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Characterization of Atmospheric Nitrogen Chemistry and the Formation/ Evolution of Particulate Matter in Houston, TX

by

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ABSTRACT

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This thesis covers laboratory experiments to study the homogeneous reduction of nitric acid (HNO$_3$) to nitrous acid (HONO) in the presence of volatile organic compounds that are surrogates for those emitted by motor vehicles. The results presented in this study focus on the impact of environmental variables on the rate of formation of HONO in this process. The homogeneous conversion of HNO$_3$ to HONO has significant atmospheric implications due to the “renoxification” of less reactive HNO$_3$ into more reactive HONO. Consecutively, this thesis describes particulate matter (PM) data collected from a month-long (September 2013) field project in Houston, TX. A mobile laboratory containing state-of-the-art PM instrumentation and auxiliary measurements was deployed. The main focus for the thesis work was to utilize this dataset to better characterize PM pollution in the city of Houston. This was achieved by several analysis approaches including cluster analysis, back-trajectory analysis, and principal component analysis to describe spatial and temporal variations in submicron PM in the Houston region. Finally, this work describes the use of a statistical source apportionment technique, positive matrix factorization, on the field dataset to apportion important constituents of atmospheric aerosols in Houston. This technique allowed the apportionment of four organic aerosol factors, two of which were associated with organic nitrates from biogenic sources.
Submicron PM plume events from on-road, industrial, and biomass burning sources in Houston also were chemically characterized. Because sources of PM pollution are still poorly understood, particularly in the highly industrial and urban city of Houston, the results from this thesis will advance PM modeling capabilities and allow improved PM control strategies in polluted urban areas similar to Houston.
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Chapter 1. Introduction

The troposphere – where we live and breathe – extends from ground level to the tropopause, which is located at altitudes of 10-15 km depending on latitude and time of year. Air quality in the troposphere is directly relevant to human health, ecosystems, hydrology, and climate change. Air pollution occurs in the form of particulate matter (PM), tropospheric ozone ($O_3$), and other trace gases at levels that are either toxic to human beings or detrimental to the environment. It can occur due to anthropogenic activities such as industrial and vehicular emissions, natural processes such as biogenic emissions and sandstorms, or a combination of both.

Particulate matter and $O_3$ are of primary interest in this thesis, due to their relative importance to human health. Atmospheric aerosols (or particulate matter) are solid and/or liquid particles suspended in the air, are made out of a variety of inorganic and organic compounds, and have varying size distributions in the atmosphere depending on its source. Tropospheric $O_3$ is caused by the photochemical interactions between atmospheric nitrogen oxides ($NO_x = \text{nitric oxide (NO)} + \text{nitrogen dioxide (NO}_2)$) and volatile organic compounds (VOCs) [Atkinson, 2000]. In addition to well-established health impacts on humans [Harrison and Yin, 2000; Lippmann, 1998], $O_3$ and PM can have important environmental impacts [Seinfeld and Pandis, 2006]. For example, tropospheric $O_3$ acts as a greenhouse gas and is reactive enough to drive other chemical processes in the atmosphere. Aerosols can result in the acidification of soil or water bodies [Duyzer, 1994] and can play an important role in climate change [IPCC, 2007].

Tropospheric $O_3$ and PM are among the criteria pollutants governed by the National Ambient Air Quality Standards (NAAQS) established by the United States
Environmental Protection Agency (EPA), aimed at protecting public health and welfare [EPA, 2012; Lippmann, 1998; Lippmann, 2012]. Due to the impact of PM and O₃ on public health and their relative importance in urban environments like Houston, TX, the intricate physical and chemical processes involving tropospheric PM and O₃ will be the overarching topics of interest in this thesis.

1.1 Introduction to PM and O₃ pollution
Pollutants that are directly emitted into the atmosphere are called primary pollutants (e.g., sulfur dioxide (SO₂) from power plant stacks and some forms of PM) whereas secondary pollutants are those such as O₃ and other forms of PM that are created in the atmosphere through chemical reactions between precursor species. The precursors for PM and O₃ can have natural/biogenic or anthropogenic sources. This section includes a brief overview of PM and O₃ pollution and why these pollutants are important, particularly in the urban/sub-urban troposphere.

1.1.1 O₃
Tropospheric O₃ correlates with mortality rates in the summer months, when O₃ levels are high compared to winter [Bell et al., 2004; Brunekreef and Holgate, 2002; Samet et al., 2000]. Ozone can have both short-term (acute) and long-term (chronic) health impacts, particularly on sensitive groups and individuals with respiratory conditions. Ozone plays a large role in the oxidative budget of the atmosphere, not only as a reactive oxidant itself but also in producing the highly reactive hydroxyl (OH⁻) and nitrate (NO₃⁻) radicals [Seinfeld and Pandis, 2006]. A large number of atmospheric processes are initiated by these oxidants, including the aging of VOCs, the growth and formation of aerosol, and the oxidation of SO₂ into sulfuric acid (H₂SO₄).
Nitrogen oxides (NO and NO$_2$) play an important role in the cycling of O$_3$ molecules in the troposphere [Atkinson, 2000; Seinfeld and Pandis, 2006]. One O$_3$ molecule is consumed each time an NO molecule gets converted into NO$_2$, and NO$_2$ in turn produces an O$_3$ molecule under UV irradiation (Figure 1). This null cycle between NO and NO$_2$ does not result in net O$_3$ production. However, certain VOCs are oxidized by OH∙, the key daytime oxidant in the atmosphere, forming hydroperoxyl (HO$_2$∙) and organic peroxy (RO$_2$∙) radicals. These radicals in turn react with NO to produce NO$_2$ without consuming O$_3$, upsetting the null cycle and resulting in the net production of O$_3$. Clearly, both VOCs and NO$_x$ play crucial roles in O$_3$ formation, and both of these compounds compete for reaction with OH∙ [Seinfeld and Pandis, 2006]. This gives rise to what are known as NO$_x$-limited and NO$_x$-saturated atmospheric conditions. In the NO$_x$-limited case (high VOC/NO$_x$ ratio), O$_3$ production scales positively with NO$_x$, and VOC reductions will have little effect on O$_3$. In contrast, under NO$_x$-saturated conditions (low VOC/NO$_x$ ratio), the addition of reactive VOCs and/or the reduction in NO$_x$ could substantially increase O$_3$ production. In order to predict accurately regional O$_3$ formation rates and for O$_3$ control strategies to be effective, the complex interactions between VOCs, atmospheric oxidants, and NO$_x$ need to be well characterized. Nitrogen oxides and VOCs can be emitted by natural/biogenic processes, but vehicular and industrial emissions also can contribute greatly to both precursor gases, thereby making them highly important in highly industrialized urban/sub-urban regions like the city of Houston.
In short, O$_3$ pollution represents a threat to public health in Houston and other urban environments around the world. Despite extensive work monitoring O$_3$ and its precursors and improving chemical models that predict O$_3$ formation, large uncertainties in predicting the response of O$_3$ to changes in VOCs, NO$_x$ and OH· levels remain [Atkinson, 2000; Rivera-Figueroa et al., 2003; Sillman, 1999]. One of the important contributors to the uncertainties of O$_3$ prediction is the lack of understanding of the trace gases nitrous acid (HONO) and nitric acid (HNO$_3$), because they both play crucial roles in the NO$_x$ budget and the oxidative capacity of the atmosphere [Atkinson, 2000; Finlayson-Pitts and Pitts, 1997]. Chapter 2 of this thesis will describe flow tube reactor experiments designed to characterize the newly proposed gas-phase reduction reaction of HNO$_3$ to HONO in the presence of proxies for vehicular VOCs.

1.1.2 PM

Particulate matter is divided broadly into fine and coarse modes based on their size. Current regulations under the NAAQS place bounds on the allowable mass concentrations of two classes of PM based on size (aerodynamic diameter, D$_p$), namely PM$_{2.5}$ and PM$_{10}$ [EPA, 2012; Lippmann, 1998]. In short, PM$_{2.5}$ refers to the total mass of
particles that have \( D_p \) smaller than 2.5 \( \mu \text{m} \), whereas \( \text{PM}_{10} \) refers to particles that have \( D_p \) smaller than 10 \( \mu \text{m} \) in diameter. This size classification of PM mass is slightly different from the definitions of fine particles (\( D_p < 2.5 \mu \text{m} \)) and coarse particles (\( 2.5 \mu \text{m} < D_p < 10 \mu \text{m} \)). The coarse mode largely consists of dust, crustal material, ash, and salts that are formed from physical processes [Seinfeld and Pandis, 2006].

Fine PM originates from secondary processes that convert gaseous species into particulate form and from primary combustion emissions [Lippmann, 1998]. Research has indicated the strong link between exposure to high levels of \( \text{PM}_{2.5} \) and increased risk of mortality, particularly due to cardiac and respiratory diseases [Laden et al., 2000; Pope et al., 2002]. Both \( \text{PM}_{10} \) and ultrafine particles (\( D_p < 0.15 \mu \text{m} \), or \( \text{PM}_{0.15} \)) have been associated with lung irritation and inflammation [EPA, 2004]. There is evidence that mortality due to PM can be exacerbated by elevated \( \text{O}_3 \) levels [Samet et al., 2000]. The NAAQS have used mass concentration (\( \mu \text{g/m}^3 \)) of PM as a metric for control, but studies have shown that the total number concentration (particles/cm\(^3\), or \#/cc) that is dominated by ultrafine particles also can be an indicator of adverse health impacts [Chen et al., 1995; Peters et al., 1997]. The control of \( \text{PM}_{2.5} \) and \( \text{PM}_{10} \) under current regulatory standards leaves submicron (\( D_p < 1 \mu \text{m} \), or \( \text{PM}_{1.0} \)) particles and ultrafine particles largely unregulated, as they represent only a small fraction of total \( \text{PM}_{2.5} \) mass due to their small size. These finer particles have been shown to be more toxic to human health [Nel, 2005] and are largely influenced by anthropogenic emissions such as from combustion and industry and by secondary aerosol formation processes. Chapters 3 and 4 of this thesis will focus on novel work characterizing submicron particles in the urban atmosphere of Houston, TX.
Atmospheric aerosol is made out of sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), organic matter (OM), black carbon (BC), metals, marine salts, marine or continental chloride (Chl), crustal material, and water [Seinfeld and Pandis, 2006]. Of primary focus in this thesis are the SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Chl, and organic portions of PM, due to their relative abundance in fine urban aerosol. Approximately 20-90 % of submicron particle mass is comprised of organic matter [Kanakidou et al., 2005].

Inorganic salts comprise a significant portion of aerosol mass in some regions [Jimenez et al., 2009] and are usually formed due to secondary reactions between acids (H$_2$SO$_4$ and HNO$_3$) and bases (primarily ammonia (NH$_3$)) either in the gas or aqueous phase [Seinfeld and Pandis, 2006; Sutton et al., 2008]. The gaseous precursors for SO$_4$, NO$_3$, and NH$_4$ salts in aerosol are SO$_2$ (oxidized to H$_2$SO$_4$), NO$_x$ (oxidized to HNO$_3$), and NH$_3$, respectively. While SO$_2$ is emitted predominantly from industrial and volcanic sources, NO$_x$ can have anthropogenic and biogenic sources. Agriculture remains the largest source of NH$_3$ globally [Clarisse et al., 2009]. The importance of the atmospheric nitrogen cycle will be stressed multiple times in this document, as species like NO$_x$, HONO, HNO$_3$, and NH$_3$ play important roles in both O$_3$ and PM chemistry.

Compared to other chemical components of PM, the sources, evolution, and removal of organic aerosols (OA) in the atmosphere are still poorly understood. OA that is directly emitted into the atmosphere are referred to as primary organic aerosol (POA), while secondary organic aerosol (SOA) is defined as organic PM formed from biogenic or anthropogenic semi-volatile or low-volatility organic gas-phase precursors. Generally, POA primarily originates from combustion processes or marine sources, while SOA is formed by the oxidation of VOCs into low-volatility compounds that partition into the
condensed phase [Jimenez et al., 2009; Kanakidou et al., 2005]. Formation of SOA can occur from photooxidation during the day [Jimenez et al., 2009] or from nocturnal oxidants [Rollins et al., 2012]. Secondary OA can either form from the partitioning of gaseous precursors into the aerosol phase (under favorable conditions) [Jimenez et al., 2009] or from the dissolution of organic vapors in liquid aerosol or cloud droplets that could be processed (through aqueous chemistry) and retained upon evaporation of the liquid water [Lim et al., 2010].

In addition to size and chemical composition, the optical properties of aerosols can have significant environmental impacts. Depending on its composition, size, and structure, a particle can both scatter and absorb light. Scattering and reflection occur more strongly in materials such as ammonium sulfate ((NH$_4$)$_2$SO$_4$) and organics, while BC and soot absorb light more efficiently [Seinfeld and Pandis, 2006]. Atmospheric aerosols impact global climate in a process referred to as radiative forcing (RF, in units of W/m$^2$), depending on their optical properties. RF is broadly defined as the change in the radiative energy budget of the Earth caused by the addition of certain materials into the atmosphere. Particulate matter is the primary contributor of uncertainties to climate models that are used to predict the RF of both natural and anthropogenic processes [IPCC, 2007]. These uncertainties are largely due to the lack of understanding of the physicochemical properties and processes involving aerosols, as well as to limited observational PM data.

