data including planetary boundary layer height, temperature, wind speed, and wind direction were tracked with a Vaisala DigiCORA tethersonde system, a Campbell Scientific HMP45C platinum resistance thermometer, and a Campbell Scientific 05103 R. M. Young wind monitor.
2.3. Results and Discussion

2.3.1. PM$_1$ overview

The total observed HR-ToF-AMS PM$_1$ mass concentration ranged between 1.1 and 16.5 µg m$^{-3}$, with a mean of 4.4 ± 2.6 (one s.d.) µg m$^{-3}$. Significant variability is observed in the time series of total PM$_1$ and of all species (Figure 2-3). The average aerosol composition was dominated by organic matter (55.0 ± 14.8%) and sulfate (30.7 ± 12.3%), followed by smaller contributions from ammonium (10.7 ± 3.8%) and nitrate (3.1 ± 1.5%).

![Figure 2-3 Time series of organic matter (green), sulfate (red), ammonium (orange), and nitrate (blue) mass concentrations (µg m$^{-3}$). Chloride is not included due to its very small concentrations.](image)

Over the campaign, the average sulfate mass concentration was 1.2 ± 0.8 µg m$^{-3}$, with a range of 0.2 to 6.7 µg m$^{-3}$. The rapid increase in the sulfate concentration on the
night of June 24 also is observed in SO\textsubscript{2} mixing ratios and particle number concentrations (Figure 2-4).

![Figure 2-4 Time series of SO\textsubscript{2} mixing ratios (gray, ppbv) and SO\textsubscript{4}²⁻ mass concentrations (red, µg m\textsuperscript{-3}).](image)

The time series of ammonium and sulfate are well correlated (R = 0.98, Figure 2-5), indicating the predominance of ammonium sulfate relative to ammonium nitrate. This is expected due to the high temperatures during the sampling period and indicates the general aged quality of the inorganic aerosol. This is confirmed by the slope of this plot being close to one regardless of the ammonia (NH\textsubscript{3}) mixing ratio.
Large spikes in concentrations are observed, particularly between June 21 and 25. The large spikes are mostly driven by increases in OA. The average OA concentration was $2.6 \pm 1.9 \, \mu\text{g m}^{-3}$, with a wide range of 0.3 to 12.8 $\mu\text{g m}^{-3}$. Organic aerosol was correlated positively with CO, likely indicating a relationship between OA and combustion activities ($R=0.81$).

The mean OA concentration diurnal profile (Figure 2-6) during daytime shows a slight increase starting from 1030 CST to 1830 CST, likely as a result of photochemical processing, with the diurnal profile more pronounced for median values. The ratios of the mean to the median OA concentrations are closer to unity between 1000 CST to 1600 CST, indicating significant variability in OA during early morning and at night. Because of the predominance of OA and its diurnal profile, significant attention is paid to OA here.
Figure 2-6 Diurnal profile plots of OA (µg m\(^{-3}\)), CO (ppbv), and OA/ΔCO (µg m\(^{-3}\) ppmv\(^{-1}\)). The points in the middle show the mean (solid) and median, and the bottom and the top of the whiskers represent the 25th and 75th percentiles, respectively.
2.3.2. OA Characterization

Both O₃ and the quantity Oₓ (Oₓ = O₃ + NO₂) are driven photochemically. However, Oₓ is a better tracer than O₃ because the reaction between NO and O₃ forms NO₂, the photolysis of which eventually reproduces O₃. Previous studies have reported correlation between O₃ and pSOA during periods of pSOA formation due to both requiring photochemical oxidation (Cabada et al., 2004, Liu et al., 2011). The positive correlation between Oₓ and pSOA also has been reported in air masses affected on relatively short timescales (less than eight hours) and with no significant local NO₂ sources (Herndon et al., 2008, Wood et al., 2010).

The times series for pSOA, O₃, and Oₓ track each other well for the DFW campaign. Correlation coefficients (R) are 0.64 and 0.71 for O₃ and Oₓ, respectively, with pSOA (Figure 2-7). The correlation of pSOA with O₃ and Oₓ confirms photochemically driven SOA formation.
The average of O:C is 0.5 ± 0.1 and reaches a value up to 0.9; the average value of H:C is 1.3 ± 0.1. The van Krevelen diagram (H:C versus O:C) indicates the oxidation mechanisms of relevance to OA. Slopes of -2, -0.5, and 0 correspond to the addition of
ketone/aldehyde, carboxylic acid, and alcohol/peroxide groups to an aliphatic (unfunctionalized) carbon, respectively (Heald et al., 2010). The slope of H:C versus O:C for DFW is -0.6 (R = 0.7); this slope falls between those for ketone/aldehyde and carboxylic acid but closer to that for carboxylic acid (Figure 2-8). It should be noted that the slope on the diagram can be a result of different combinations of reactions; therefore, the slope only gives information on the range of oxidation processes that are responsible for the aging of the OA. Slopes of ambient data usually range between -0.5 to -1. The slope observed in DFW is similar to those observed in Pasadena, CA (-0.64) (Hayes et al., 2013) and Changdao, China (-0.63) (Hu et al., 2013).

![Image of Van Krevelen diagram](image)

**Figure 2-8** Van Krevelen diagram of elemental ratios (O:C vs. H:C) estimated from HR-ToF-AMS measurements of OA.

Carbon oxidation state (OS\(_c\) = 2*O:C - H:C) describes the extent of OA processing and usually ranges between -2 to +1 for observed OA (Kroll et al., 2011). Lower OS\(_c\) represents HOA (between -1.7 to -1.6), while OOA typically has an OS\(_c\) between -0.5 to +0.9 (Kroll et al., 2011). In this dataset most of the OS\(_c\) values fall
between -0.5 and +0.5, with a mean of -0.2. The mean and median values are close to each other, which suggests relatively little impact of events characterized by atypical levels of either type of OA. Figure 2-9 shows the diurnal profile of OS$_c$ values. OS$_c$ starts increasing in the morning at 0830 CST and shows a decrease after 1930 CST suggesting a higher oxidation state during daytime, as expected.

![Graph showing diurnal profile of OS$_c$ values](image)

Figure 2-9 Diurnal profile of OS$_c$, with formatting as described in Figure 2-6.

### 2.3.3. OA/ΔCO Analysis

To calculate the OA/ΔCO ($\mu$g m$^{-3}$ ppmv$^{-1}$) ratio, the fifth percentile of CO mixing ratio (ppmv) is used as a background level (0.085 ppmv) and subtracted from measured values in this study (Cottrell et al., 2008). A CO threshold of 0.102 ppbv (20% larger than background level) is applied to data, and any CO value smaller than the threshold is removed. Weekday and weekend data were analyzed separately to account for any distortion to OA/ΔCO and aging relations caused by different contributions of diesel and
gasoline vehicles in the two different times of the week. Only weekday data are reported here due to the small number of data points available for weekend data.

OA mass concentrations and CO mixing ratios generally track each other (Figure 2-10). A diurnal trend can be observed in OA time series, except the period with large spikes between June 21 and 25. The OA/ΔCO time series shows greater variability than the individual OA and CO time series, with lower values between June 21 and June 25 despite both species being enhanced.

The average OA/ΔCO in the DFW region was 88.9 ± 37.6 µg m⁻³ ppmv⁻¹, with a range of 11.9 and 248.3 µg m⁻³ ppmv⁻¹ (Table 2-1). Figure 2-5 shows a diurnal profile of the ratio, along with diurnal profiles of OA and CO alone. Organic aerosol enhancement with respect to CO starts in the morning (increased photochemical activity) at 0830 CST and shows a decrease after 1730 CST. However, values remain relatively consistent overnight. If the premise of this approach regarding co-location of CO and POA emissions is correct, this consistency at night potentially can be explained by OA formation at night to counter particle deposition and enhancement of CO in the shallower nocturnal boundary layer. An increase of OOA/ΔCO at night was observed during a field campaign in Houston in 2006 (Cleveland et al., 2012). The CO diurnal profile shows its first peak during morning rush hour between 0530 CST and 0930 CST, starts increasing at 1430 CST, keeps increasing until midnight, and then remains low.
Figure 2-10 Time series of OA/ΔCO (gray, µg m⁻³ ppmv⁻¹), mass concentrations of OA (black, µg m⁻³), and the mixing ratio of CO (ppbv).
Table 2-1 Statistics of OA/ΔCO and other aging metrics.