There are multiple ways in which PM impacts climate [Kanakidou et al., 2005]. The direct effect involves the scattering of incoming sunlight back into space by reflective aerosol (cooling effect) or the absorption of radiation by absorbing aerosols (warming effect). Indirect climate effects of aerosols refer to the processes through which particles
interact with clouds, thereby affecting the albedo (reflectiveness) of the Earth and the cloud lifetime and hence the radiative budget. In other words, fine particles can act as cloud condensation nuclei (CCN) or ice nuclei (IN) to more efficiently form clouds or increase cloud albedo (cooling). Finally, the semi-direct effect involves cloud burn-off due to radiative heating from light-absorbing soot or BC aerosol (warming). In addition to climate effects, elevated levels of PM that scatters and absorbs light effectively reduce visibility, depending on its composition and optical properties.

Large uncertainties still exist in the source apportionment, chemical modeling, and environmental impacts of atmospheric aerosols. A combination of chamber experimentation, modeling, and field observation efforts over the past two decades has improved our understanding of the formation, evolution and removal of aerosols, with particular focus on the organic submicron fraction [Holmes, 2007; Jimenez et al., 2009; Kanakidou et al., 2005]. Chapters 3 and 4 of this thesis focus on novel data-collection using a mobile platform and results from an extensive analysis of the resulting spatially diverse dataset obtained during September 2013 in Houston, TX. This mobile PM$_1$ dataset was coupled with a large suite of concurrent/co-located measurements to further our knowledge of the major constituents and sources of urban/sub-urban aerosols.

1.2 Air Quality in Houston, TX

Since the NAAQS were established in 1971, numerous cities in the U.S. have been in non-compliance with the O$_3$ and PM standards. Much effort has been devoted to the development and revision of State Implementation Plans (SIPs) to improve air quality in these cities and achieve compliance. The Houston-Galveston-Brazoria (HGB) area, which includes eight counties in the vicinity of the city of Houston, has made significant
effort to reduce PM and O₃ pollution. However, due to complex meteorological conditions and large amounts of industrial and vehicular emissions, the area has faced significant challenges to achieve compliance with these standards [Banta et al., 2005; Lefer et al., 2010].

The HGB area has long faced non-attainment challenges with the EPA O₃ standards [Lefer et al., 2010]. The highest number of 8-hr O₃ exceedance days in the HGB area from 1990 to 2005 occurred during summer, particularly from late-July to late-September [Estes, 2006; Fast et al., 2006]. As a result, most modeling efforts and field studies have focused on oxidant photochemistry during summer months (e.g., the Texas Air Quality Studies TexAQS-2000 and TexAQS-II in 2006). In the TexAQS-2000 study, O₃ was formed at unusually rapid rates in industrial plumes in Houston due to large petrochemical point sources of highly reactive VOCs (HRVOCs) [Jiang and Fast, 2004; Ryerson et al., 2003]. It was found in TexAQS-II that despite localized control strategies, the achievable background O₃ levels could still exceed the new 8-hr O₃ standard of 75 ppbv established in 2008 [Parrish et al., 2009]. In the month-long intensive TexAQS-II Radical and Aerosol Measurement Project (TRAMP), Ziemba et al. [2010] observed HONO production that was hypothesized to result from heterogeneous reactions on POA. This raises the question of whether PM could potentially impact O₃ formation through important intermediates like HONO; this topic will be discussed in detail in Chapter 2.

The four-year annual average for PM₂.₅ in the period 2012 – 2014 was 11.3 µg/m³ at the Clinton Drive EPA monitoring site near East Houston (calculated from hourly air pollution data from the Texas Commission on Environmental Quality (TCEQ) website, www.tceq.texas.gov), which barely complies with the newly tightened annual primary
NAAQS of 12.0 µg/m³. This shows that although Houston has been in compliance with PM standards, there is still a need for better controls to reduce the mass loadings for PM\textsubscript{2.5} as well as for finer, unregulated particulates like PM\textsubscript{1.0}. In order to achieve this, both primary and secondary aerosol in the HGB area must be characterized both near and far away from sources.

The contribution of the HGB petrochemical industry to HRVOC loadings not only exacerbates O\textsubscript{3} pollution, it can have profound impacts on primary and secondary PM. Additionally, the Houston metropolitan area has an extensive network of local and interstate freeways that contributes to primary and secondary aerosol pollution. To study the impact of local traffic and industrial activity on PM pollution in HGB, numerous ground-based, airborne, and mobile datasets of PM also were collected in both TexAQS studies in 2000 and 2006.

For example, in TexAQS-2000 Brock et al. [2003] showed that a large portion of PM mass downwind of the urban area was linked to industrial and power plant emissions. Another study during the same period attempted to model aerosol RF in the region but was complicated by the lack of understanding of SOA chemistry, complex meteorology, and uncertainties in primary aerosol emission in Houston [Fast et al., 2006].

During the TRAMP 2006 intensive, PM\textsubscript{1} was found to consist mostly of SO\textsubscript{4} and OM (in this context equivalent to OA), while proton nuclear magnetic resonance (NMR) spectroscopy data showed that aerosols in the HGB area have a unique fingerprint that was likely distinguished by its urban and industrial sources [Cleveland et al., 2012]. During the same intensive period, primary traffic emissions were shown to contribute to
total aerosol mass (dominated by organic matter), especially during the morning rush hour (MRH) [Ziemba et al., 2010]. During TexAQS-II, Bahreini et al. [2009] found that industrial plumes generated higher PM mass than urban plumes and that anthropogenic VOCs (not biogenic VOCs) contributed significantly to SOA formation and enhancement in OA mass. In 2006, the urban and industrial sources in HGB also were shown to impact CCN activity in aerosols, especially as aging occurs downwind and the content of water-soluble organic carbon (WSOC) increases [Asa-Awuku et al., 2011]. The CCN activity could affect cloud radiative properties and regional hydrological cycles.

In addition to findings from TexAQS 2000 and 2006, several other studies in Houston provided relevant air quality data and are summarized here. Tunnel measurements near Houston apportioned PM$_{2.5}$ emissions to diesel, gasoline and road-dust sources, with diesel vehicles being heavy PM$_{2.5}$ emitters [Fraser et al., 2003a]. Additionally, Fraser et al. [2003b] identified diesel, gasoline, road-dust, cooking, and biomass burning (wood) emissions as important sources of PM$_{2.5}$ at several sites in Houston. More recently (2009), submicron PM in Houston was found to be internal mixtures of mostly OA and SO$_4$, while particle physical properties and new particle formation were influenced by meteorology [Levy et al., 2013]. Gong et al. [2013a] showed that local ammonia emissions (from power plants) contribute to formation of particles and PM$_{1}$ mass concentrations.

In general, modeled SOA yields based on laboratory data and using measured concentrations of precursor VOCs could underestimate SOA formation by several orders of magnitude [de Gouw et al., 2008; de Gouw et al., 2005; Heald et al., 2005; Kleinman et al., 2008; Volkamer et al., 2006]. Volkamer et al. [2006] also showed that
anthropogenic HRVOCs produced higher quantities of SOA than predicted by these models, which may be the case for the highly industrialized atmosphere in Houston. A modeling study in TexAQS-2000 using the then-updated Community Multi-scale Air Quality (CMAQ) model by EPA still under-predicted SOA when compared with observations [Zhang and Ying, 2011]. The National Emissions Inventory (NEI) by EPA, which estimates the emission of air pollutants, does not have speciated primary PM data [EPA, 2014]. In addition to an incomplete representation of SOA formation pathways in these models, the lack of speciated emissions inventories of primary PM and the complex meteorology in Houston could exacerbate the errors when predicting PM levels. The uncertainties in current PM models limit the effectiveness of state control policies in reducing current PM levels, which may hinder the ability of the city of Houston to improve its air quality and to maintain compliance with potentially tighter PM standards.

1.3 NASA DISCOVER-AQ

To address the knowledge and data gaps in O$_3$ and PM pollution, the National Aeronautics and Space Administration (NASA) seeks to continually improve methods to measure these pollutants and their respective precursors through satellite remote sensing. It also is important to determine accurately the vertical distribution of these pollutants in the troposphere. To support these efforts, the four-year program Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ; www.nasa.gov/mission_pages/discover-aq/), which consists mostly of simultaneous satellite, airborne, and ground-based/mobile sampling of atmospheric data, was established. Previous DISCOVER-AQ projects were held in the mid-Atlantic Coast region (2011) and the Central Valley of California (2013). A
subsequent project was held in the Denver area (2014). Chapters 3 and 4 of this thesis focus on a one-month project held in Houston during September 2013. A variety of atmospheric data was collected (with a focus on chemical composition of PM) during DISCOVER-AQ Houston, using a ground-based mobile platform henceforth referred to as the University of Houston/Rice University Mobile Air Quality Laboratory (MAQL, Figure 2). Details on the instrumentation and techniques used for the trace gas and PM measurements will be discussed in detail in section 3.2. In short, the MAQL provided ground-based measurement to answer scientific questions pertaining to air quality at the surface, while also providing data for comparison with satellite and aircraft measurements.

Figure 2. The MAQL with the sampling mast in the upright/stationary position (left) and in the forward/mobile position (right)

1.4 Research questions

Several scientific questions pertaining to urban air quality (particularly that of Houston, TX) that will be addressed in each chapter of this thesis are listed here:
Chapter 2. Impact of environmental variables on the reduction of HNO$_3$ by proxies for VOCs emitted by motor vehicles

Recent work in our laboratory has indicated that the reduction of HNO$_3$ to HONO can occur homogeneously in the presence of VOCs that are surrogates for those emitted by motor vehicles. The primary scientific question is: How do environmental variables impact the rate of formation of HONO in this process? It was hypothesized that the following environmental variables impact the HONO formation reaction rate (positively or negatively): temperature (positive), HNO$_3$ concentration (neutral), gas-phase ammonia levels (negative), UV irradiation (positive), and the presence of reactive aerosol (positive).

Chapter 3. Overview of Surface Measurements and Spatial Characterization of Submicron Particulate Matter during the DISCOVER-AQ 2013 Campaign

The purpose of this study was to improve the understanding of the sources and transformation processes of particulate pollutants in the urban and suburban regions of the HGB area. This study was based on the data collected using a mobile platform that housed aerosol instrumentation as part of the NASA DISCOVER-AQ field campaign in Houston, TX. The main research questions addressed by this study were: 1) Does PM pollution in Houston have specific patterns spatially, temporally, and in relation to meteorological conditions? 2) Can principal component analysis (PCA) identify factors that describe meteorological, emissions, and chemical processes governing PM pollution in Houston? It was hypothesized that PM chemical composition in Houston was highly variable temporally and spatially depending on meteorology and as a result of the multitude of primary/secondary sources throughout the expansive area. Primary PM
sources were expected to dominate in the populated city, particularly in the urban core. The various sources of PM were hypothesized to manifest as interpretable factors from PCA of combined PM, trace gas, and meteorology data.

Chapter 4. Source Apportionment of Organic and Nitrate Aerosols using Factor Analysis of High Resolution Mass Spectrometry Data during DISCOVER-AQ 2013 Texas

The goals in this chapter are similar to the ones above: to characterize sources and transformation of PM in Houston. However, this chapter describes a statistical factor analysis method to analyze the spatial PM data generated during DISCOVER-AQ. The key scientific questions were: 1) What are the major sources of OA in Houston and how do they compare with previous findings in Houston or in other similar urban environments? 2) Can factor analysis be used to reliably apportion NO$_3$ aerosol in Houston? 3) Can mass spectral analysis of individual emission plumes help characterize major primary sources of PM$_1$ in Houston? It was hypothesized that an established factor analysis model could apportion major primary/secondary sources of OA and NO$_3$ in Houston, and that a mobile plume sampling approach would allow characterization of anthropogenic, primary PM$_1$ sources throughout the region. Additionally, it was expected that SOA formation processes were highest in the forested area north of Houston and the resulting oxidation state of OA would be higher in that region.
Chapter 2. Impact of environmental variables on the reduction of HNO$_3$ by proxies for VOCs emitted by motor vehicles

2.1 Literature review

HONO is an important trace gas in the regional and global troposphere. It can have significant air quality implications due to its photolysis, yielding NO and the OH· radical [Atkinson, 2000]:

$$\text{HONO} + hv \rightarrow \text{OH} + \text{NO} \quad \text{(R1)}$$

The OH· radical serves as a strong oxidant in the atmosphere and is partly responsible for the chemical processes that lead to the formation O$_3$ [Finlayson-Pitts and Pitts, 1997] and secondary PM [Kanakidou et al., 2005]. The potential of a regional air mass to produce O$_3$ depends strongly on the relative abundance of volatile organic compounds (VOCs) and NO$_x$. Because HONO influences NO$_x$ levels and the oxidative capacity of the atmosphere, O$_3$ levels are highly sensitive to HONO levels under particular conditions [Carter and Seinfeld, 2012; Harris et al., 1982; Lei et al., 2004]. Harris et al. [1982] observed increases in O$_3$ dosages (i.e. O$_3$ exposure received by a population; units of ppm min) up to a factor of 3 when 10 ppb of HONO is included in model simulations. Using a three-dimensional chemical transport model, Lei et al. [2004] estimated up to 12 ppb enhancements in O$_3$ levels in Houston, TX, due to a proposed heterogeneous source of HONO. Zero-dimensional model simulations of O$_3$ formation episodes in the Upper Green River Basin in Wyoming during winter predicted strong O$_3$ sensitivity to HONO levels [Carter and Seinfeld, 2012].
Nitrous acid mixing ratios observed at various urban sites range from 0.4 to 8.0 ppb at night and approximately 100 to 300 ppt during the day [Harris et al., 1982; Harrison et al., 1996; Indarto, 2012; Kleffmann, 2007; Wong et al., 2011], while concentrations at rural sites were consistently lower, at 10-200 ppt [Cape et al., 1992; Zhou et al., 2002; Zhou et al., 2011]. A known source of HONO during daytime in polluted environments is the reaction between OH and NO [Atkinson, 2000]:

$$\text{OH} + \text{NO} \rightarrow \text{HONO} \quad (R2)$$

Nitrous acid builds up overnight from (R2) (if OH persists without sunlight) and other sources and photolyzes in the morning, causing a spike in OH and NO$_x$, resulting in accelerated O$_3$ production [Harris et al., 1982]. Nitrous acid sources other than (R2) are thus highly important due to their potential to contribute to both daytime and nighttime HONO levels. Modeling studies have concluded that HONO sources are still missing from current HO$_x$ and NO$_x$ chemistry models, resulting in the underprediction of HONO or O$_3$ levels [Carter and Seinfeld, 2012; Grannas et al., 2007; Wong et al., 2011].