<table>
<thead>
<tr>
<th></th>
<th>OA/ΔCO (µg m⁻³ ppm⁻¹)</th>
<th>-log(NOₓ/NOᵧ)</th>
<th>SOₓ₂⁻ / (SO₂ + SO₄²⁻)</th>
<th>Photochemical Age (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>88.9</td>
<td>0.3</td>
<td>0.6</td>
<td>26.7</td>
</tr>
<tr>
<td>Median</td>
<td>85.6</td>
<td>0.3</td>
<td>0.7</td>
<td>26.9</td>
</tr>
<tr>
<td>Std Dev</td>
<td>37.6</td>
<td>0.2</td>
<td>0.1</td>
<td>5.3</td>
</tr>
<tr>
<td>Std Error</td>
<td>0.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Min</td>
<td>11.9</td>
<td>0.0</td>
<td>0.4</td>
<td>13.9</td>
</tr>
<tr>
<td>Max</td>
<td>248.3</td>
<td>0.8</td>
<td>0.8</td>
<td>38.1</td>
</tr>
</tbody>
</table>

2.3.4. Airmass Aging Metrics

Photochemical age and other aging surrogates were used to evaluate the extent of processing and for intercomparison in the DFW area. It is important to note that these values are only approximations/proxies of the airmass age because the calculation of the real age is more complicated, requires reaction rates and oxidant levels, and depends on atmospheric conditions. However, it should be noted that all metrics presented here are expected to increase with airmass aging. In addition, it is hypothesized that relationships between OA/ΔCO and any of these age metrics may allow insight into processes relevant for pSOA. An error and statistical analysis is presented in Section 2.3.4.1.
2.3.4.1. Uncertainty Analysis

The upper-lower bound method was used to estimate the maximum uncertainties in OA/ΔCO and age metrics. Analytical uncertainties of relevant measurements and estimated maximum uncertainties of OA/ΔCO, \( \text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2) \), \(-\log(\text{NO}_x/\text{NO}_y)\) and photochemical age are summarized in Table 2-2. Differences in diurnal profiles and in the comparisons shown in Figures 2.11.b and 2.12.b were evaluated using a student’s t-test; results supported statistical differences from hour to hour in diurnal profiles and in the relationships shown in Figures 2.11.b and 2.12.b.

Table 2-2 Analytical uncertainties in relevant measurements and estimated uncertainties in OA/ΔCO, \( \text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2) \), \(-\log(\text{NO}_x/\text{NO}_y)\) and photochemical age.

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Analytical Uncertainty</th>
<th>OA/ΔCO and Age Metrics</th>
<th>Estimated Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA</td>
<td>10%</td>
<td>OA/ΔCO</td>
<td>15%</td>
</tr>
<tr>
<td>CO</td>
<td>5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_2)</td>
<td>4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>8%</td>
<td>( \text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2) )</td>
<td>6%</td>
</tr>
<tr>
<td>NO</td>
<td>5%</td>
<td>-(\log(\text{NO}_x/\text{NO}_y))</td>
<td></td>
</tr>
<tr>
<td>NO(_2)</td>
<td>7%</td>
<td></td>
<td>24%</td>
</tr>
<tr>
<td>NO(_y)</td>
<td>5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>15%</td>
<td>Photochemical Age</td>
<td>26%</td>
</tr>
<tr>
<td>Benzene</td>
<td>(Kim et al., 2015)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Sulfur

The SO$_4^{2-}/$(SO$_4^{2-}$+SO$_2$) values range between 0.4 and 0.8, and no significant diurnal profile is observed. The average sulfate aging metric is 0.6 ± 0.1 (Table 2-1). The observed sulfate aging metric values were comparable to those measured in Ontario, Canada (Hayden et al., 2011).

Figure 2-11 shows the time series of OA/ΔCO as a function of the sulfate aging metric. Most SO$_4^{2-}/$(SO$_4^{2-}$+SO$_2$) data fall near the average value, and no consistent monotonic linear relationship between the ΔOA/ΔCO values and the sulfate aging metric can be observed (Figure 2-11). As illustrated Figure 2-11, overall only a very slight positive correlation can be observed between the two metrics when OA/ΔCO values are averaged within binned values of the sulfur aging metric. This suggests that processing mechanisms required for sulfate formation likely contribute to enhancements in OA indirectly by altering the nature of the aerosol. The poor correlation also can be explained by the relatively long lifetimes of SO$_2$ with respect to aqueous- and gas-phase oxidation, which are approximately 70 hours and 7 days, respectively (Wojcik and Chang, 1997). The sulfur aging metric therefore does not reflect more local processes.
Figure 2-11 a.) OA/ΔCO (µg m⁻³ppmv⁻¹) ratios color coded by SO₄²⁻/(SO₂ + SO₄²⁻) 
b.) OA/ΔCO (µg m⁻³ppmv⁻¹) vs. (SO₄²⁻/(SO₂ + SO₄²⁻)). The OA/ΔCO ratios are 
averaged into ten bins according to SO₄²⁻/(SO₂ + SO₄²⁻). The lack of data points that 
approach zero for the x-axis indicates consistently aged air with respect to sulfur. Error 
bars show the range of data.
Figure 2-12 OA factors /ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻).

Figure 2-12 shows the time series of the ratio of three OA factors contributing to total OA to ΔCO as a function of the sulfate aging metric. While HOA and SVOOA show no relationship with SO₄²⁻ / (SO₂ + SO₄²⁻), LVOOA shows an overall increasing trend with the aging metric (Figure 2-13). This positive relationship indicates that the LVOOA factor at the site is likely regional in character, as is sulfate aerosol is due to the long relative time for its formation.

**NOₓ/NOᵧ**

Co-located measurements of NOₓ and NOᵧ were used to estimate this aging metric (Figure 2-13). The -log(NOₓ/NOᵧ) ranged between 0.0 and 0.8 and showed a significant diurnal profile. The aging metric starts to increases at 0630 CST, peaks around 1530
CST, and keeps decreasing overnight. The average metric value was 0.3 ± 0.2 (Table 2-1). The observed -log(NO\textsubscript{x}/NO\textsubscript{y}) values were similar to those observed by Slowik et al. (2011) in southwestern Ontario and smaller than those observed by Kleinman et al. (2007) in New England.

![Figure 2-13 Time series of NO\textsubscript{x} (gray) and NO\textsubscript{y} (black) mixing ratios (ppbv).](image)

Figure 2-14 shows the same OA/ΔCO time series but colored by the aging metric with respect to NO\textsubscript{x}. As illustrated in Figure 2-14, values smaller than 0.2 are more likely when low OA/ΔCO ratios are observed; accordingly, values higher than 0.4 mostly correspond to higher OA/ΔCO values. This is intuitive as one would expect less OA enhancement in fresher airmasses. A significant positive correlation exists between -log (NO\textsubscript{x}/NO\textsubscript{y}) and OA/ΔCO (Figure 2-14), but the slope of this relationship changes when – log(NO\textsubscript{x}/NO\textsubscript{y}) lies between 0.3 and 0.4. A steeper slope indicates that enhancement in
OA occurs more rapidly as the airmass ages; a gentler slope indicates slower OA enhancement as the airmass ages. The larger slope in this case occurs with fresher airmass age, likely signifying that OA processing and formation are more rapid in fresher airmasses. Compared to the sulfur aging metric, the NO\textsubscript{x} aging metric is more likely to reflect local processes. Kleinman et al. (2007, 2008) observed similar trends in New England and Mexico City.

Figure 2-15 shows the time series of OA factors / ΔCO as a function of –log(NO\textsubscript{x}/NO\textsubscript{y}). Similar to sulfate aging metric, HOA shows no correlation with –log(NO\textsubscript{x}/NO\textsubscript{y}). Between OOA factors, SVOOA shows the most consistent relationship, with an increase as the aging metric increases. While, the increase in the ratio reaches a plateau between –log(NO\textsubscript{x}/NO\textsubscript{y}) values 0.2 and 0.5, it keeps increasing afterwards.
Figure 2-14 OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by –log(NOₓ/NOᵧ) b.) OA/ΔCO (µg m⁻³ ppmv⁻¹) vs. –log(NOₓ/NOᵧ). The measured ratios OA/ΔCO are averaged into ten bins according to –log(NOₓ/NOᵧ). Error bars show the range of data.
Figure 2-15 OA factors /ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by −log(NOₓ/NOᵧ).

**Photochemical Age**

Photochemical age is estimated using Equation 1.2 where brackets represent mixing ratios (Figure 2-16 shows the PTR-ToF-MS ambient measurements of toluene and benzene in ppbv) or number densities (for OH, assumed for the entire data set to be 3x10⁶ molecules cm⁻³) and kᵣ and kₛ are the rate coefficients (not temperature-corrected) for the reaction of OH with toluene (5.63×10⁻¹² cm³ molecule⁻¹ s⁻¹) and benzene (1.22 ×10⁻¹² cm³ molecule⁻¹ s⁻¹), respectively (Atkinson and Arey, 2003, de Gouw et al., 2005). The initial ratio of toluene to benzene is assumed to be 1.4 based on Texas emission inventories (Zhou et al., 2012). Photochemical age values are zero when the toluene to benzene ratio is equal to that at the point of emission.
Figure 2-16 Time series of toluene (gray) and benzene (black) mixing ratios (ppbv).

Photochemical age values ranges between 13.9 and 38.1 hours. Table 2-1 shows the average photochemical age was 26.7 ± 5.3 hours. The photochemical age range is similar but slightly higher than values calculated by Cottrell et al. (2008) at Thompson Farm in semi-rural New England, which is slightly further from a major metropolitan area, Hayes et al. (2013) in Pasadena, CA, and Hu et al. (2013) in Changdao Island, China.
Figure 2-17 OA/ΔCO (µg m\(^{-3}\) ppmv\(^{-1}\)) ratios color coded by photochemical age (hr).

Figure 2-17 shows the time series of OA/ΔCO colored as a function of photochemical age with respect to the toluene to benzene (predominantly anthropogenic hydrocarbons) ratio. While a decrease in OA/ΔCO ratio is observed between June 17 and 21, after June 21, a more pronounced positive relation is observed. Unlike the other metrics, however, the binned OA/ΔCO-photochemical age relationship is not statistically significant, indicating that increases in OA/ΔCO beyond those from aromatics (or related compounds) are controlled by biogenic hydrocarbons or by inorganic-influenced (i.e., NO\(_x\)) chemistry.

2.4. Conclusions

The average aerosol composition in DFW was dominated by OA and sulfate. A detailed analysis of OA concentrations shows a tight correlation with CO. Elemental analysis indicates the probable importance of carboxylic acid in OOA, but the wide range of OSe values observed suggests HOA also is important. The time series for pSOA, O\(_3\), and O\(_x\) track each other well and suggest photochemical SOA formation. Overall, a
positive correlation can be observed between OA/ΔCO values and -log (NO_x/NO_y). More rapid OA enhancement is observed with lower values (between 0 and 0.35) of -log (NO_x/NO_y), signifying OA processing and formation are more rapid in fresher airmasses. However, OA/ΔCO values do not show a significant correlation with sulfate aging metric and photochemical age with respect to hydrocarbons. While LVOOA/ΔCO shows a positive correlation with sulfate aging metric, SVOOA/ΔCO shows an overall increase with -log (NO_x/NO_y), indicating the different origin of the two OA factors, regional and local, respectively. These aging-OA/ΔCO relationships warrant further investigation and highlight that caution must be used when describing an airmass as “aged.”
Chapter 3

Characterization of Ambient Aerosols and Evolution of Organic Aerosol during the Southern Oxidant and Aerosol Study (SOAS)

3.1. Introduction

The Southern Oxidant and Aerosol Study (SOAS) was conducted as a part of a larger study, the Southeast Atmosphere Study (SAS), which was one of the largest atmospheric chemistry studies ever performed in North America. This extensive collaborative study of biosphere-atmosphere interactions was conducted, organized, and funded by a broad number of organizations such as the Environmental Protection Agency (EPA), the National Science Foundation, the National Oceanic and Atmospheric Administration, the Electric Power Research Institute, and several U.S. and international research institutions.

The scientific questions that motivated SOAS, as stated in the SOAS White Paper, were:

- What are the magnitudes, variations, and controlling processes for biosphere-atmosphere fluxes of oxidants and reactive carbon and nitrogen across spatial scales relevant to air quality and climate?
• What are the chemical and physical processes that control the oxidation of BVOCs? How do anthropogenic emissions alter the distribution of the BVOC oxidation products, and what are the implications for the formation of O₃, reactive nitrogen, and aerosol precursors?
• To what extent do anthropogenic influences impact biogenic SOA formation?
• How do aqueous chemistry and cloud processing of BVOCs and related aerosols influence atmospheric SOA?
• What are the climate-relevant properties of biogenic aerosol (VOC of biogenic origin)?

Field and airborne measurements for SOAS were conducted from June 1 through July 15, 2013. Ground field sites included Centreville and Alabama Aquatic Biodiversity Centre (AABC), Alabama; Look Rock, Tennessee; and Research Triangle Park (RTP), North Carolina. Large emission rates of isoprene coupled with a range of observed NOₓ and SO₂ levels in Centreville, the major ground site, made it an ideal place to study the scientific questions stated above. A variety of trace gas and aerosol data was collected at this site by different institutions. This proposal will focus on the submicron PM data collected using a HR-ToF-AMS in a forested area in Centreville, which is located in Talladega National Forest. The main objectives of this study are to (i) determine the contribution of various sources to the total OA mass concentrations in Centreville using a PMF model, (ii) to evaluate quantitatively the photochemical age dependencies of SOA formation in a region subject to both large emission rates of BVOCs and anthropogenic
pollution sources, iv) to compare results with previously published studies in other regions.

3.1.1. Air Quality in Southeast US

The Southeastern U.S. is characterized by large emissions of VOCs (mainly isoprene and monoterpenes) from vegetation. High concentrations of BVOCs and the near-field presence of anthropogenic pollutants such as SO₂ and NOₓ make the region susceptible to secondary pollutants such as O₃ and secondary aerosols (Goldstein et al., 2009). A relatively high intensity of solar radiation, poor vertical mixing due to low wind speeds, and a high frequency of air stagnation in the region contribute to the O₃ and PM2.5 accumulation and the resulting haze events (Zhang et al., 2006, Goldstein et al., 2009, Hidy et al., 2014).

The Southeastern U.S. has been the focus of intensive atmospheric field studies for more than two decades. The SOS was the first major study that took place in this region with the motivation of understanding the O₃-related chemical and meteorological factors that are characteristic for the region. Several field studies were conducted starting from 1992 in Alabama, Florida, Georgia, Kentucky, Louisiana, Mississippi, North Carolina, South Carolina, Tennessee, and Texas (Chameides and Cowling, 1995).

After the U.S. EPA established annual and daily National Ambient Air Quality Standards (NAAQS) for PM₂.₅ in 1997, the scope of SOS was extended to include both O₃ and PM. In 1998, the Southeastern Aerosol Research and Characterization Study (SEARCH) was initiated as a part of SOS to characterize concentrations, sources, and health impacts of PM and gases in the southeastern U.S (Hansen et al., 2003).
Eight selected monitoring sites including Centreville were coupled as urban-rural pairs in Alabama (North Birmingham and Centreville), Georgia (Atlanta and Yorkville), Mississippi (Gulfport and Oak Grove), and Florida (Pensacola and suburban Pensacola) (Hansen et al., 2003). The findings from these field campaigns have been published in several scientific papers and reports and also used to evaluate air quality models (Zhang et al., 2004, Morris et al., 2006, Yu et al., 2007, Zhang et al., 2013).

Annual emission rates of CO, NO$_x$, and SO$_2$ in the four states decreased by ~ 50% between 1999 and 2008 (Blanchard et al., 2013). Measurements from the SEARCH sites between 1999 and 2010 reflect the decreases in emission rates. Blanchard et al. (2013) estimated the rates of decrease of mean annual concentrations of the major pollutants between 1999 and 2010. The mean annual concentrations of SO$_2$, aerosol sulfate (SO$_4^{2-}$), and aerosol organic mass for all eight sites decreased significantly by an average rate of 7.2%, 4.9%, and 4.8% per year, respectively. The CO concentrations show a much stronger rate of decrease in the four urban sites (6.2% per year) compared to rural sites (1.7 % per year).

The four-year (1999-2002) daily average of PM$_{2.5}$ mass concentrations in Centreville and Birmingham were 14.17 µg/m$^3$ and 20.32 µg/m$^3$, respectively. In the period of 2009-2012, these numbers declined to 8.89 and 11.88 µg/m$^3$. Organic matter and SO$_4^{2-}$ were the most abundant species in both periods. The eight-hour daily maximum O$_3$ mixing ratios for Centreville and Birmingham were 36.97 ppbv and 23.27 ppbv in the 1999-2002 period and 32.93 ppbv and 24.74 ppbv in the 2009-2012 period, respectively (Hidy et al., 2014).
3.2. Experimental

3.2.1. Sampling Site and Meteorology

As part of SOAS, an Aerodyne HR-ToF-AMS and a BMI PILS were deployed at the SEARCH site in Centreville, Alabama from 1 June to 15 July 2013. The location of the site is shown in Figure 3-1. The site is located in a forested area that is part of the Talladega National Forest and is situated at 32.9030 N, 87.2500 W, and at an elevation of 126 m. The site is ~80km SW of Birmingham and ~55 km SE of Tuscaloosa. The anthropogenic pollutant sources in the region include power plants, pulp and paper mills, and metal processing (Hidy, 2014). BVOC emissions are highly dominated by isoprene followed by monoterpenes such as α-pinene and β-pinene. Historically, the site has been influenced by a range of NOx mixing ratios and a range of aerosol acidity conditions due to variable SO2 and aerosol sulfate levels.