A number of recent studies have documented possible sources of HONO from HNO$_3$ or NO$_2$. Kleffmann [2007] proposed several HONO formation mechanisms: heterogeneously on surfaces treated with HNO$_3$, from the reduction of NO$_2$ on photosensititized organic surfaces, and via homogeneous photolysis of ortho-substituted nitroaromatics. Similarly, photolytic conversion of NO$_2$ to HONO on polycyclic aromatic hydrocarbon films was observed by Cazoir et al. [2014]. Grannas et al. [2007] summarized several HONO formation mechanisms in a snowpack. Based on urban field measurements in New Zealand, Reisinger [2000] observed a good correlation between
HONO/NO\textsubscript{2} (a metric for the relative abundance of HONO) and aerosol surface density, which indicated a heterogeneous HONO formation reaction. HONO forms on the surface of soot particles from NO\textsubscript{2}, but the reaction rapidly terminates under typical ambient conditions and is not considered a major contributor to HONO [Ammann et al., 1998; Kalberer et al., 1999]. Kirchstetter et al. [1996] measured vehicular emissions of HONO in the Caldecott Tunnel, but the observed HONO/NO\textsubscript{2} ratios were much lower than the nighttime values measured under ambient conditions. In addition, recent airborne measurements coupled with zero-dimensional model simulations inferred a strong gas-phase source within the residual layer with formation rates that scaled with HONO photolysis rates [Li et al., 2014]. The authors argued that this unknown source could dominate overall HONO production in the planetary boundary layer, exceeding surface HONO sources. The proposed ultraviolet (UV)-dependent HONO source was likely internal (from the reaction of NO\textsubscript{x} and/or HO\textsubscript{x}). Liu et al. [2014] proposed a substantial heterogeneous HONO source from the hydrolytic disproportionation of NO\textsubscript{2} on aerosol to help explain missing daytime HONO sources in China. Flow tube studies by VandenBoer et al. [2015] suggested a nighttime soil sink of HONO, leading to daytime acid displacement and release of HONO. A review of the current state of the science for HONO can be found in Spataro and Ianniello [2014].

During field measurements in September 2006 in Houston, TX, Ziemba et al. [2010] observed HNO\textsubscript{3} depletion that was concurrent with increases in both HONO concentrations and aerosol surface area dominated by a proxy for POA. The authors hypothesized a heterogeneous reaction between HNO\textsubscript{3} and POA to form HONO, which supports the findings from several other studies that document the reduction of HNO\textsubscript{3}
through heterogeneous reactions [Rivera-Figueroa et al., 2003; Zhou et al., 2003; Zhou et al., 2002; Zhou et al., 2011]

In an effort to better understand the phenomenon observed by Ziemba et al. [2010], Rutter et al. [2014] performed a series of flow tube experiments in which gaseous HNO$_3$ was observed to be reduced homogeneously to HONO by VOCs representative of those emitted from motor vehicles. The proposed reaction mechanism was:

$$\text{HNO}_3 + \text{VOC} \rightarrow \text{HONO} + \text{VOC}_{\text{ox}} \quad \text{(R3)}$$

The reported formation rate of HONO in the reactor was $0.3 \pm 0.1$ ppb hr$^{-1}$ under a defined base case of 25.0 °C and relative humidity (RH) of ~20 %. The HONO formation rates decreased with increasing RH. Increased surface area in the flow-tube (Teflon© Raschig rings and/or a surrogate for vehicular POA) had no impact on HONO formation. The experiments described here used a slightly modified and improved version of the flow-tube system described in Rutter et al. [2014] to further characterize this HONO formation reaction by varying temperatures and HNO$_3$ concentrations, irradiating, or adding ammonia (NH$_3$) or mineral dust surrogates. These experiments are designed to improve our understanding of the importance of the proposed HONO formation reaction under varying ambient conditions and to assess its potential to enhance HONO levels in the atmosphere.
2.2 Methodology for this study

2.2.1 General Information

The flow-tube system used in this study is described by Rutter et al. [2014], with improvements and additional instrumentation described below. Briefly, HNO$_3$ gas and VOCs from a specific blend of vehicle engine oil (Table 1) were introduced into a quartz flow reactor, which is located in a temperature-controlled chamber. Nitric acid was generated from a permeation device (Dynacal, VICI Metronics, Poulsbo, WA), and engine oil particles along with VOCs were introduced using a TSI 3076 atomizer (Shoreview, MN) with a Teflon® filter in-line when the particles were not desired. A combustion VOC surrogate was not used for this study as the original intent was to use reduced organics from motor oil [Rutter et al., 2014]; this avoids possible HONO artifacts from combustion exhaust [Kirchstetter et al., 1996]. A recent tunnel study showed that a large portion of vehicular POA is similar in composition to unburned motor oil [Worton et al., 2014]. The VOCs used in this study were intended to serve as surrogates for VOCs produced from the volatilization of vehicular POA under ambient conditions. The outflow from the flow-tube was sampled by a refurbished on-line mist chamber-ion chromatograph (MC/IC) system [Rutter et al., 2014] to obtain 10-minute HONO and HNO$_3$ concentrations. This measurement technique has been tested and characterized extensively [Dibb et al., 2002; Dibb et al., 1994; Dibb et al., 1998; Talbot et al., 1990] and showed good comparison with Differential Optical Absorption Spectroscopy [Stutz et al., 2010]. A new quartz flow-tube with dimensions identical to those of the reactor in Rutter et al. [2014] was used and was passivated by a non-reactive halocarbon wax coating to minimize wall reactions. Instrumentation used to measure
temperature, RH, and particle number concentration were outlined in Rutter et al. [2014].

The instrumentation for measuring NH$_3$ is described below.

Table 1. The blend of engine oils used to generate the VOCs in this study (adapted from Rutter et al. [2014])

<table>
<thead>
<tr>
<th>Name</th>
<th>Grade</th>
<th>Intended Engine Type</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castrol GTX</td>
<td>5W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Castrol GTX</td>
<td>10W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Mobil 1 High Mileage</td>
<td>5W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Mobil 1 High Mileage</td>
<td>10W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Mobil 1 Extended Performance</td>
<td>5W-20</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Valvoline Premium Conventional</td>
<td>5W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Valvoline Premium Conventional</td>
<td>10W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Quaker State Advanced Durability</td>
<td>5W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Quaker State Advanced Durability</td>
<td>10W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Pennzoil Active</td>
<td>5W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Pennzoil Active</td>
<td>10W-30</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Pennzoil Active</td>
<td>5W-20</td>
<td>Gasoline</td>
<td>25</td>
</tr>
<tr>
<td>Castrol GTX Diesel</td>
<td>15W-40</td>
<td>Diesel</td>
<td>115</td>
</tr>
</tbody>
</table>

In this study, the base case experiments were conducted at a temperature of 25°C and a RH of ~20% while maintaining a mean HNO$_3$ concentration of 2.4 ppb and a constant level of VOCs in the flow-tube reactor. For each experiment, the flow-tube reactor was allowed to equilibrate at the desired conditions (concentrations of HNO$_3$ and VOCs, temperature, RH, and other variables). The formation rates of HONO ($f_{HONO}$, ppb hr$^{-1}$) were calculated using the step change in HONO concentrations when VOCs were removed:

$$f_{HONO} = ([HONO]_t - [HONO]_0) / t_{res}$$

Equation 1
where \([HONO]_t\) (in ppb) was the average steady-state HONO concentration measured when VOCs were present to react with HNO₃, \([HONO]_0\) was measured after VOCs were removed and only HNO₃ was present, and \(t_{res}\) is the average residence time of all gases in the flow-tube (150 s). Detailed descriptions of a typical experiment can be found in Rutter et al. [2014], and all experiments described in this study follow the same procedures except the modifications mentioned below. Additional experimental information is provided in section 2.3.6 and details on individual experiments and error propagation in Table 2.
Table 2. Detailed measurement uncertainties and propagated errors in experiments. ‘Unc’ values for individual experiments represent errors propagated from measurement uncertainties. Rows denoted with ‘Stdev.’ refer to standard deviations of the calculated average values; rows denoted with ‘Prop.’ refer to the propagated errors of the average.

<table>
<thead>
<tr>
<th>Expt No.</th>
<th>Category</th>
<th>Initial [HNO₃] (ppt)</th>
<th>Unc type</th>
<th>Unc (ppt)</th>
<th>Initial [HONO] (ppt)</th>
<th>Unc (ppt)</th>
<th>f[HONO] (ppb hr⁻¹)</th>
<th>Unc (ppb hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Base case, High HNO₃</td>
<td>4608</td>
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<td>77</td>
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<td>0.55</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>Base case, High HNO₃</td>
<td>4428</td>
<td></td>
<td>30</td>
<td>67.4</td>
<td>0.8</td>
<td>0.65</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>Base case, High HNO₃</td>
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<td></td>
<td>29</td>
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<td>1.9</td>
<td>0.59</td>
<td>0.24</td>
</tr>
<tr>
<td>Avg</td>
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<td>Stdev.</td>
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<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Prop.</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Base case, Med HNO₃</td>
<td>1471</td>
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</tr>
<tr>
<td>5</td>
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<td></td>
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<td>1.1</td>
<td>0.54</td>
<td>0.12</td>
</tr>
<tr>
<td>6</td>
<td>Base case, Med HNO₃</td>
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<td></td>
<td>8</td>
<td>43.9</td>
<td>1.0</td>
<td>0.42</td>
<td>0.18</td>
</tr>
<tr>
<td>Avg</td>
<td>Base case, Med HNO₃</td>
<td>1522</td>
<td>Stdev.</td>
<td>159</td>
<td>41.4</td>
<td>2.2</td>
<td>0.51</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Prop.</td>
<td>10</td>
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<td>0.5</td>
<td></td>
<td></td>
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<tr>
<td>7</td>
<td>Base case, Low HNO₃</td>
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<td>1.9</td>
<td>0.43</td>
<td>0.25</td>
</tr>
<tr>
<td>Avg</td>
<td>Base case, all HNO₃</td>
<td>2415</td>
<td>Stdev.</td>
<td>1613</td>
<td>53.3</td>
<td>13.4</td>
<td>0.54</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Prop.</td>
<td>15</td>
<td></td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>T = 20.0 °C</td>
<td>2704</td>
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<td>35</td>
<td>45.2</td>
<td>0.9</td>
<td>1.14</td>
<td>0.20</td>
</tr>
<tr>
<td>9</td>
<td>T = 20.0 °C</td>
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<td>27</td>
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<td>1.7</td>
<td>0.93</td>
<td>0.23</td>
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<tr>
<td>10</td>
<td>T = 20.0 °C</td>
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<td>79</td>
<td>51.1</td>
<td>1.1</td>
<td>0.93</td>
<td>0.22</td>
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<tr>
<td>11</td>
<td>T = 20.0 °C</td>
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<td>55</td>
<td>58.5</td>
<td>2.1</td>
<td>0.91</td>
<td>0.30</td>
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<tr>
<td>Avg</td>
<td>T = 20.0 °C</td>
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<td>6.1</td>
<td>0.98</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Prop.</td>
<td>35</td>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
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<tr>
<td>12</td>
<td>T = 30.0 °C</td>
<td>4741</td>
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<td>22</td>
<td>75.4</td>
<td>4.2</td>
<td>0.78</td>
<td>0.41</td>
</tr>
<tr>
<td>13</td>
<td>T = 30.0 °C</td>
<td>4505</td>
<td></td>
<td>24</td>
<td>95.2</td>
<td>3.5</td>
<td>0.36</td>
<td>0.35</td>
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<tr>
<td>14</td>
<td>T = 30.0 °C</td>
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<td>27</td>
<td>75.5</td>
<td>1.9</td>
<td>0.78</td>
<td>0.30</td>
</tr>
<tr>
<td>15</td>
<td>T = 30.0 °C</td>
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<td>76.8</td>
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<tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Prop.</td>
<td>16</td>
<td></td>
<td>2.1</td>
<td></td>
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<tr>
<td>16</td>
<td>T = 35.0 °C</td>
<td>4389</td>
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<td>21</td>
<td>104.3</td>
<td>3.0</td>
<td>0.59</td>
<td>0.27</td>
</tr>
<tr>
<td>17</td>
<td>T = 35.0 °C</td>
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<td>0.37</td>
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<td>69.1</td>
<td>1.5</td>
<td>0.77</td>
<td>0.17</td>
</tr>
<tr>
<td>19</td>
<td>T = 35.0 °C</td>
<td>3343</td>
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<td>42</td>
<td>76.2</td>
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<td>0.47</td>
<td>0.13</td>
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<tr>
<td>Avg</td>
<td>T = 35.0 °C</td>
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<td>Stdev.</td>
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<td>80.2</td>
<td>16.4</td>
<td>0.59</td>
<td>0.13</td>
</tr>
<tr>
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<td></td>
<td></td>
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<td></td>
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<tr>
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<td>UV Irradiation</td>
<td>2886</td>
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<td>71</td>
<td>315.1</td>
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<td>UV Irradiation</td>
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<td>263.4</td>
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<td>0.33</td>
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<tr>
<td>Avg</td>
<td>UV Irradiation (uncorrected)</td>
<td>3405</td>
<td>Stdev.</td>
<td>451</td>
<td>276.5</td>
<td>34.0</td>
<td>0.29</td>
<td>0.04</td>
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<tr>
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<td>UV Irradiation (corrected, Eq. (2))</td>
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<td>Prop.</td>
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<td></td>
<td></td>
<td>0.37</td>
<td>0.17</td>
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</table>
Table 2. (continued)