Figure 3-1 The location of Centreville field site and photo of SOAS field site.
3.2.2. Instrumentation

The concentrations of submicron non-refractory aerosols were measured with HR-ToF-AMS online, and samples containing water-soluble inorganic ions collected with PILS were analyzed off-site using Dionex ICs. The instruments sampled from two copper tubing inlets that were equipped with a 2.5-µm cyclone. The HR-ToF-AMS ion path alternated between V and W (better m/z resolution) mode, and the concentrations were averaged over 2.5 min intervals. The V mode data have been used for the reported concentrations here. All data were analyzed using standard HR-ToF-AMS software (SQUIRREL v1.53 and PIKA v1.12) within Igor Pro 6.22A (WaveMetrics, Lake Oswego, OR). Real-time corrections for ionization efficiency and composition-dependent collection efficiency were applied when calculating HR-ToF-AMS mass loadings (µg/m³); PILS aerosol SO₄²⁻ was used for a quality assurance comparison.

3.3. Results and Discussions

3.3.1. PM₁ Overview

The total observed HR-ToF-AMS PM₁ average mass concentration was 7.91 ± 3.47 µg m⁻³. Time series of mass concentrations of OA, sulfate, ammonium, nitrate, and chloride measured with HR-ToF-AMS are shown in Figure 3-2. Statistics of PM₁ components can be found in Table 3-1. The average aerosol composition was dominated by organic matter (73%), followed by smaller contributions from sulfate (19%), ammonium (5%), and nitrate (3 %).
Figure 3-2 Time series of organic matter (green), sulfate(red), ammonium (orange), and nitrate (blue) mass concentrations (µg m\(^{-3}\)).

Table 3-1 Statistics of PM\(_1\) components

<table>
<thead>
<tr>
<th>Variable</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Mean</th>
<th>Mode</th>
<th>Median</th>
<th>Lower Quartile</th>
<th>Upper Quartile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organics</td>
<td>76.24</td>
<td>0.15</td>
<td>5.45</td>
<td>1.54</td>
<td>5.28</td>
<td>3.34</td>
<td>6.97</td>
</tr>
<tr>
<td>Nitrate</td>
<td>1.54</td>
<td>0.01</td>
<td>0.11</td>
<td>0.10</td>
<td>0.09</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>Sulfate</td>
<td>10.74</td>
<td>0.01</td>
<td>2.05</td>
<td>2.03</td>
<td>2.01</td>
<td>1.15</td>
<td>2.71</td>
</tr>
<tr>
<td>Ammonium</td>
<td>1.67</td>
<td>0.00</td>
<td>0.41</td>
<td>0.00</td>
<td>0.39</td>
<td>0.21</td>
<td>0.56</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.20</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>
The average OA concentration during campaign was $5.45 \pm 3.34 \, \mu g \, m^{-3}$, with a range of 0.15 to 76.24 $\mu g \, m^{-3}$. OA concentrations were significantly higher than the DFW OA concentrations. The highest OA peak during the campaign (June 4th) was driven by an open burning event. OA concentration correlated well with CO mixing ratio ($R=0.71$). The concentrations of SVOOA, which was identified as one of the four OA components at the site (see section 3.3.3) track the CO mixing ratio. Similar correlations between OOA factors and CO have been observed in previous field studies (Weber et al., 2007). These observations were thought to be caused by the anthropogenic influence on SOA formation from BVOCs as explained previously. Diurnal profile of OA shows that OA concentrations were slightly higher at night (Figure 3-3).

The average sulfate and ammonium concentrations were $2.05 \pm 1.22$ and $0.41 \pm 0.27 \, \mu g \, m^{-3}$, respectively, and their concentrations were slightly larger during the day. On June 26, large sulfate concentrations were observed as a result of a power plant plume coming from the southwest. The slope (1.38) of the regression line between molar equivalents of major cations and anions ([NH4+] and [NO3-] + 2[SO42-]) suggests that ambient aerosols were acidic (Figure 3-4).

Average nitrate concentration during campaign was $0.11 \pm 0.08 \, \mu g \, m^{-3}$ with a range of 0.01 to 1.54 $\mu g \, m^{-3}$. Nitrate concentrations were higher during night and showed significant variability compared to daytime. Lower concentrations during day can be explained by higher temperature levels during daytime considering higher volatility of nitrate with respect to other inorganic components.
Figure 3-3 Diurnal profiles of PM$_1$ components: organics (top left), nitrate (top right), sulfate (bottom left) and ammonium (bottom left). Error bars on the data represent standard deviation of the data during the corresponding hour.

Figure 3-4 The molar equivalents of major cations vs. anions ([NH$_4^+$] and [NO$_3^-$] + 2[SO$_4^{2-}$]).
3.3.2. OA Characterization

The average of O:C of OA in the sampling site was 0.52 ± 0.06 and reaches a maximum of 1.05; the average value of H:C is 1.41 ± 0.05. The slope of H:C versus O:C for Centreville is -0.49 ± 0.008; this slope falls between those ketone/aldehyde and carboxylic acid (Figure 3-5). The slope on the diagram can be a result of different combinations of reactions; therefore, the slope only gives information on the range of oxidation processes that are responsible for the aging of the OA. The slope of Centreville data is similar to that observed in DFW but closer to carboxylic acid, which signifies the more oxidized nature of OA in the region.

Diurnal profiles of elemental ratios are shown in Figure 3-6. The diurnal profiles of OM:OC (organic mass to organic carbon) and O:C show almost identical diurnal trends, which start to increase after 6:00 AM in the early morning, peak between 12:00 PM and 01:00 PM, and start decreasing with the sunset. The similar trends between OM:OC and O:C ratios also suggest the importance of OOA in the sampling site. The diurnal trend of H:C is close to a flat line at night and shows a slight increase after 8:30 AM. The ratio does not change until 07:00 pm, which could be explained by the local traffic at the site due to the SOAS community.
Figure 3-5 Van Krevelen diagram of elemental ratios (O:C vs. H:C) estimated from HR-ToF-AMS measurements of OA.

Figure 3-6 Diurnal profile of elemental ratios of OA with formatting as described in Figure 3-3.
3.3.3. PMF Results

Four OA factors were identified using PMF including isoprene-derived OA (IEPOX OA), biomass burning organic aerosol (BBOA), SVOOA, and LVOOA. Mass spectra and diurnal profiles, tracer ions for different OA factors, and comparison of time series of the OA factors with other tracers were used for identification process.

IEPOX OA was identified by the contribution of tracer ions $C_4H_5^+$ (m/z 53) and $C_5H_6O_5^+$ (m/z 82) (Figure 3-7). The main formation mechanism of IEPOX OA was suggested to be uptake of isoprene epoxydiols (formed by the oxidation of isoprene by OH under low-NO conditions) by acidic aerosols. This factor accounted for 22% of total OA. Time series of IEPOX OA and sulfate tracked each other well, and the R value between the two time series was 0.73. The diurnal profile of the factor shows significant dynamics, which shows an increase at 6:00 AM in the morning and a peak in the afternoon (Figure 3-8).

The mass spectra profile of the two OOA factors is shown in Figure 3-7. The factor with higher $f_{44/43}$ (the ratio between the fraction of m/z 44 and m/z 43) represents LVOOA. LVOOA and SVOOA factors account for 31% and 31% of total OA, respectively. The diurnal profile of LVOOA is very similar to the diurnal profile of IEPOX OA and shows an increase with photochemical activity. However, the diurnal profile of SVOOA started to increase after 18:00 PM and kept increasing till early morning. The BBOA factor was identified by the tracer ions $C_2H_4O_2^+$ (m/z 60) and $C_3H_5O_2^+$ (m/z 73). A significant peak in the time series of BBOA factor was observed in the morning of June 4, which was a result of an open burning event near the field site.
Figure 3-7 Mass spectra profiles show the fraction of each m/z in total OA factor mass. b) Mass spectra for the four OA factors identified using PMF analysis and time series of the corresponding factors.
3.3.4. OOA-Aging Relationships

3.3.4.1. Sulfur

The SO$_4^{2-}$/ (SO$_4^{2-}$+SO$_2$) values range between 0.04 and 1, with a mean of 0.69 ± 0.18 (Table 3-2). The sulfate aging metric values were slightly higher but comparable to those measured in DFW. The aging metric did not show a significant diurnal trend.
Table 3-2 Statistics of aging metrics.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Mean</th>
<th>Mode</th>
<th>Median</th>
<th>Lower Quartile</th>
<th>Upper Quartile</th>
</tr>
</thead>
<tbody>
<tr>
<td>-log(NOₓ/NOᵧ)</td>
<td>0.96</td>
<td>0</td>
<td>0.37</td>
<td>0.15</td>
<td>0.34</td>
<td>0.20</td>
<td>0.54</td>
</tr>
<tr>
<td>SO₄²⁻/(SO₄²⁻ + SO₂)</td>
<td>1.00</td>
<td>0.04</td>
<td>0.69</td>
<td>1.00</td>
<td>0.72</td>
<td>0.59</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Figure 3-9 and Figure 3-10 show the time series of OA/ΔCO and OA factors/ΔCO as a function of the sulfate aging metric. As seen in the graphs, there were no consistent relationships between the aging metric and OA/ΔCO and OA factors/ΔCO values, in contrast to DFW where a positive relationship was observed between LVOOA/ΔCO and the sulfate aging metric.

Figure 3-9 OA/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻)
3.3.4.2. NO$_x$/NO$_y$

The average -log(NO$_x$/NO$_y$) during the SOAS campaign was 0.37 ± 0.2, with a range of 0 to 0.96. The aging metric shows a strong diurnal profile. It starts to increase at 07:30 AM and peaks around 15:00 PM (Figure 3-11). The OA/ΔCO time series as a function of -log(NO$_x$/NO$_y$) is shown in Figure 3-12. Similar to DFW data, values smaller than 0.2 are more likely when low OA/ΔCO ratios are observed. A significant positive correlation was observed between -log (NO$_x$/NO$_y$) and OA/ΔCO (Figure 3-13). The slope of this relationship is steeper when –log(NO$_x$/NO$_y$) lies between 0 and 0.4. Rapid enhancement of OA occurring with fresher airmass age was more prominent in Centreville than in DFW.
Figure 3-11 Diurnal profile of $-\log(\text{NO}_x/\text{NO}_y)$ with formatting as described in Figure 3-3.

Figure 3-12 OA/ΔCO (µg m$^{-3}$ ppmv$^{-1}$) ratios color coded by $-\log(\text{NO}_x/\text{NO}_y)$. 
Figure 3-13 OA/ΔCO (µg m⁻³ ppmv⁻¹) vs –log(NOₓ/NOᵧ). The measured ratios OA/ΔCO are averaged into 10 bins according to –log(NOₓ/NOᵧ). Error bars show the error of the mean.

Figure 3-14 shows the time series of OA factors/ΔCO as a function of –log(NOₓ/NOᵧ). All OA factors in Centreville show a significant relationship with –log(NOₓ/NOᵧ) with the exception of BBOA. While low LVOOA/ΔCO and IEPOX OA/ΔCO values were observed with –log(NOₓ/NOᵧ) values between 0 and 0.2 (Figure 3-14), high values of those ratios were observed with –log(NOₓ/NOᵧ) values 0.3 and higher. However, SVOOA shows a negative relation with the –log(NOₓ/NOᵧ) aging metric. As shown in Figure 3-14, –log(NOₓ/NOᵧ) values between 0 and 0.2 usually correspond to high SVOOA/ΔCO ratios.
Figure 3-14 OA factors/ΔCO (µg m⁻³ ppmv⁻¹) ratios color coded by –log(NOₓ/NO₂).

Figure 3-15 shows LV0OA/ΔCO, SV0OA/ΔCO and IEPOX OA/ΔCO ratios which are averaged into 10 bins according to –log(NOₓ/NO₂). LV0OA/ΔCO in Centreville has a strong positive correlation with the aging metric, which suggests LV0OA in the region is produced locally, in contrast to DFW.
Figure 3-15 LVOOA/ΔCO, SVOOA/ΔCO and IEPOX OA/ΔCO ratios averaged into 10 bins according to \(-\log(\text{NO}_x/\text{NO}_y)\). Error bars show the error of the mean.
IEPOX OA/∆CO shows an overall increase with an increase in $-\log(\text{NO}_x/\text{NO}_y)$, with a steeper slope up to 0.4. While SVOOA in DFW shows an increase with $-\log(\text{NO}_x/\text{NO}_y)$, SVOOA in Centreville shows a strong negative correlation with the same aging metric (Figure 3-15). This trend can be explained by rapid oxidation of SVOOA to form LVOOA with photochemical activity.

3.4. Conclusions

The average aerosol composition was dominated by organic matter (73%) followed by smaller contributions from sulfate (19%), ammonium (5%), and nitrate (3%). Positive matrix factorization analysis of the high-resolution mass spectra resolved four components from the total organic mass: BBOA, IEPOX OA, SVOOA, and LVOOA. A large majority of the OA mass is classified as oxygenated (SVOOA 31% and LVOOA 31%); there are also important contributions from IEPOX OA and BBOA, accounting for 22% and 15% of the total OA mass, respectively. The LVOOA and IEPOX OA diurnal profiles show a classic photochemical profile. The SVOOA diurnal profile shows an enhancement during nighttime and remains low during the day, while BBOA does not show a significant diurnal trend.

A significant positive correlation is observed between LVOOA/∆CO and the $-\log(\text{NO}_x/\text{NO}_y)$ aging metric, which signifies the local characteristic of LVOOA. IEPOX OA shows an increasing trend with increasing values of $-\log(\text{NO}_x/\text{NO}_y)$. In contrast to DFW, SVOOA shows a strong negative relation with the $-\log(\text{NO}_x/\text{NO}_y)$ aging metric. OA/∆CO and OA factors /∆CO values do not show any relationship with the sulfate
aging metric. Unfortunately, we do not have benzene data for this location and could not study photochemical age with respect to hydrocarbons.
Chapter 4

Characterization of Ambient Aerosols and Evolution of Organic Aerosol in Houston

4.1. Introduction

Real-time measurements of submicron particles were taken with a HR-ToF-AMS from May 12 to May 29, 2015, in Houston, TX, with a time resolution of 20 seconds. The goals of this work were to investigate the chemical characterization of submicron particles near industrial facilities, to determine the different OA factors that contribute to total OA, and to study the OA processing and aging metric relationships. In addition, researchers from the University of Iowa collected high-volume filter samples at the site to characterize OA at the molecular level. These data will be useful for comparison of HR-ToF-AMS data and aging metrics to specific organic marker compounds.

4.2. Experimental

4.2.1. Sampling site and Instrumentation

The HR-ToF-AMS measurements were performed continuously between May 12 and May 29, 2015, at the Clinton Drive TCEQ monitoring site. The site has an elevation of 6m above sea level, is near East Houston, and is located at 32° 59’16” N, 97° 28’ 37”
W. Houston is one of most populous cities in the U.S., with a population close to 2.2 million. The city dominates U.S. oil and gas production/processing and is one of the biggest petrochemical manufacturing centers in the world. The location and a photograph of the site are shown in Figure 4.1.

The HR-ToF-AMS measurements were performed continuously between May 12 and May 29, 2015, at the Clinton Drive TCEQ monitoring site. The site has an elevation of 6m above sea level, is near East Houston, and is located at 32° 59’16” N, 97° 28’ 37” W. Houston is one of most populous cities in the U.S., with a population close to 2.2 million. The city dominates U.S. oil and gas production/processing and is one of the biggest petrochemical manufacturing centers in the world. The location and a photograph of the site are shown in Figure 4.1.

Figure 4-1 The location (red pin) and a photograph of the Clinton Drive TCEQ field site
4.3. Results and Discussions

4.3.1. PM$_1$ Overview

The time series of five non-refractory components (organics, sulfate, ammonium, nitrate, and chloride) of PM$_1$ measured by the HR-ToF-AMS are shown in Figure 4-2. The average total concentration of the five components was 5.7 ± 4.4 µg m$^{-3}$, with a range up to 69.3 µg m$^{-3}$. Organics and sulfate aerosol were the two most abundant species, with relative average contributions of 47.1 ± 19.6% and 39.9 ± 15.1% to total measured PM$_1$, respectively. Organics and sulfate “events” with significantly high peaks were observed throughout campaign (Figure 4-2). Ammonium and nitrate mass accounted for only 11.0 ± 5.5% and 1.7 ± 4.2% of total PM$_1$.

![Figure 4-2 Time series of mass concentrations of organic matter, sulfate, ammonium, nitrate, and chloride at Clinton Drive (µg m$^{-3}$).](image-url)

Figure 4-2 Time series of mass concentrations of organic matter, sulfate, ammonium, nitrate, and chloride at Clinton Drive (µg m$^{-3}$).
The average OA concentration during the campaign was 2.6 ± 2.9 µg m⁻³ with a maximum of 63.9 µg m⁻³ during the high organic peak events in the first week. Backward trajectories calculated using the NOAA HYSPLIT model (Figure 4-3) indicate that the air with high organic concentrations came to the sampling site from the east and northeast directions, coincident with the Houston Ship Channel. This suggests that high organic peak events on those days are likely driven by industrial emissions and characterized by HOA; PMF results given in detail in the next section confirm that HOA is the most dominant OA factor during these events. The diurnal profile of OA (Figure 4-4) shows that median values for OA concentrations follow a diurnal trend, with higher concentrations between 8AM and 6PM, likely a result of photochemical processing. The OA concentrations show the highest variability during early morning hours.