<table>
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<tr>
<th>Expt No.</th>
<th>Category</th>
<th>Initial [HNO₃] (ppt)</th>
<th>Unc type</th>
<th>Unc (ppt)</th>
<th>Initial [HONO] (ppt)</th>
<th>Unc (ppt)</th>
<th>( \text{f}_{\text{HONO}} ) (ppb hr⁻¹)</th>
<th>Unc (ppb hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>Ammonia</td>
<td>3370</td>
<td>53</td>
<td>95.4</td>
<td>1.6</td>
<td>0.58</td>
<td>0.17</td>
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<tr>
<td>24</td>
<td>Ammonia</td>
<td>3717</td>
<td>71</td>
<td>96.1</td>
<td>1.4</td>
<td>0.61</td>
<td>0.20</td>
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</tr>
<tr>
<td>25</td>
<td>Ammonia</td>
<td>3909</td>
<td>66</td>
<td>97.9</td>
<td>1.1</td>
<td>0.60</td>
<td>0.20</td>
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</tr>
<tr>
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<td>3666</td>
<td>Stdev.</td>
<td>273</td>
<td>96.5</td>
<td>1.3</td>
<td>0.60</td>
<td>0.01</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>Prop.</td>
<td>37</td>
<td>8</td>
<td>0.8</td>
<td>0.11</td>
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</tr>
<tr>
<td>26</td>
<td>Alumina aerosol</td>
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<td>29</td>
<td>88.5</td>
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<td>0.40</td>
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<td>Alumina aerosol</td>
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<td>Alumina aerosol</td>
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<td>Stdev.</td>
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<tr>
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<td>Prop.</td>
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<tr>
<td>29</td>
<td>Silica aerosol</td>
<td>3541</td>
<td>24</td>
<td>90.0</td>
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<td>0.36</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Silica aerosol</td>
<td>3393</td>
<td>15</td>
<td>91.3</td>
<td>1.2</td>
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<tr>
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<td>Silica aerosol</td>
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<td>18</td>
<td>89.6</td>
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<tr>
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<td>Silica aerosol</td>
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<td>Stdev.</td>
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<td>0.43</td>
<td>0.11</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>Prop.</td>
<td>11</td>
<td>0.5</td>
<td></td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>

Engine oil particles (100 nm, < 150 #/cm³) were shown in Rutter et al. [2014] to have no effect on the reaction. During several tests, larger concentrations of motor oil particles were injected (up to 1400 #/cm³) into the mixture of VOCs and HNO₃, and the particles had no observable impact on HONO levels. Therefore, for all experiments presented here motor oil particles were not considered relevant and were excluded by filtering the output from the atomizer upstream of the flow tube reactor. Figure 3 depicts the experimental setup used in this study. A detailed diagram for the delivery of HNO₃ and VOCs can be found in Rutter et al. [2014].
Variations to the base case experiments were achieved by independently varying chamber temperature or HNO₃ concentration or by introducing UV irradiation, NH₃, or mineral dust aerosol to the system. When a parameter was altered or a new constituent was added, all other base case variables remained unchanged. Apart from HNO₃ and NH₃ experiments discussed in sections 2.3 and 2.4, all experiments in this study were conducted at initial HNO₃ concentrations of ~2-4 ppb for consistency with the experiments of Rutter et al. [2014] and the field measurements of Ziemba et al. [2010].
2.2.2 Temperature

This study aims to investigate the sensitivity of $f_{HONO}$ to reaction temperature. Because the proposed reduction reaction of HNO$_3$ by VOCs may involve simultaneous reactions of different reactive VOCs of the engine oil blend, the temperature dependence of the overall formation rate is not expected to follow Arrhenius behavior. Investigation of temperature dependence is achieved by a temperature-controlled environmental test chamber (Espec North America Inc., Hudsonville, MI). The flow-tube and other components were allowed to equilibrate at the desired set-point temperature before an experiment. The measured reactor outflow temperatures were within ~1°C of the set-point chamber temperatures. The temperature range tested here (20.0 to 35.0°C) is relevant for the conditions observed in the 2006 Houston field study. Temperatures outside of this range also resulted in compromised seals in the reactor setup.

2.2.3 HNO$_3$ concentration

Initial HNO$_3$ mixing ratios were kept relatively constant in the experiments by Rutter et al. [2014], but minor fluctuations in HNO$_3$ between experiments were impossible to avoid. Nitric acid concentration was not considered important by Rutter et al. [2014] because the HNO$_3$ levels were in excess of the estimated 200 - 300 ppt reactive VOCs in the reactor. Here, experiments conducted at different initial concentrations of HNO$_3$ were used to probe this hypothesis and to investigate potential impacts of HNO$_3$ levels on the proposed reaction.
The steady-state HNO$_3$ concentrations in the flow-tube were varied in these experiments by operating the permeation device at different temperatures or by shutting off its supply entirely. Holding other parameters constant, HNO$_3$ mixing ratios of approximately 4.0 ppb, 1.5 ppb, and 0.4 ppb were achieved. The corresponding experiments are henceforth referred to as high HNO$_3$, medium HNO$_3$, and low HNO$_3$ experiments.

2.2.4 Ammonia

Ammonia reacts with HNO$_3$ to form ammonium nitrate (NH$_4$NO$_3$), which transitions to the particulate phase when specific thermodynamic criteria are met. This reaction is hypothesized as a potential competing reaction and was studied in the flow-tube reactor by the addition of NH$_3$. Experiments were performed by injecting 118.0 ± 2.0 ppb of gas-phase NH$_3$ to the flow-tube reactor. A 1-ppm NH$_3$ cylinder supplied the NH$_3$ gas stream, which was diluted upon entering the reactor. Ammonia concentrations were monitored using a 10.4-µm external cavity quantum cascade laser that has been well characterized and tested [Gong et al., 2011; Gong et al., 2013a]. The instrument has a detection limit of 0.7 ppb and an accuracy of 7%, with a maximum time-resolution of 1 s. Because the MC collection efficiencies for HNO$_3$ and HONO already exceed 95% [Dibb et al., 1994], NH$_3$ is not expected to cause interferences in HNO$_3$ and HONO measurements. There was no evidence of artifacts from particulate NH$_4$NO$_3$ because the MC/IC sample stream was filtered.
2.2.5 UV Irradiation

A HONO artifact at a forested field site correlated with UV intensity, possibly due to the photochemical conversion of HNO$_3$ to HONO on the wall of a glass sampling manifold [Zhou et al., 2002]. Laboratory experiments conducted by Zhou et al. [2003] found evidence that photolysis of adsorbed HNO$_3$ on Pyrex surfaces yields HONO, and Zhou et al. [2011] found a significant HONO daytime source from the photolysis of HNO$_3$ on forest canopies. These findings emphasize the potential role of UV irradiation in the conversion of HNO$_3$ to HONO. Despite the observations of Rutter et al. [2014] and Ziemba et al. [2010] that light is not required for the proposed (R3) to proceed, it is hypothesized that UV irradiation may either accelerate (R3) or dampen it by consuming the reactive VOCs involved. Thus, experiments were conducted to test the sensitivity of $f_{\text{HONO}}$ to UV irradiation.

Four 4-ft, 40W Sylvania 350BL lights (Osram Sylvania, Danvers, MA) irradiated the flow-tube reactor for one set of experiments. Totaling 160W of output, these tubes were mounted above the reactor and were distributed evenly along the length of the reactor. The reactor and lights were encased in Mylar reflective material to maximize light intensity and to ensure uniform distribution of the artificial light (peak $\lambda = 350$ nm). The same type of lights was used in the chamber experiments of Cocker et al. [2001]. This wavelength produces maximum NO$_2$ photolysis rates [Carter et al., 1995] and falls within the UV-A spectrum (320 to 400 nm), which has been reported to photolyze species such HONO [Alicke et al., 2002; Stutz et al., 2000]. Thus, the lamps were considered a viable
starting point to test for direct interferences on the hypothesized HONO formation reaction.

2.2.6 Mineral dust aerosol surfaces

Field data collected in Houston during 2006 showed the potential for heterogeneous reduction of HNO₃ into HONO on urban aerosol [Ziemba et al., 2010]. However, Rutter et al. [2014] showed that the HONO formation reaction does not occur heterogeneously on engine oil particles or on a large surface area of Teflon® material. Grassian [2002] observed HNO₃ heterogeneous uptake on mineral dust (alumina (Al₂O₃) and silica (SiO₂)) surfaces and heterogeneous HONO production reactions from NO₂ on soot or SiO₂ particles. Gustafsson et al. [2008] observed heterogeneous production of HONO on mineral dust (from the Gobi desert) from NO₂ and water. Because mineral dust aerosols have more polar surfaces when compared to the engine oil and Teflon® surfaces, they are hypothesized to be better candidates for heterogeneous conversion of HNO₃ to HONO.

Two types of atmospherically abundant mineral dust materials were chosen for these experiments: carboxylate-doped SiO₂ and Al₂O₃.

Aqueous dispersions of size-calibrated 100-nm monodisperse spherical particles composed of either carboxylated-SiO₂ or pure Al₂O₃ (Corpuscular Inc., Cold Spring, NY) were used to generate aerosols for these experiments. These solutions were nebulized using an atomizer and subsequently dried using a diffusion-dryer and a heater (87.5 ± 1.5°C).
2.3 Main findings

2.3.1 Base Case Results

Compared with the previous flow-tube study, the average base case $f_{\text{HONO}}$ of $0.54 \pm 0.09$ ppb hr$^{-1}$ (Table 3) agrees better with the observed 2006 Houston value of $0.6 \pm 0.3$ ppb hr$^{-1}$ [Rutter et al., 2014; Ziemba et al., 2010]. This could be attributed to improved measurement accuracy due to the refurbished MC/IC system. This observation also suggests that the reduction of HNO$_3$ to HONO by the reactive components of vehicular VOCs that were co-emitted with POA [Rutter et al., 2014] could be a dominant contributor to HONO formation events observed in Houston. The comparison here is qualitative because meteorology and vertical mixing conditions are highly variable in the atmosphere, and temperature ranged from 20.0 to 35.0°C during this field campaign [Lefer et al., 2010]. Additionally, it is worth noting that experiments conducted using pure VOCs (toluene, isoprene, and hexadecane) in place of motor oil VOCs did not result in net HONO production, ruling out these VOCs as potential reactants. These experiments also rule out HONO artifacts from reactions other than (R3). In other words, despite the <10% HNO$_3$-to-HONO conversion efficiency we generally observe in the flow-tube system [Rutter et al., 2014], other nitrogen-containing compounds originating from HNO$_3$ reduction likely did not contribute to HONO production in this system. Table 3 summarizes experimental data for each type of experiment. Mean values are reported for initial HNO$_3$ concentrations, $f_{\text{HONO}}$, and water vapor mixing ratios with $N \geq 3$. All error bars and uncertainties reported here were propagated from measurement uncertainties, except those for initial HNO$_3$ concentrations with $N \geq 3$, which are reported as standard deviations from the mean. The measurement uncertainties were larger than
the standard deviations for \( f_{\text{HONO}} \) in most experiment types, indicating high repeatability. Additional information on uncertainty is included in section 2.3.6.

Table 3. Summary of experimental conditions and HONO formation rates.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial HNO(_3) (ppt)</th>
<th>Unc/stdev (ppt)</th>
<th>N(^a)</th>
<th>( f_{\text{HONO}} ) (ppb/hr)</th>
<th>Unc/stdev (ppb/hr)</th>
<th>Water vapor mixing ratio (%)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case, High HNO(_3)</td>
<td>3980</td>
<td>936</td>
<td>3</td>
<td>0.60</td>
<td>0.16</td>
<td>0.67</td>
<td>T = 25.0 °C</td>
</tr>
<tr>
<td>Base case, Moderate HNO(_3)</td>
<td>1522</td>
<td>159</td>
<td>3</td>
<td>0.51</td>
<td>0.08</td>
<td>0.63</td>
<td>T = 25.0 °C</td>
</tr>
<tr>
<td>Base case, Low HNO(_3)</td>
<td>399</td>
<td>53</td>
<td>1</td>
<td>0.43</td>
<td>0.25</td>
<td>0.58</td>
<td>T = 25.0 °C</td>
</tr>
<tr>
<td>Base case, all HNO(_3) levels</td>
<td>N/A</td>
<td>N/A</td>
<td>7</td>
<td>0.54</td>
<td>0.09</td>
<td>0.64</td>
<td>T = 25.0 °C</td>
</tr>
<tr>
<td>T = 20.0 °C</td>
<td>2763</td>
<td>52</td>
<td>3</td>
<td>0.98</td>
<td>0.16</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>T = 30.0 °C</td>
<td>4344</td>
<td>361</td>
<td>4</td>
<td>0.64</td>
<td>0.22</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>T = 35.0 °C</td>
<td>3755</td>
<td>474</td>
<td>4</td>
<td>0.59</td>
<td>0.17</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>UV Irradiation</td>
<td>3405</td>
<td>451</td>
<td>3</td>
<td>0.37</td>
<td>0.17</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>680</td>
<td>52</td>
<td>3</td>
<td>0.60</td>
<td>0.11</td>
<td>0.73</td>
<td>NH(_3) = 118.0 ± 2.0 ppb</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average count = 1600 ##/cm(^3)</td>
</tr>
<tr>
<td>Alumina aerosol</td>
<td>3356</td>
<td>346</td>
<td>3</td>
<td>0.45</td>
<td>0.07</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average count = 1600 ##/cm(^3)</td>
</tr>
<tr>
<td>Silica-COOH aerosol</td>
<td>3443</td>
<td>85</td>
<td>3</td>
<td>0.43</td>
<td>0.10</td>
<td>0.60</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) N = number of experiments conducted

The average HONO formation rates are not statistically different (within 1σ) when initial HNO\(_3\) concentrations were ~400, 1500, and 4000 ppt, suggesting that the 200 - 300 ppt of reactive VOCs previously estimated by Rutter et al. [2014] (assuming a 1-to-1 stoichiometric ratio) remains the limiting factor. The lowest HNO\(_3\) concentrations achieved in these experiments were ~400 ppt (by shutting off HNO\(_3\) supply), which likely reflects the presence of HNO\(_3\) in the air source or the desorption of HNO\(_3\) from the supply tubing, since reactor walls were first rinsed with deionized water and baked under
UV lights. A regression showing the weak relationship between $f_{HONO}$ and HNO$_3$ mixing ratio is shown in Figure 4. Because HNO$_3$ concentrations above 400 ppt do not appear to significantly impact $f_{HONO}$, all seven HNO$_3$ experiments were grouped into one base case category (Table 3). This base case and the Houston 2006 average provide the benchmarks for comparison with other experiments (Figure 5).

Figure 4. Least squares linear regression between $f_{HONO}$ and initial HNO$_3$ concentration from seven experiments conducted at varying HNO$_3$ concentrations. The slope and intercept are reported with standard error estimated from the linear regression and have units of ppb hr$^{-1}$ ppt$^{-1}$ and ppb hr$^{-1}$ respectively.
Figure 5. HONO formation rates for each category of experiments with error bars for comparison with the base case scenario and field results from Ziemba et al. [2010]. HighN, ModN, and LowN represent experiments with high HNO$_3$, moderate HNO$_3$, and low HNO$_3$, respectively, and are combined to generate the base case output. Solid and dotted horizontal lines indicate averages and 1σ bands for the base case (blue) and Ziemba et al. [2010] field (red) results.

2.3.2 Temperature

Although the mean $f_{HONO}$ value for the combined base case experiments (T= 25°C) was lower than that for other temperatures, the $f_{HONO}$ at 30.0°C and 35.0°C are not statistically different (within 1σ) than that of the base case. However, experiments at 20.0°C yielded significantly higher $f_{HONO}$ (above 1σ). This could mean that the reaction rate increases at lower temperatures, but as mentioned previously this dependence may not follow an Arrhenius trend. This trend suggests the possibility that multiple reactions involving
different reactive VOCs become more important at various temperatures. Sampling lines were insulated and heated such that HONO wall losses would be as small as possible, but it should be noted that any bias due to wall losses would likely decrease $f_{\text{HONO}}$ at lower temperatures. The enhanced rate at lower temperatures could make the proposed reaction mechanism even more important at night.

2.3.3 NH$_3$

The presence of NH$_3$ had no observable impact on the reaction. Nitric acid concentrations were at ~3500 ppt before NH$_3$ was introduced. After addition of NH$_3$, the system equilibrated at $118.0 \pm 2.0$ ppb NH$_3$ and $680 \pm 52$ ppt HNO$_3$. The formation of NH$_4$NO$_3$ and its subsequent partitioning into the solid phase is the likely cause for the observed consumption of HNO$_3$; any NH$_4$NO$_3$ particles formed would be filtered prior to entering the MC/IC. The $f_{\text{HONO}}$ for these experiments also were similar to the base case, likely because HNO$_3$ was still in excess compared to the VOCs. This indicates that the neutralization reaction between ammonia and HNO$_3$ does not directly interfere with the HONO formation reaction beyond the competition for HNO$_3$. Consistent with the experiments under varying HNO$_3$ levels, a lower $f_{\text{HONO}}$ is not observed due to the decrease in HNO$_3$.

2.3.4 UV Light

When UV lights were turned on prior to experiments, a constant photolytic source of HONO from HNO$_3$ was observed, contributing to background HONO levels (net production of ~226 ppt or ~5.42 ppb hr$^{-1}$) in the reactor. Several sources could explain
this HONO production, for example direct photolysis of HNO$_3$ sorbed on the reactor walls [Zhou et al., 2003] or from photolysis of nitrophenols [Bejan et al., 2006] that could be present in lubricating oil. We do not have the capability to isolate these sources, but they are not expected to bias $f_{HONO}$ as defined here because formation rates are calculated using a step change in HONO when VOCs were removed during an experiment (Equation 1). In other words, the HONO formation observed when VOCs were introduced under UV Irradiation occurs above and beyond the background photolytic sources.

The observed average $f_{HONO,obs}$ under UV irradiation of 0.29 ± 0.17 ppb hr$^{-1}$ was obtained using the change in HONO levels when VOCs were removed, similar to other experiments. However, according to a simplified mass balance (Equation 2), the actual HONO production rate ($f_{HONO,UV}$) must correct for photolytic losses of HONO generated when VOCs were present to react with HNO$_3$:

$$f_{HONO,UV} = f_{HONO,obs} + J_{HONO} (HONO_{UV+VOCs} - HONO_{UV})$$

Equation 2

where $J_{HONO}$ is the photolysis rate of HONO, and the term in brackets represents the difference in measured HONO mixing ratios with and without VOCs when the lights are illuminated. A spectroradiometer was not available to determine $J_{HONO}$. In Equation 2, an average $J_{HONO}$ value of 1.75 x 10$^{-3}$ s$^{-1}$ was used. This value was derived from an average of measured ambient noon-time $J_{HONO}$ (1.75 x 10$^{-3}$ s$^{-1}$ [Alicke et al., 2003] and 1.60 x 10$^{-3}$ s$^{-1}$ [Lee et al., 2013]) and $J_{HONO}$ estimated using the method from Kraus and
Hofzumahaus [1998] (1.90 x \(10^{3}\) s\(^{-1}\)) from NO\(_2\) photolysis rates reported in an environmental chamber [Nakao et al., 2011] that utilized the same model of lights as this study. When corrected, the average \(f_{HONO, UV}\) is 0.37 ± 0.17 ppb hr\(^{-1}\) (Table 3 and Figure 5). However, the \(J_{HONO}\) used here is likely much higher than the actual value from only four 40W UV lights, indicating that the \(f_{HONO, UV}\) is likely an upper bound. To further test the uncertainty, the estimated value of \(J_{HONO}\) used was adjusted by factors of 0.5 and 2 to provide a range of 0.33 ± 0.17 to 0.44 ± 0.17 ppb hr\(^{-1}\) for the potential average \(f_{HONO,UV}\) values.

Although \(f_{HONO, UV}\) is within the uncertainty range of the base case \(f_{HONO}\), it is likely that the reported \(f_{HONO, UV}\) represents an upper bound and that the UV wavelengths studied here could directly interfere with the reduction reaction of HNO\(_3\) to HONO. One explanation for this observation is that under UV irradiation, relevant organic compounds undergo oxidation by radicals formed in the reactor [Atkinson, 2000] or are photolyzed directly. This could alter the reactivity of the VOCs or reduce the total concentration of reactive VOCs available for reaction, hence slowing the overall reaction rate. This and additional tests (section 2.3.6) support the hypothesis that VOCs are the limiting reactants in the reaction proposed here.

### 2.3.5 Mineral dust aerosol surfaces

Neither carboxylated-SiO\(_2\) nor Al\(_2\)O\(_3\) particles (at concentrations of \(~1600 \#/cm^3\)) yielded significantly different \(f_{HONO}\) (above 1σ) than the base case (Figure 5). The slight decrease observed is counterintuitive if the surfaces are expected to enhance the reaction, indicating that the surfaces are potential minor loss sites for the reactive VOCs involved.
or for the HONO produced [Romanias et al., 2012]. This further affirms the probability that a surface is not required to convert HNO$_3$ to HONO via the proposed pathway.

### 2.3.6 Additional experiments and information

Section 2.4 of our previous manuscript [Rutter et al., 2014] provides a detailed discussion of the choice of engine oil VOCs used as proxies for vehicular emissions. Background levels of HONO (~30 ppt) and HNO$_3$ (~400 ppt) in the reactor were achieved upon rinsing the system with water and baking with UV lights for ~8 hours.

Three experiments were conducted at T = 20 °C and by diluting the source of VOCs with clean air prior to injection to the flow-tube reactor (other conditions were identical to the T = 20 °C experiments). The diluted concentration of reactive VOCs in the reactor was estimated based on mass balance to be ~55% of the nominal concentration used. The dilution of VOCs resulted in $f_{\text{HONO}}$ of 0.72 ± 0.22 ppb hr$^{-1}$, which is lower when compared with $f_{\text{HONO}}$ of 0.96 ± 0.18 ppb hr$^{-1}$ for the nominal T= 20°C experiments (Table 3 and Figure 5). This comparison provides supporting evidence that the concentration of VOCs was the limiting factor for the reaction discussed here. However, these experiments were not used in direct comparison with the other experimental categories because two variables (temperature and concentration of VOCs) were changed simultaneously.

Tests were also conducted to rule out heterogeneous reactions in the flow tube reactor, by measuring $f_{\text{HONO}}$ under varying residence times while keeping other parameters constant. The $f_{\text{HONO}}$ for different residence times were statistically similar, which lends support to our case that HONO formation occurred predominantly in the gas phase.
Weekly calibrations for the mist chamber/ion-chromatography (MC/IC) were conducted to minimize systematic errors in HONO mixing ratio measurements ([HONO] in ppt). The overall measurement uncertainties in \([HONO]_i\) and \([HONO]_0\) in Equation 1 were estimated from the standard deviation of 1-hour averages of steady-state [HONO] (immediately prior to and after the removal of VOCs). These uncertainties were propagated to the \(f_{HONO}\) “Unc” values for individual experiments as shown in Table 2. When calculating the mean \(f_{HONO}\) value for each experimental category, the individual uncertainties are again propagated to give an estimate of the uncertainty in the averaged \(f_{HONO}\) value (“Prop”). These propagated measurement uncertainties are larger than the spread in \(f_{HONO}\) values for each category (standard deviation of the average, “Stdev”), indicating good repeatability. The same procedures were used to calculate initial [HNO₃] and [HONO] values (also shown in Table 2). The larger of either the ‘Stdev.’ or ‘Prop.’ values for initial [HNO₃] or \(f_{HONO}\) were used to represent their respective uncertainty ranges in Table 3 and Figure 5 in the main text.