Figure 4-3 HYSPLIT 24-hour backward trajectories for the days with high OA concentration events.
The average sulfate and ammonium concentrations during the campaign were 2.4 ± 2.4 µg m⁻³ and 0.7 ± 0.7 µg m⁻³, respectively. Similar to OA, sulfate aerosol shows significant variability during the campaign, with concentrations reaching up to 40.7 µg m⁻³. The air with high sulfate concentrations typically was transported to the sampling location from the south and southeast of the location. Figure 4-5 shows the HYSPLIT 24-hour backward trajectories for the days with high sulfate concentration events. Large spikes of sulfate occur on days when the site is in downwind of Gulf of Mexico. Local SO₂ emissions also may contribute to this observation. The diurnal profiles of sulfate and ammonium tracked each other, and the mean and median values of these components show a slight increase during the day (Figure 4-4). The concentrations of both compounds have higher variability during the night.

Figure 4-4 Diurnal profiles of OA, sulfate, ammonium, and nitrate during the Clinton Drive sampling campaign. Mean values are plotted with solid lines; median values are plotted with squares and bars showing the standard deviation.
The concentration of nitrate was low for most of the campaign, with an average nitrate concentration of 0.07 ± 0.08 µg m⁻³. The median values of nitrate in each hour were close to a flat line; however, mean values show two peaks around 9AM and 12:30PM (Figure 4-4). The two peaks hours show the greatest variability, which indicates that the mean values were skewed as a result of high nitrate events.

Figure 4-5 HYSPLIT 24-hour backward trajectories for the days with high sulfate concentration events.

4.3.2. OA Characterization

Diurnal profiles of elemental ratios (H:C, O:C, and OM:OC) are shown in Figure 4-6. The H:C diurnal profile shows an early morning peak, matching morning rush hour, and remains mostly consistent for the rest of the day. The O:C and OM:OC ratios show
daytime peaks as expected (between 8AM and 8PM) due to photochemistry and second peaks after midnight. This nighttime peak could be related to nocturnal processing of organic compounds by nitrate radical (Cleveland et al., 2012). The average of O:C and H:C ratios for Clinton Drive site were 0.6 ± 0.2 and 1.6 ± 0.2, respectively. The slope of H:C versus O:C was -0.67 which was similar to that observed in DFW but closer to carboxylic acid. H:C versus O:C has shown significant variability on the diagram, which reflects the variability of different OA factors throughout campaign.

Figure 4-6 Diurnal profiles of elemental ratios OM:OC, O:C, and H:C of OA during the Clinton Drive sampling campaign.
4.3.3. PMF Results

Three OA components were identified using PMF: HOA, SVOOA and LVOOA. Figure 4-8 shows the mass spectral profiles of the identified components. The first factor is dominated by ions with m/z ratios of 41, 43, 55, 57, and 69 (C_nH_{2n+1}^+ and C_nH_{2n-1}^+), which are typical signatures of urban primary emissions. Both OOA components have significant contribution from m/z 44 (CO_2^+), which is a tracer for oxidized organics. To differentiate between SVOOA and LVOOA, the relative contributions of m/z 44 and m/z 43 (mostly C_2H_3O^+) to mass spectral profiles of the two components were used. The LVOOA, which is more oxidized than SVOOA, has a higher f_{44/43} (ratio of m/z 44 to m/z 43).
Figure 4-8 Mass spectra for the three components identified in the PMF analysis for OA during the Clinton Drive sampling period. Each color in the plot represents a certain type of OA factor that contributes to total OA.

Figures 4-9 and 4-10 show the corresponding time series of mass concentrations and diurnal profiles of the three OA components. Mass concentrations of HOA varied significantly during the sampling period, and most OA peaks were driven by the increase in HOA concentrations. The HOA accounted for an average of $31.7 \pm 21.8\%$ of the total OA. The diurnal profile of this factor shows a significant increase during morning rush hour (7 to 9 AM), similar to the H:C diurnal profile, and a smaller increase during evening rush hour (5 to 6 PM). More significant contributions to total OA were made by the OOA factors, with contributions of $38.7 \pm 24.1\%$ and $28.9 \pm 21.4\%$ for LVOOA and SVOOA, respectively.

The SVOOA factor diurnal profile shows an increase during the daytime, when SOA formation is expected due to photochemical activity. A smaller increase in the
LVVooA factor concentration is observed both during daytime (11 AM to 6 PM) and after midnight. These relationships and profiles indicate that even in highly industrialized areas, processing is quite important.

Figure 4-9 Time series of the three organic aerosol components.
4.3.4. OOA-Aging Relationships

4.3.4.1. Sulfur

The $\text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2)$ values range between 0.02 and 1, with a mean of $0.69 \pm 0.12$ (Table 4-1). The aging metric did not show a significant diurnal trend.
Table 4-1 Statistics of aging metrics.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Mean</th>
<th>Mode</th>
<th>Median</th>
<th>Lower Quartile</th>
<th>Upper Quartile</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4^2-$ / (SO$_4^2+$SO$_2$)</td>
<td>1</td>
<td>0.02</td>
<td>0.6</td>
<td>0.4</td>
<td>0.56</td>
<td>0.20</td>
<td>0.54</td>
</tr>
<tr>
<td>Photochemical Age (hrs)</td>
<td>72.4</td>
<td>0.2</td>
<td>15.7</td>
<td>7.2</td>
<td>13.9</td>
<td>8.6</td>
<td>20</td>
</tr>
</tbody>
</table>

Figures 4-11 and 4-12 show the time series of OA/ΔCO and OA factors/ΔCO as a function of the sulfate aging metric. As seen in the graphs, there were no consistent relationships between the sulfate aging metric and OA/ΔCO and OA factors/ΔCO values. Similar to the other two sites in this work, sulfate aging metric was not able to reflect local processes in Houston. For the OA factors, only LVOOA shows an overall increase as sulfate age increases signifying the regional characteristic of the factor. Unfortunately, NO$_y$ data were not available at the Clinton site; therefore, we were not able to study the NO$_x$/NO$_y$ aging metric.
Figure 4-11 OA/ΔCO (µg m⁻³ ppbv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻)

Figure 4-12 OA factors/ΔCO (µg m⁻³ ppbv⁻¹) ratios color coded by SO₄²⁻ / (SO₂ + SO₄²⁻)
4.3.4.2. Photochemical Age

Photochemical age values range between 0.2 and 72.4 hours. Table 4-1 shows the average photochemical age was 15.7 ± 5.8 hours. Figure 4-12 shows the time series of OA/ΔCO colored as a function of photochemical age with respect to the toluene to benzene (predominantly anthropogenic hydrocarbons) ratio. The time resolution of the toluene and benzene measurements was 1-hr, limiting the number of data points throughout the campaign and requiring averaging of higher time-resolution data. For the limited data, Figure 4-13 shows no relationship between OA/ΔCO and photochemical age.

Figure 4-13 OA/ΔCO (µg m\(^{-3}\)ppmv\(^{-1}\)) ratios color coded by \(\text{SO}_4^{2-} / (\text{SO}_2 + \text{SO}_4^{2-})\)
4.4. Conclusions

The average aerosol composition in Houston was dominated by OA and sulfate, and they accounted for $47.1 \pm 19.6\%$ and $39.9 \pm 15.1\%$ of total PM$_1$, respectively. High concentrations of OA were observed when the sampling location was downwind of the Houston Ship Channel, and high concentrations of the HOA component were observed during the same events, suggesting that primary emissions of OA cause high OA peaks. High concentrations of sulfate events occurred when the site was in the downwind of Gulf of Mexico.

Three OA factors were identified using the PMF model: HOA, SVOOA, and LVOOA. Total OA was dominated by the OAA factors, which accounted for approximately two-thirds of the total OA, very consistent with the estimates of Cleveland et al. (2012) at a location closer to downtown Houston. However, the HOA factor showed the highest variability during the campaign and dominated high concentration OA events. The HOA likely represents a background mobile emission source coupled with large industrial events. Given the diurnal profiles, SVOOA likely represents more rapid local SOA formation from industrial and mobile source VOC emissions, while LVOOA likely represents a significantly aged regional SOA.

Both the sulfate aging metric and the photochemical age with respect to toluene and benzene did not show significant relationships with OA processing. Only the LVOOA factor showed an increase with sulfate aging metric, signifying its regional characteristic.
Chapter 5

Field Site Comparisons and Implications

Overviews of PM$_1$ composition and concentration, diurnal profiles, PMF results, and OA enhancement and aging metric relationships for the three field sites were given in detail in previous sections. Thus, in this chapter, data from the three field sites are compared in terms of PM$_1$ characteristics, OA factors and OA enhancement and aging metric relations. The goal is to generalize the findings of the study, if possible. After these comparisons, the novelty and larger implications of this work are discussed.