2.3.7 Summary of results

Estimates of base case (25°C, ~20% RH) \(f_{HONO}\) derived from the reduction of HNO₃ by VOCs agree well with data from a 2006 field study in Houston [Ziemba et al., 2010] during which enhancements in HONO during morning rush hour were observed. The hypothesized reaction (R3) studied here could have been the main HONO source during the HONO formation events.

The HONO formation rate was relatively enhanced (~1.0 ppb hr⁻¹) at a lower temperature of ~20°C but statistically the same (~0.6 ppb hr⁻¹) in experiments at 25, 30 and 35°C. The
assumption that multiple reactive components of the VOCs react with HNO$_3$ is supported by this observation, and the relative importance of each reactive species in the reaction may vary with temperature. The reaction rate is independent of initial HNO$_3$ concentration (> 400 ppt), suggesting that the concentration of reactive VOCs was the limiting factor. However, future work testing this reaction under HNO$_3$ concentrations < 400 ppt may provide insights into its relevance in cleaner environments. Ammonia gas consumed HNO$_3$ in the reactor (down to 680 ppt) but did not have a direct impact on the HONO formation reaction, providing further evidence that the rate is limited by the availability of VOCs in the experimental system. The $f_{HONO,UV}$ from (R3) was likely impeded by UV irradiation. Possible explanations for this observation include the photolysis/deactivation of the reactive VOCs involved in (R3) or the direct interference of UV light on (R3). Nonetheless, this observation must be confirmed by conducting a similar flow-tube study that focuses on constraining the reactive VOCs involved and quantifying HONO photolysis rates. The test of multiple atmospherically-relevant particle surfaces confirmed that the reaction proposed here does not require surfaces to proceed, despite the correlation that was observed in Houston in 2006 [Ziemba et al., 2010]. Given the uncertainties, we observe substantial percentage changes in $f_{HONO}$ between the base case and the 20°C and UV experiments, even when compared to the change when RH was varied from the base case to 1% or 50% in Rutter et al. [2014]. The reduced sensitivity of $f_{HONO}$ to other environmental variables tested here is also an important finding, especially in future modeling work aiming at incorporating this new HONO source to existing atmospheric models.
The HONO formation process studied here is likely homogeneous, but the results presented here do not rule out the possibility of a heterogeneous reaction pathway occurring in the atmosphere. Also, it is important to note that the net production of HONO observed in the UV experiments is in addition to background photolytic reactions that appear to be occurring on the wax-coated tube walls.

The gas-phase conversion of HNO$_3$ to HONO has significant air quality implications due to the “renoxification” of less reactive HNO$_3$ into more reactive HONO and should be tested in future modeling and field efforts. This pathway proceeds rapidly in the laboratory when compared with previously identified mechanisms (Table 4) and could potentially be an important source of HONO in the lower atmosphere ($2^{nd}$ order rate constant $\sim 1.0 \times 10^{-7}$ ppt$^{-1}$ s$^{-1}$ estimated in Gall et al. [2015], in revision for Atmospheric Environment). Its role in HONO production aloft (synonymous to the unknown gas-phase HONO source proposed by Li et al. [2014]) cannot yet be ruled out and should be evaluated in future work.
Table 4. Estimated rates of previously identified HONO formation mechanisms using observed or typical ambient parameters. Parameters used in the source strength calculations are included below.

<table>
<thead>
<tr>
<th>Source rank</th>
<th>HONO source mechanism</th>
<th>Estimated source strength (ppb hr&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Input parameters</th>
<th>Daytime/Nighttime</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gas-phase source that scales with (J_{\text{HONO}})</td>
<td>0.69 (S_{\text{HONO}}, J_{\text{HONO}})</td>
<td>Day</td>
<td>Li et al. [2014]</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Homogeneous source (HNO&lt;sub&gt;3&lt;/sub&gt; and VOCs)</td>
<td>0.54 (P_{\text{HNO3}}, [\text{HNO3}])</td>
<td>Day/Night</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Photolysis of surface-adsorbed HNO&lt;sub&gt;3&lt;/sub&gt; (scaled by [HNO&lt;sub&gt;3&lt;/sub&gt;])</td>
<td>0.54 (k_{\text{OH-NO3}})</td>
<td>Day</td>
<td>Zhou et al. [2003]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Reaction between OH and NO</td>
<td>0.33 (P_{\text{OH}}, [\text{OH}], [\text{NO}])</td>
<td>Day</td>
<td>Atkinson et al. [2004]</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>NO&lt;sub&gt;2&lt;/sub&gt; surface production</td>
<td>0.004 (S_{\text{NO2}}, S/V, [\text{NO2}])</td>
<td>Day/Night</td>
<td>VandenBoer et al. [2013]</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>NO&lt;sub&gt;2&lt;/sub&gt; hydrolysis on aerosol surface</td>
<td>0.0002 (k_{\text{NO2}}, S/V, [\text{NO2}])</td>
<td>Day/Night</td>
<td>Kurtenbach et al. [2001]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HONO production rate</td>
<td>(S_{\text{HONO}})</td>
<td>ppt s h&lt;sup&gt;-1&lt;/sup&gt; × (J_{\text{HONO}})</td>
<td>4.05E+05</td>
<td>Li et al. [2014]</td>
</tr>
<tr>
<td>Ambient noon-time HONO photolysis rate</td>
<td>(J_{\text{HONO}})</td>
<td>s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>1.70E-03</td>
<td>Aicke et al. [2003]; Lee et al. [2013]</td>
</tr>
<tr>
<td>HONO production (700 ppt HNO&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>(P_{\text{HNO3}})</td>
<td>ppb hr&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>1.50E-01</td>
<td>Zhou et al. [2003]</td>
</tr>
<tr>
<td>Rate constant</td>
<td>(k_{\text{OH-NO3}})</td>
<td>[N&lt;sub&gt;2&lt;/sub&gt;] cm&lt;sup&gt;3&lt;/sup&gt; molecule&lt;sup&gt;-1&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>7.52E-31</td>
<td>Atkinson et al. [2004]</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt; uptake coefficient</td>
<td>(S_{\text{NO2}})</td>
<td>-</td>
<td>2.00E-06</td>
<td>VandenBoer et al. [2013]</td>
</tr>
<tr>
<td>Rate constant</td>
<td>(k_{\text{NO2}})</td>
<td>(S/V) min&lt;sup&gt;-1&lt;/sup&gt; m&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>3.00E-03</td>
<td>Kurtenbach et al. [2001]</td>
</tr>
<tr>
<td>Experimental nitric acid levels</td>
<td>[HNO&lt;sub&gt;3&lt;/sub&gt;]</td>
<td>ppt</td>
<td>2500</td>
<td>This study</td>
</tr>
<tr>
<td>12-hr daytime hydroxyl radical</td>
<td>[OH]</td>
<td>ppt</td>
<td>0.08</td>
<td>Atkinson [2000]</td>
</tr>
<tr>
<td>Assumed daytime nitrogen oxide</td>
<td>[NO]</td>
<td>ppb</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>Assumed daytime nitrogen dioxide</td>
<td>[NO&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>ppb</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Daytime boundary layer height, Houston</td>
<td>(h)</td>
<td>m</td>
<td>400</td>
<td>Banta et al. [2005]</td>
</tr>
<tr>
<td>Median aerosol surface area, Houston</td>
<td>(S/V)</td>
<td>mm&lt;sup&gt;2&lt;/sup&gt; cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>232</td>
<td>Ziemba et al. [2010]</td>
</tr>
</tbody>
</table>

In addition to their direct impact on O<sub>3</sub> formation and secondary organic aerosol formation, vehicular VOCs could also regulate the oxidative capacity of the atmosphere through the redox reaction studied here. These different processes have significant implications in terms of regional and global air quality. Hence, future experimental work
focusing on the quantification of individual reactive components of the VOCs (e.g. utilizing mass spectrometry techniques coupled with proton transfer reaction or gas chromatography) that were involved in the reaction studied here (under varying environmental conditions) would allow detailed characterization of the HONO formation mechanism(s) and determination of reaction yields.
Chapter 3. Overview of Surface Measurements and Spatial Characterization of Submicron Particulate Matter during the DISCOVER-AQ 2013 Campaign

3.1 Literature review

3.1.1 PM measurement techniques

Historically, among the first techniques used to quantify PM mass for regulatory purposes was the use of high-volume sampling equipment to capture particles on filter media [Chow, 1995]. In addition to obtaining total PM mass (by measuring the change in weight of filter samples), filter samples can be analyzed by various analytical techniques to determine PM chemical composition and other properties. Although sufficient for the determination of PM mass for compliance with NAAQS, filter sampling methods have low time-resolution (usually > 1 hour for each sample), have low selectivity with respect to particle size, require extensive manual labor, and can be biased by both positive and negative artifacts. The scanning mobility particle sizer (SMPS) or similar instruments enable real-time determination of aerosol size distribution and total aerosol volume based on the principle of electrical mobility but lacks chemical speciation capabilities [McMurry, 2000]. On the other hand, the particle-into-liquid-sampler (PILS) combined with an ion-chromatography (IC) technique allows online (real-time/automated) chemical speciation of water-soluble aerosols, but lacks the ability to resolve particles by size and only allows sampling of water-soluble material. The PILS-IC system generally offers limited information regarding organic material as well. The drawbacks in these techniques presented so far necessitate the development of a sampling technique capable of measuring real-time chemical composition and size distribution of atmospheric particles.
The novel aerosol mass spectrometer (AMS) was developed by Aerodyne Research Inc. (ARI, Billerica, MA) and is capable of high time-resolution, size-resolved chemical speciation of submicron, non-refractory atmospheric aerosols [Jayne et al., 2000]. The first version of the Aerodyne AMS instrument known as the Quadrupole AMS (Q-AMS) features a particle time-of-flight (PToF) portion to resolve particle size and a quadrupole mass spectrometer to separate ions obtained from sampled PM by their differences in mass-to-charge ratios (m/z). The High-Resolution Time-of-Flight AMS (HR-ToF-AMS, herein HR-AMS) was used in this study. The HR-AMS instrument features an ion time-of-flight (IToF) mass analyzer, replacing the quadrupole and delivering much higher mass-resolution (a term used to describe the ability of a mass spectrometer to distinguish small differences in ion mass (e.g. CO$^+$ at m/z 27.99492 and N$_2^+$ at m/z 28.00614)) than the Q-AMS [DeCarlo et al., 2006]. The HR-AMS produces real-time, size-resolved averages of mass spectra (MS) over very short time intervals (down to 1s). This translates to a time series of the organic and inorganic fractions of PM and size distributions of different chemical compositions at different time points. Several other techniques can be used to expand the utility of the data collected by the HR-AMS and will be discussed below.

The HR-AMS and similar iterations have characterized PM$_1$ evolution and sources through atmospheric chamber studies [Aiken et al., 2010; Aiken et al., 2009; Ng et al., 2010; Sato et al., 2010; Xu et al., 2015a; Zhang et al., 2005b] and field measurements in major urban areas (e.g. Los Angeles, USA [Craven et al., 2013], Zurich, Switzerland [Mohr et al., 2011], and Mexico City, Mexico [Aiken et al., 2009]), resulting in improved characterization and prediction of local PM sources. These datasets have contributed
greatly to the understanding of spatial and temporal variability of aerosol components, nucleation and growth of particles, PM source profiles, and chemical processing and aging of aerosols. Refractory PM species including BC/soot, soil, and metals that are not measured by the HR-AMS.

Basic data products from the analysis of HR-AMS data include: 1) time series of the mass concentrations of individual aerosol fragments (or a collection of fragments, e.g. the aerosol species NO$_3$ that is primarily the sum of the NO$^+$ and NO$_2^+$ fragments); 2) averaged MS graphs over specific time periods (e.g. 1hr, 1 day); 3) averaged size distributions of different aerosol species or fragments over specific time periods; and 4) averaged MS graphs over specific size bins (e.g. MS graph of all species at $D_p = 300$-$350$nm). These data products are useful for comparison with other atmospheric parameters and to derive information such as PM$_1$ composition (OA, NO$_3$, SO$_4$, NH$_4$, and Chl) averaged over certain time periods or by location.

3.1.2 Particulate organic nitrate formation

Organic nitrates (ON) can be produced from the oxidation of VOCs by photochemical oxidants in the presence of NO$_x$ during the day [O'Brien et al., 1997] and by nitrate radicals (NO$_3^\cdot$) at night [Bruns et al., 2010; Hallquist et al., 1999; Spittler et al., 2006], with subsequent partitioning into the aerosol phase. The NO$_3^\cdot$ radical is produced from the reaction between NO$_2$ and O$_3$, photolyses rapidly during daytime, and is an important oxidant at night due to its fast reaction with unsaturated organics such as biogenic VOCs (BVOCs; e.g. isoprene and monoterpenes) [Winer et al., 1984]. The formation of particulate ON and SOA through NO$_3^\cdot$ reactions with BVOCs has been observed in
chamber studies [Boyd et al., 2015; Fry et al., 2009; Liu et al., 2012], from ground measurements in forested/urban areas in California [Rollins et al., 2012; Rollins et al., 2013; Shilling et al., 2013] and in the southeast US [Xu et al., 2015a; Xu et al., 2015b], and aloft in Houston [Brown et al., 2013]. ON can also form favorably from photooxidation of AVOCs in the presence of NO$_x$ [Liu et al., 2012]. The production of low-volatility and semi-volatile precursors from these NO$_3^·$ radical reactions results in high SOA and ON aerosol yields. For example, Xu et al. [2015a] estimated ~17 times higher SOA yields from NO$_3^·$ oxidation of β-pinene (a monoterpenie) when compared with the use of OH or O$_3$ as oxidants. The authors also estimated up to 40-60% contribution of ON to a nighttime SOA surrogate at a forested site in the southeast US, indicating the importance of ON at such locations.