Figure 5-1 shows a summary of average concentrations of total measured PM$_1$ and PM$_1$ components throughout the campaigns at the three field sites. The DFW site was the cleanest with respect to PM pollution. The lowest concentrations of OA, sulfate, and total PM$_1$ were observed at this site. However, it had the highest average nitrate concentration. This could be a result of the cattle near the site providing excess NH$_3$ (Gong et al., 2013). The highest average concentrations of OA and total PM$_1$ were observed in Centreville, which is by far the most rural site. This indicates significant transport of material from urban locations and the influence of local biogenic VOC emissions (Hidy et al., 2014, Xu et al., 2015). As a result of being located in a highly industrialized area, the Clinton Drive site was influenced by frequent high peak events of organics and sulfate, likely resulting from point source emissions. The Clinton Drive site had the highest average sulfate concentration when the site was downwind of the Gulf of
Mexico; this is likely a result of industrial facilities in this direction (for example, in Texas City) as opposed to marine sulfur. The OA events occurred when the site was downwind of the Houston Ship Channel.

Prior to comparing PMF factors, it is important to consider whether they are chemically similar at each location, as SVOOA and LVOOA typically represent less oxidized and more oxidized OA, respectively. Given that “less” and “more” are relative terms, their definitions should be considered compared to some sort of standard. In this case, mass spectra of the OA factors given the same category name were compared for all the sites. Figure 5-2 shows scatter plots of the fractional contribution of given m/z signals to the total OA signal for each of the factors. Each plot represents a comparison of a given PMF factor between two of the field sites. As shown in Figure 5-2, mass spectra of the OA factors were consistent for all the three sites. They were significantly correlated with each other, with Pearson’s r values between 0.84 and 0.99. Slopes are generally close to unity, with deviation for m/z values at the low end of the fractional signal range. At these low values, uncertainty increases due to decreased signal (relative to noise) and slight changes in instrument operation between the field campaigns. As such, it is assumed for this analysis that the factors are chemically similar between the field campaigns.

The PMF results indicate that the so-called HOA factor was observed for both the DFW and Clinton sites while OOA factors, SVOOA and LVOOA, were observed at all three sites. The SOAS field site exhibited the largest fraction of total OOA (Figure 5-3). The Centerville site also had the most distinctive PMF results. As opposed to DFW and
Clinton Drive, an HOA factor was not discernible in Centreville; this is likely due to the dilution and/or oxidation of POA from non-local sources during transport. In addition, the IEPOX OA factor formed as a result of isoprene oxidation was only observed at this site. These results are explained by large emissions of BVOCs (mostly isoprene) in the presence of $SO_2$ and $NO_x$ transported from upwind anthropogenic sources. Meteorological conditions also favored photochemical activity. Houston also had the highest HOA contribution to total OA. The PMF results indicate that high OA concentration events were driven mostly by primary OA.

While the analyses shown above demonstrate that the OA factors are chemically consistent between the sites and relatively important at each of the sites, an investigation of the OOA factor enhancement with respect to the aging metrics provides some insight into the origin of different OOA factors at the different sites. For example, LVOOA showed a positive correlation with the sulfate aging metric in DFW, while it showed a strong correlation with the $NO_x/NO_y$ aging metric in Centreville. This indicates that the origin of the LVOOA at the two different field sites is different, despite being similar chemically. The LVOOA in DFW is mostly regional, while the LVOOA in Centreville is mostly local. This provides insight into the use of AMS data in past and future field studies. It is generally assumed that LVOOA is aged/regional OA due to its more oxidized nature (which typically requires a longer period of time to form). However, this work indicates that LVOOA can form more rapidly under certain scenarios and therefore represents a local source of more oxidized OA.
The SVOOA also showed different characteristics at the DFW and SOAS sites. The SVOOA in DFW showed an overall positive relationship with the NO\textsubscript{x}/NO\textsubscript{y} aging metric. That is, as NO\textsubscript{x} is chemically processed, more SVOOA is formed. As with the discussion above, this implies local formation. What is particularly interesting is that the slope of this relationship changes such that it appears that more rapid changes in SVOOA are observed in fresher airmasses compared to when older airmasses are further aged. The steeper slope of SVOOA enhancement in the abundance of NO\textsubscript{x} could be explained by NO\textsubscript{x} altering SOA formation indirectly by impacting O\textsubscript{3} formation (through its photochemical interactions with VOCs). Ozone, an oxidant itself, also contributes atmosphere’s oxidative budget by producing OH radical. Therefore, controlling local anthropogenic NO\textsubscript{x} emissions, which is mostly dominated by mobile sources (Kim et al., 2011) in DFW, could limit both O\textsubscript{3} and SVOOA formation.

In Centreville, the SVOOA-NO\textsubscript{x} aging relationship showed a strong negative correlation. Centreville is characterized by high abundance of isoprene and monoterpenes and further-field presence of anthropogenic pollutants. As stated previously, NO\textsubscript{3} oxidation of isoprene and monoterpenes creates SOA in large yields (Ng et al., 2008, Fry et al., 2009). Because NO\textsubscript{3} radical is formed through the NO\textsubscript{2} plus O\textsubscript{3} reaction and subsists at night due to the lack of photolysis, high concentrations of SVOOA in Centreville during night time can be explained by formation of SOA by NO\textsubscript{3} oxidation of BVOCs. Therefore, when NO\textsubscript{2} is present (and thus, the airmass appears fresh), an enhanced mixing ratio of NO\textsubscript{3} is expected, leading to enhanced SVOOA. Prevention of SVOOA in rural areas would then depend on limiting the amount of NO\textsubscript{2} present. This emphasizes the need for regional, in addition to local as specified for urban areas, NO\textsubscript{x}
control. However, one must be careful when recommending NO$_x$ control in isolation, as decreases in NO$_x$ can lead to increases in O$_3$, depending on a location’s position on the O$_3$ isopleth.

While OA enhancement and aging metric relationships have been studied previously (Weber et al., 2007, Kleinman et al., 2008, Slowik et al., 2011, Hayes et al., 2013), most of these studies include investigation of either dependence of OA enhancement on only one specific aging metric, total OA (as opposed to a PMF factor) enhancement, or a particular location in isolation. Thus, this work is novel as we compare the relation between various SOA factor enhancements and various aging metrics in three areas characterized by highly varying emissions profiles and meteorology. The results summarized in previous paragraphs emphasized that the relation of aging metrics and OA enhancements are likely differ significantly based on the OA factor and aging metric studied. The relationships between OA factor enhancements and aging metrics helped us to characterize the OA factors based on nocturnal chemistry or photochemistry and based on local or regional production. A major emphasis of these results with regard to air quality is the need to focus on both local and regional NO$_x$ control, again assuming no resulting increases in O$_3$ (which would need to be evaluated by air quality modeling).

It should be noted there are additional techniques that can be used to approximate airmass aging such as the ratios alkyl nitrates /alkanes (anthropogenic photochemistry) and isoprene oxidation products/isoprene (biogenic photochemistry). As shown here, using various aging metrics with respect to different emission sources and comparing
them with OA enhancement provides insight into SOA formation. When considering future air quality, it is probable that the frequency, duration, and spatial extent of wildfires will increase. Globally, a significant fraction (90%) of POA is attributed to biomass burning; however, evolution of BBOA in the atmosphere and aging of biomass burning plumes are not well understood (Jolleys et al., 2012). Thus, it is recommended that future air quality campaigns include methodologies to measure the impact of BBOA to a greater extent, including molecular speciation of specific BBOA tracers. This would then allow the ratio of levoglucosan and its isomers to free methoxyphenols to be used as a metric of plume aging because of the different degradation rates of the compounds (Myers-Pigg et al., 2016). This metric could then be considered with the PMF results to evaluate the impact on OA factor enhancement of the processing of plume emissions. Such measurements would have been useful for SOAS. A rapid increase of OA concentration was observed during a biomass burning event in the first week of SOAS campaign, with OA concentration levels in excess 70 µg m⁻³.

The findings of this work show that SOA was consistently a substantial fraction of total OA and that a significant fraction of total SOA for all three sites exhibited local characteristics. This implies that control strategies for PM also should focus on the VOCs that act as SOA precursors, in addition to the NOₓ discussed above. DFW and Houston, two highly urbanized cities, are subject to VOC emissions of both biogenic and anthropogenic origin.