Due to the mix of anthropogenic and biogenic emissions in the forested area north of Houston, these NO$_3^·$ driven ON and SOA formation processes are likely very important at night. However, apart from an aircraft survey of ON processes above the forested area north of Houston [Brown et al., 2013], there is a lack of published data characterizing temporal trends for ON formation at the ground level in that region. In this chapter and in chapter 4, we provide evidence of rapid nighttime SOA and ON formation and processing in Houston that was strongly linked to NO$_3^·$ radical reactions, utilizing data collected during DISCOVER-AQ. The impact of anthropogenic and biomass burning (BB) emissions on ON formation also will be evaluated in these chapters.

### 3.1.3 Spatial and temporal characterization of PM$_1$ composition

The HGB area is influenced heavily by both local and regional PM sources [Russell et al., 2004]. Based on previous field missions conducted since 2000 [Brock et al., 2003;
Olaguer et al., 2014; Parrish et al., 2009], a key identified feature of the Houston atmosphere is the abundance of HRVOCs, NO\textsubscript{x}, and SO\textsubscript{2} from petrochemical, power plant, vehicular, and ship emissions. HRVOCs contribute to unusually fast ozone production in Houston [Jiang and Fast, 2004; Ryerson et al., 2003] and likely play a significant role in local/regional SOA formation [Alicke et al., 2003; Bahreini et al., 2009; de Gouw et al., 2008; de Gouw et al., 2005; Volkamer et al., 2006]. Additionally, the presence of significant vegetation results in the prevalence of BVOCs north of HGB that likely enhance SOA formation [Brown et al., 2013; Russell and Allen, 2005], particularly when mixed with anthropogenic emissions – a phenomenon observed in other urban/forested areas such as Sacramento, CA [Shilling et al., 2013] and Bakersfield, CA [Rollins et al., 2012; Rollins et al., 2013].

Aircraft observations of PM\textsubscript{1} in Houston [Bahreini et al., 2009; Brock et al., 2003] found enhanced particle growth and formation in industrial plumes, primarily in the form of OA and sulfate (SO\textsubscript{4}), relative to less-polluted urban plumes. Another aircraft study observed strong biogenic SOA formation in the forested north [Brown et al., 2013]. On top of an 18-story building near downtown, Cleveland et al. [2012] sampled aerosols that were dominated by SO\textsubscript{4} and OA (which has a unique industrial/urban NMR signature), while [Levy et al., 2013] observed strong diurnal and meteorology-driven variations in aerosol physical and optical properties. Wood et al. [2010] reported strong correlations between formation metrics for SOA and O\textsubscript{3} that were formed on similar timescales at an industrial site (La Porte, TX) during daytime. However, there remains limited surface PM composition data in the sub-urban, forested regions in HGB.
Previous work based on routine measurements at different sites in HGB [Russell et al., 2004] indicated spatial uniformity in annually/seasonally averaged fine aerosol mass/composition, though there was large spatial variability in hourly/daily PM composition due to the abundance of local/regional sources in the area. Because previous PM studies in the HGB area were limited in spatial resolution (e.g. [Cleveland et al., 2012] and [Wood et al., 2010]) or were conducted aloft [Bahreini et al., 2009; Brock et al., 2003; Brown et al., 2013] or in the Gulf of Mexico [Bates et al., 2008; Russell et al., 2009], there are limited data characterizing spatial variations in ground-level PM chemical composition in HGB. Thus, the spatial variability of local versus regional, primary versus secondary, and biogenic versus anthropogenic sources of PM remains uncertain in the area, which complicates PM modeling and control efforts in Houston.

The MAQL was deployed during DISCOVER-AQ in order to investigate the spatial distribution and temporal variability of PM$_1$ levels and composition in Houston. This study combined both on-road sampling and short-term stationary measurements at multiple urban, industrial, and sub-urban/forested sites in HGB. This sampling strategy specifically aimed to achieve both spatial and temporal characterization of PM$_1$ composition in Houston. In addition to this broad characterization, application of clustering algorithms to the aerosol mass loadings at sixteen stationary sampling sites led to the definition of distinct PM$_1$ pollution zones in the Houston area. The specific character and dynamics of PM$_1$ in each of these zones was studied, and important physical/chemical processes that drive the variability in PM$_1$ and trace gas pollutants in these were investigated by application of principal component analysis (PCA) on combined stationary and mobile datasets.
3.2 Methodology for this study

3.2.1 Mobile PM$_1$ and trace gas measurements

The driving paths covered by the MAQL during the month-long campaign are shown on a map of Houston in Figure 6 with major stationary sampling sites (Table 5). During days when NASA deployed atmospheric research aircraft (ten flight days), the MAQL sampled pollutants to the northwest of Houston near spiral sites and flight paths. On non-flight days, the mobility of the MAQL allowed the strategic sampling of on-road emissions, petrochemical plumes, and regional air masses upwind/downwind of the city to capture the evolution of PM and trace gases. A stationary, ground-based monitoring site also was established at the TCEQ Manvel Croix location (Figure 6 and Table 5) to measure water-soluble aerosol composition for data quality control purposes. The MAQL spent considerable time sampling PM$_1$ in the Manvel and Conroe sites (Figure 6, north of Houston) to characterize the distinct character of PM$_1$ in these urban and sub-urban sites, respectively.

Table 5. GPS coordinates for major stationary sites during DISCOVER-AQ.

<table>
<thead>
<tr>
<th>Location</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conroe Airport</td>
<td>30.35030</td>
<td>-95.42512</td>
</tr>
<tr>
<td>Spring Creek Park</td>
<td>30.10073</td>
<td>-95.65303</td>
</tr>
<tr>
<td>Manvel Croix</td>
<td>29.5204</td>
<td>-95.3925</td>
</tr>
<tr>
<td>Galveston</td>
<td>29.2545</td>
<td>-94.8613</td>
</tr>
<tr>
<td>San Jacinto</td>
<td>29.75203</td>
<td>-95.09056</td>
</tr>
</tbody>
</table>
Figure 6. Map of the HGB area, showing major stationary field sites and MAQL sampling paths (in red) during DISCOVER-AQ 2013. Table 5 lists these major sites by coordinates.

A size-resolved, non-refractory (NR) PM$_1$ mass spectral dataset was collected using the HR-AMS [DeCarlo et al., 2006] aboard the MAQL (Figure 2). The MAQL was operated under mobile mode (inlet mast lowered) for on-road driving or stationary mode (inlet mast raised) for extended stationary sampling. A Teflon®-coated aluminum cyclone
URG corporation, Chapel Hill, NC) was installed as the aerosol inlet at the front of the MAQL inlet mast. This inlet cyclone removes most aerosol particles larger than a specific cut-off size (diameter) that was determined by flow-rate, while minimizing losses of the smaller particles. The total air flow-rate through the inlet cyclone was controlled at ~8 liters-per-minute (LPM), which resulted in a size cut of ~2-µm that was equivalent to losses of ~50% of 2-µm particles and negligible losses of submicron PM. The inlet lines consist mainly of copper and stainless steel tubing and fittings, with the appropriate inner diameters (ID) to maintain laminar flow in the aerosol stream to minimize wall losses. The aerosol stream was passed through ~30 feet of 1/2-inch ID metal tubing before it enters the truck body of the MAQL, upon which it was dried using a 24-inch Permapure© MD-110 Nafion dryer unit to relative humidities (RH) below 40%. All lines and fittings within the air-conditioned space were insulated to prevent condensation of water on the inner walls. Drying the aerosol stream and insulating inlet lines reduce particle losses and avoids RH-dependent fluctuations in particle collection efficiency (CE) [Middlebrook et al., 2012]. Upon drying, the aerosol stream was split into a HR-AMS sample stream (~0.08 LPM), a Grimm SMPS stream (0.3 LPM), an EcoChem Analytics Photoelectric Aerosol Sensor (PAS) stream (2 LPM), and the excess stream that flows towards the GAST oil-free vacuum pump (GAST Manufacturing Inc., Benton Harbor, MI) that pulls the flow of aerosol from the inlet to the instruments. Ancillary trace-gas measurements of carbon monoxide (CO), SO2, NOx, O3, and meteorological parameters onboard the MAQL are summarized in Table 6. Estimated aerosol residence time in the copper inlet tubing system prior to arriving at the AMS was ~15 s, while ancillary measurements were synchronized to the AMS data. The AMS was programmed
to sample every 20 seconds during mobile measurements and every 60 seconds during most stationary measurements. Based on an estimated average driving speed of 45 miles per hour, the mobile 20-second resolution results in a spatial resolution of 0.25 miles or 400 meters.

Table 6. Summary of relevant measurements made by the MAQL during DISCOVER-AQ 2013. Also included are measurements from two independent studies in zones 1 and 2 for qualitative comparison.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Instrumentation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>University of Houston/Rice Mobile Air Quality Laboratory (MAQL)</strong></td>
<td></td>
</tr>
<tr>
<td>Submicron non-refractory PM</td>
<td>Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)</td>
</tr>
<tr>
<td>PAHs in soot</td>
<td>Ecochem PAS2000 analyzer (soot particle-bound polycyclic aromatic hydrocarbons)</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>AeroLaser (Garmisch-Partenkirchen, Germany) AL-5001 CO Monitor</td>
</tr>
<tr>
<td>Sulfur dioxide (SO\textsubscript{2})</td>
<td>Thermo Electron Corp. 43C Trace Level SO\textsubscript{2} Analyzer (pulsed fluorescence)</td>
</tr>
<tr>
<td>Nitrogen oxides (NO\textsubscript{x})</td>
<td>Air Quality Design (Golden, CO, United States) NO-NO\textsubscript{2}-NO\textsubscript{x} Analyzers (High sensitivity chemiluminescence)</td>
</tr>
<tr>
<td>Ozone (O\textsubscript{3})</td>
<td>Thermo Electron Corp. 49C O\textsubscript{3} Analyzer (ultraviolet photometry)</td>
</tr>
<tr>
<td>T, P, RH, wind speed/direction</td>
<td>RM Young meteorological station + RM Young translator (to calculate true wind speed using vehicle motion)</td>
</tr>
<tr>
<td>GPS coordinates</td>
<td>High-resolution marine GPS</td>
</tr>
<tr>
<td><strong>Rice University Manvel ground site</strong></td>
<td></td>
</tr>
<tr>
<td>Soluble submicron PM</td>
<td>Particle-into-liquid sampler (PILS; BMI Inc., Hayward, CA) and ion-chromatograph (ICS-1600; Dionex, Sunnyvale, CA)</td>
</tr>
<tr>
<td><strong>University of Texas (UT) Conroe ground site</strong></td>
<td></td>
</tr>
<tr>
<td>Submicron non-refractory PM</td>
<td>Aerodyne Aerosol Chemical Speciation Monitor (ACSM); see Ng et al. [2011b] for instrument description</td>
</tr>
<tr>
<td><strong>Aerodyne Research, Inc. (ARI) mobile laboratory</strong></td>
<td></td>
</tr>
<tr>
<td>Submicron refractory and non-refractory PM</td>
<td>Aerodyne high-resolution Soot-Particle Aerosol Mass Spectrometer (SP-AMS); see Onasch et al. [2012] for instrument and Dallmann et al. [2012] for mobile laboratory descriptions</td>
</tr>
</tbody>
</table>
Aerosol was sampled by the HR-AMS through an inlet orifice (limiting the volumetric flow rate at ~1.4 cm$^3$ s$^{-1}$) into a vacuum chamber, and the aerosol stream (consisting of ambient particles and ambient gases at 1 atm) was focused into a narrow beam by an aerodynamic focusing lens (Figure 7). The aerosol beam enters the PToF chamber and passes through a spinning disk (chopper) with two slits. Particles achieve a terminal velocity and arrive at the end of the chamber to be vaporized (at T = 600 °C, which efficiently vaporizes most non-refractory aerosol material) and ionized by electron impact (70 eV). The resulting ions are then delivered into the IToF mass spectrometric chamber, where the ions travel either in a shorter V-shaped path (V-mode, lower m/z resolution) or a longer W-shaped path (W-mode, higher m/z resolution) before arriving at the ion detector. The instrument was operated either in MS mode or PToF mode. In MS mode, the chopper was moved away from the particle beam to an “open” position, allowing continuous detection of the ions from ambient PM and generating real-time MS graphs (y-axis = signal intensity or concentration; x-axis = m/z). In MS mode, the chopper was also operated in a “closed” position to determine the aerosol background signal in the instrument, which was subtracted from the “open” signal to yield the final MS signal used for quantification. In PToF mode, the spinning chopper allows bursts of particles through, and the time it takes for particles to travel a specific distance in the PToF chamber can then be calculated. This information translates into the vacuum terminal velocity of the particles (which is proportional to particle size) and ultimately provides aerodynamic size distributions of the different components of the sampled PM. The HR-AMS was shock-mounted in the air-conditioned laboratory space of the MAQL during
DISCOVER-AQ, protecting the sensitive electronics from damage while the vehicle was in transit.