The BVOC emissions in both cities are dominated by isoprene and monoterpenes (Buzcu and Fraser, 2006, Rutter et al., 2014). Although their contribution to total VOC
emissions is small and uncontrollable, oxidation of BVOCs can result in high yields of SOA production with the presence of anthropogenic emissions.

A significant amount of VOC reactivity at the DFW site was related to natural gas operations (mostly short alkanes such as ethane, butane and propane) and mobile sources (2,2,4-trimethylpentane, benzene, toluene and C₈ and C₉ aromatics). In addition, VOC levels in Houston are impacted by petrochemical production facilities (mostly ethylene and propylene) and refineries (ethane, propane, n-butane and isobutane) (Buzcu and Fraser, 2006). Highly reactive VOC emissions from these facilities have been shown to contribute to rapid O₃ production rates (Ryerson et al., 2003), which consequently enhance SOA formation.

Thus, in Houston and DFW, reduction in secondary PM requires controlling both NOₓ and anthropogenic VOC emissions. A reduction in both VOC and NOₓ also would ensure decreases in O₃ based on the shape of the O₃ isopleth.

Although the bulk of the fine PM in these urban areas appear to be secondary in nature, it is important to consider control of primary PM. In DFW, the most important contributor to POA was mobile sources. Controlling mobile POA emissions both in DFW and Houston can reduce POA levels. In Houston, it also was observed that emissions of fine OA and SO₄ from industrial sources resulted in high (up to levels of 69 µg m⁻³) PM concentration events. These results emphasize the need for clean technologies to reduce industrial primary fine PM concentrations in Houston. Based on this, a multi-pollutant (VOC, NOₓ, and primary PM) and multi-source (mobile sources, industrial sources) control strategy likely will be necessary to decrease PM in urban areas.
For the SOAS site, control of local VOCs is not possible. Tight correlations of LVOOA and the NO$_x$/NO$_y$ aging metric and increased levels of SVOOA at night in Centreville underscore the importance of NO$_x$ in the region. Moreover, Xu et al. (2015) suggested isoprene-derived SOA is altered directly by the abundance of sulfate. These observations emphasize that controlling regional anthropogenic pollutants such as NO$_x$ and SO$_2$ is critical to control fine PM levels in the Southeast US.

These results also indicate that design of PM control strategies likely needs to be location specific. It is also possible that control strategies need to be time specific for these locations. However, because these studies were limited in their duration, no comment can be made on this aspect. The Houston Aerosol Characterization and Health Experiment, which occurred from 2013-2015 and for which data currently are being analyzed, should allow insight into temporal issues (daily, weekly, monthly, and seasonally) associated with PM in Houston.

The fundamental motivation of this work is that PM in the troposphere impacts climate, visibility, and public health. However, the quantification of these impacts includes significant uncertainties because of deficiencies in the understanding of the sources, formation mechanisms, and aging processes associated with OA, which constitutes a significant fraction of PM. Evaluation of these impacts and their uncertainties is beyond the scope of this work, as is photochemical modeling. Instead, the implications of this work relate more to providing guidance for future research.

More specifically, laboratory experiments are necessary to determine the optical properties (impact on climate and visibility), cloud or ice nucleation properties (impact
on climate), or assay response (impact on health) of SOA factors represented by SVOOA and LVOOA. In order to ensure applicability to the atmosphere, the SOA generated in the experiments must be representative. The relationships derived in this work provide relevant information. For example, nitrate radical oxidation of VOC should be included in experiments, as it appears based on the data presented here that such a phenomenon leads to formation of OOA to a much greater extent than thought previously. In addition, it has been shown that SOA formation is more rapid when there is an abundance of NOₓ, even if the overall amount of SOA is expected to increase with lower concentrations of NOₓ. This implies both kinetic as well as product-distribution effects of NOₓ on SOA formation. Therefore, the effect of a full range of atmospherically relevant NOₓ/NOᵧ ratios on SOA formation rates should also be investigated in laboratory experiments.

Figure 5-1 Comparison plot of average concentrations of total PM₁ and PM₁ components at the three field sites investigated in this work.
Figure 5-2 Average fractions of OA components over the campaigns at the three sites investigated in this work.
Figure 5-3. Comparisons of mass spectra of OA factors at the three sites investigated in this work.
Chapter 6

Conclusions

The main objectives of this study were to improve the understanding of the sources and transformation processes of PM$_1$ components, with an emphasis on OA and relationships between enhanced OA/OA factor concentrations and various aging metrics in three US cities: Fort Worth, Centreville and Houston. The HR-ToF-AMS was used to measure PM$_1$ chemical composition and concentrations at all the field sites.

OA and sulfate were the most dominant PM$_1$ components at all three sites. The OA in DFW and Houston was apportioned into three OA factors including HOA, SVOOA, and LVOOA. HOA was more prominent in Houston compared to DFW, which reflects the significant effect of industrial emissions on primary OA in Houston. In both cities, total OOA comprised a large fraction of total OA. In Centreville, total OA was apportioned into four factors: BBOA, IEPOX OA, SVOOA, and LVOOA. OA in Centreville was also dominated by OOA. These results show that SOA formation and aging processes are critical, no matter if it is a forested, urban or an industrialized area.

The OA factor /ΔCO enhancements with respect to age metrics were investigated for DFW, Centreville and Houston. In DFW, LVOOA/ΔCO shows a positive correlation with sulfate aging metric and SVOOA/ΔCO shows an overall increase with -log (NO$_x$/NO$_y$), indicating the different origin of the two OA factors, regional and local, respectively. In Centreville, a significant positive correlation is observed between
LVOOA/ΔCO and the \( \text{–log}(\text{NO}_x/\text{NO}_y) \) aging metric, which signifies the local characteristic of LVOOA. IEPOX OA shows an increasing trend with increasing values of \( \text{–log}(\text{NO}_x/\text{NO}_y) \). In contrast to DFW, SVOOA shows a strong negative relation with the \( \text{–log}(\text{NO}_x/\text{NO}_y) \) aging metric which could be explained by the night time production of SOA by NO\(_3\) oxidation which formed mostly at night through NO\(_2\)+O\(_3\) reaction. The LVOOA in Houston shows an increasing trend with increasing values sulfate aging metric. These aging-OA/ΔCO relationships warrant further investigation and highlight that caution must be used when describing an airmass as “aged.”

In the future, I plan to continue conducting atmospheric field studies in Turkey by using the knowledge and skills I gained during my graduate studies in the U.S. PM pollution is an emerging environmental concern in many cities in Turkey. The European Environment Agency (EEA) reported that 97% of the urban population in Turkey is exposed to PM levels higher than EU standards and the World Health Organization (WHO) recommendations for PM\(_{2.5}\) and PM\(_{10}\). My goal is to conduct field studies to improve the understanding of chemical characterization, sources and transformation processes of PM in Turkey.
References

The Southern Oxidant and Aerosol Study (SOAS): Measuring and modeling at the interface of air quality and climate change to understand biosphere-atmosphere interactions [Online].
[Accessed].


HATAKEYAMA, S., IZUMI, K., FUKUYAMA, T., AKIMOTO, H. & WASHIDA, N. 1991. REACTIONS OF OH WITH ALPHA-PINENE AND BETA-PINENE IN


of petrochemical industrial emissions of reactive alkenes and NOx on tropospheric ozone formation in Houston, Texas. *Journal of Geophysical Research-Atmospheres*, 108.


Appendix

Peer-reviewed publications in print


Scientific presentations

B. Karakurt Cevik, Y.J. Leong, C. Hernandez, R.J. Griffin, Characterization of Ambient Aerosol Concentration, Composition, and Aging during the Southern Oxidant and Aerosol Study, American Association for Aerosol Research Annual Conference, Minneapolis, MN, October 2015. (poster)

B. Karakurt Cevik, Y.J. Leong, C. Hernandez, R.J. Griffin, Characterization of ambient aerosols during the Southern Oxidant and Aerosol Study (SOAS) in Centreville, AL, with a high-resolution time-of-flight aerosol mass spectrometer, *American Geophysical Union Winter Meeting*, San Francisco, CA, December 2013. (poster)

**Contributed presentations**


R. Sheesley, T. Barrett, S. Yoon, A. Clark, L. Hildebrandt-Ruiz, R. Griffin, B. Karakurt Cevik, R. Long, R. Duvall, and S. Usenko, Spatial trends in surface-based carbonaceous aerosol, including organic, water-soluble, and elemental carbon,
during DISCOVER-AQ in Houston, TX, *American Geophysical Union Winter Meeting*, San Francisco, CA, December 2014. (poster)


B.C. Sive, X. Lan, D. Anderson, Y. Zhou, M. Camp, R.J. Griffin, Chemical characterization of submicron aerosol emissions in the greater Houston area using
an aerosol mass spectrometer on a mobile platform, *American Geophysical Union Winter Meeting*, San Francisco, CA, December 2013. (poster)