Figure 7. Schematic of the HR-ToF-AMS [DeCarlo et al., 2006].

The Griffin group personnel were primarily in charge of the operation of the HR-AMS, while also monitoring the MAQL to maintain continuous data acquisition for as close to 24 hours per day as possible during September 2013. The HR-AMS was the instrument of primary focus in this study, but comparisons of AMS data with other co-located measurements can provide useful information. In addition to the aforementioned instruments housed within the MAQL, multiple datasets from DISCOVER-AQ 2013 was available for comparison: 1) submicron water-soluble PM composition from the BMI (Brechtel Manufacturing Inc., Hayward, CA) PILS coupled with Dionex IC (Dionex, Sunnyvale, CA) located at the Manvel Croix measurement site (Figure 6), which was also operated by the Griffin group; 2) satellite data from DISCOVER-AQ; 3) airborne data from the heavily instrumented (gas phase and particulate phase) P-3B NASA aircraft on
flight days; 4) gas-phase measurements and speciated PM collected by Professor Lea Hildebrandt Ruiz of the University of Texas at Austin (UT Austin) using the Chemical Ionization Mass Spectrometer (CIMS) and Aerosol Chemical Speciation Monitor (ACSM) respectively, located at the Lone Star Executive Airport site in Conroe, TX (Figure 6); and 5) various gas-phase and PM$_1$ data from similar mobile platforms deployed during the same period including MLs operated by Princeton University and Aerodyne Research, Inc. Only select measurements were used for comparison in the studies presented in this thesis, though there are ample opportunities for future collaborative studies with the data originators above.

To reiterate, the main PM$_1$ chemical constituents identified using the HR-AMS include OA constituents, SO$_4$, NO$_3$, NH$_4$, and Chl [DeCarlo et al., 2006]. These constituents are quantified using high-resolution MS collected by the HR-AMS in V-mode, up to a mass-to-charge ratio (m/z) of 120 during each averaging interval. Detection limits and uncertainties for key measurements aboard the mobile platform are shown in Table 7. The sampled organic MS also allow estimates of organic elemental ratios such as oxygen:carbon (O:C) and hydrogen:carbon (H:C) and of the organic mass:organic carbon (OM:OC) ratio at much higher time-resolution compared to conventional sampling techniques [Aiken et al., 2007; Aiken et al., 2008]. The O:C and H:C allow quantification of the average oxidation state of carbon in OA (OS$_c$) [Heald et al., 2010; Kroll et al., 2011], which is not confounded by non-oxidative processes (e.g. hydration reactions). These elemental parameters are important metrics for characterizing OA sources and aging processes. The elemental ratios and OS$_c$ values presented here were calculated using the updated Improved-Ambient method [Canagaratna et al., 2015] for samples with
OA concentrations above 1.5 µg/m$^3$. The Improved-Ambient method accounts for thermal fragmentation of organics in the AMS vaporizer for more accurate elemental estimates. The H:C and O:C ratios calculated using this method were 27% and 11% higher respectively [Canagaratna et al., 2015].

Table 7. Measurement detection limits (LOD) for 1-minute averages and calculated/literature uncertainties for major PM$_1$ and trace gas parameters measured by the MAQL

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LOD</th>
<th>Units</th>
<th>Uncertainties</th>
<th>Unc. reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AMS PM$_1$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OA</td>
<td>0.110</td>
<td>µg/m$^3$</td>
<td>37%</td>
<td>[Bahreini et al., 2009]</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>0.018</td>
<td>µg/m$^3$</td>
<td>35%</td>
<td>[Bahreini et al., 2009]</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>0.010</td>
<td>µg/m$^3$</td>
<td>33%</td>
<td>[Bahreini et al., 2009]</td>
</tr>
<tr>
<td>Total NO$_3$</td>
<td>0.010</td>
<td>µg/m$^3$</td>
<td>33%</td>
<td>[Bahreini et al., 2009]</td>
</tr>
<tr>
<td>Chl</td>
<td>0.011</td>
<td>µg/m$^3$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NO$^+$</td>
<td>0.008</td>
<td>µg/m$^3$</td>
<td>33%</td>
<td>[Bahreini et al., 2009]</td>
</tr>
<tr>
<td>NO$_2^+$</td>
<td>0.004</td>
<td>µg/m$^3$</td>
<td>33%</td>
<td>[Bahreini et al., 2009]</td>
</tr>
<tr>
<td>O:C ratio</td>
<td>Min. OA 1.5 µg/m$^3$</td>
<td>12%</td>
<td>[Canagaratna et al., 2015]</td>
<td></td>
</tr>
<tr>
<td>H:C ratio</td>
<td>Min. OA 1.5 µg/m$^3$</td>
<td>4%</td>
<td>[Canagaratna et al., 2015]</td>
<td></td>
</tr>
<tr>
<td><strong>Trace gases and other</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_2$</td>
<td>150</td>
<td>pptv</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>50</td>
<td>pptv</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td>NO$_2$</td>
<td>150</td>
<td>pptv</td>
<td>12%</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>50</td>
<td>pptv</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td>O$_3$</td>
<td>1.5</td>
<td>ppbv</td>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>PAHs in soot</td>
<td>0.010</td>
<td>µg/m$^3$</td>
<td>22%</td>
<td></td>
</tr>
</tbody>
</table>

The MAQL sampled size-resolved NR PM$_1$ composition and trace gas data continuously in mobile and stationary-mode operation from September 6 to September 29, 2013.

Approximately 30% of NR PM$_1$ samples (comprising ~70 hours of sampling) were collected during mobile-mode operation, while approximately 190 hours of sampling
corresponded to stationary data sampled at sixteen main locations (Table 8). Figure 6 illustrates the spatial coverage of AMS PM$_1$ measurements during the campaign, illustrating the mobile lab driving path as well as five major stationary field sites where a major fraction of the stationary-mode data was collected (Conroe, Spring, San Jacinto, Galveston and Manvel).

Table 8. Distribution of sampling time and measurement days during DISCOVER-AQ 2013 by zones/sites and under mobile/stationary modes.

<table>
<thead>
<tr>
<th>Zone/site</th>
<th>Data type</th>
<th>PM$_1$ sampling time, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>All data</td>
<td>Stationary/Mobile</td>
<td>263</td>
</tr>
<tr>
<td>All data</td>
<td>Stationary</td>
<td>193</td>
</tr>
<tr>
<td>All data</td>
<td>Mobile</td>
<td>70</td>
</tr>
<tr>
<td>Zone 1</td>
<td>Stationary (5 selected points, Figure 11)</td>
<td>112</td>
</tr>
<tr>
<td>Zone 1</td>
<td>Mobile</td>
<td>32</td>
</tr>
<tr>
<td>Zone 1: Conroe site</td>
<td>Stationary</td>
<td>62</td>
</tr>
<tr>
<td>Zone 2</td>
<td>Stationary (11 selected points, Figure 11)</td>
<td>79</td>
</tr>
<tr>
<td>Zone 2</td>
<td>Mobile</td>
<td>36</td>
</tr>
<tr>
<td>Zone 2: Manvel site</td>
<td>Stationary</td>
<td>42</td>
</tr>
</tbody>
</table>

3.2.2 Data analysis and interpretation

3.2.2.1 Data processing

Standard data analysis procedures were applied using AMS software packages SQUIRREL v1.56D and PIKA 1.15D in Igor Pro 6.36 (WaveMetrics Inc., Lake Oswego, OR, USA), including the application of relative ionization efficiencies (RIE) for OA (1.4), SO$_4$ (1.2), NO$_3$ (1.1), NH$_4$ (4.1), and Chl (1.3) and the use of composition-dependent CE corrections for acidic particles [Middlebrook et al., 2012]. Eight ammonium nitrate mass
calibrations were performed throughout the sampling period, and the calibrated signals from the sampled m/z range allow quantification of PM$_1$ chemical components in mass concentration units of nitrate-equivalent µg per standard m$^3$ of air (µg/m$^3$). The chemically-resolved particle size distributions are calibrated with commercial NIST-traceable monodisperse polystyrene latex particles (Thermo Fisher Scientific, Waltham, MA, USA). Corrections for background interferences of CO$_2$(g), CO$_2$(g) and isotopic nitrogen ($^{15}$N$^{14}$N$_{(g)}$) on OA signals were also applied to this dataset.

The PIKA software package for high resolution (HR) MS analysis allows the integration of the raw MS collected at every time point into graphs of meaningful ‘sticks’ at each m/z, with each stick corresponding to a mass loading of individual fragments (e.g. CO$^+$ at m/z 27.99492 as shown in Figure 8). Background interferences from CO$_2$(g) and $^{15}$N$^{14}$N in air on important organic fragments CO$_2$$^+$ and CHO$^+$ (due to similar m/z) were corrected in the HR-AMS data. V-mode was used during the majority of the project, due to its stronger signal-to-noise ratio and thus better quantification capability. When the MAQL was sampling at a stationary location for extended periods, the instrument was programmed to alternate between V- and W-modes, with the sole purpose of improving the separation of similar fragments in W-mode during data analysis. Additionally, PToF mode was utilized whenever the instrument was running in V-mode to collect size distributions of all ions sampled by the AMS. For the DISCOVER-AQ project, integrated stick MS graphs are available at every data point, with averaging time intervals ranging from 20s (while sampling mobile) to 60s (while stationary).
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Figure 8. Example HR MS “sticks” graph of an arbitrary ambient sample in V-mode from DISCOVER-AQ, indicating the ability of the HR-AMS to separate ions that have very similar m/z (Org = OA)

Using meteorological parameters (temperature and RH) and inorganic PM$_1$ composition (SO$_4$, NH$_4$, and NO$_3$) as input, aerosol liquid water content (LWC, in µg/m$^3$) was estimated using the ISORROPIA thermodynamic model assuming metastable phase states (i.e., allowing supersaturated aqueous solutions) [Nenes et al., 1998]. A three-dimensional chemical transport model (WRF-SMOKE-CMAQ) [Pan et al., 2015] was applied to estimate isoprene and monoterpenes mixing ratios during the DISCOVER-AQ study for grid-cells corresponding to the real-time location of the MAQL.

3.2.2.2 Filtering of data

A rainy period (Sep 19 – 21, 2013; Figure 9) resulting in low PM$_1$ and trace gas concentrations primarily at the Manvel site was not included for zonal, site, and diurnal
A short contamination episode from a nearby diesel generator in the early morning of Sep 15 at the San Jacinto site was excluded from the stationary analysis presented here.

The Improved-Ambient elemental ratios H:C, O:C, OM:OC, and OS\textsubscript{c} discussed in the main text were calculated for data points with at least of 1.5 µg/m\textsuperscript{3} OA. The 1.5 µg/m\textsuperscript{3} threshold in this study was determined based on correlation plots between O:C and \( f_{CO2^+} \) (fraction of CO\textsubscript{2}\textsuperscript{+} signal to total OA). Robust O:C ratios are expected to correlate with \( f_{CO2^+} \) [Aiken et al., 2008; Canagaratna et al., 2015], and applying the 1.5 µg/m\textsuperscript{3} threshold here removes most noisy O:C data points, resulting in the good correlation that was expected between O:C and \( f_{CO2^+} \) in the stationary dataset (R= 0.735). Most of the low OA data points corresponded to rainy periods during the campaign (Figure 9). It should be noted also that organic NO\textsubscript{3} groups were not included in the OS\textsubscript{c} calculations here due to remaining uncertainties on the correct RIE that should be applied on organic NO\textsubscript{3} groups (based on ~2-3x disagreements in the quantification of organic NO\textsubscript{3} group when compared with other techniques, such as FTIR [Liu et al., 2012]). Inclusion of the organic NO\textsubscript{3} fragments for elemental calculations could increase O:C and OS\textsubscript{c} values by ~5% [Fry et al., 2013].
Figure 9. Time series of AMS PM$_1$ species and meteorology measurements aboard the MAQL during DISCOVER-AQ 2013. From top to bottom: AMS PM$_1$ constituents (pie chart shows campaign-averaged PM$_1$ composition) and O:C elemental ratio (black dots); PM$_1$ neutralization parameter (NH$_4^+$,measured/NH$_4^+$,predicted); local precipitation events (1 = substantial rain event); MAQL temperature (T) and relative humidity (RH) measurements. Shaded regions indicate mobile measurements.

The PM$_1$ neutralization parameter (NH$_4$$_4$,measured/NH$_4$$_4$,predicted) discussed in the text was calculated based on the assumption that ions other than NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$ are negligible because PILS-IC measurements at Manvel yielded below-detection levels for these ions throughout the campaign. Values of NH$_4$$_4$,measured/NH$_4$$_4$,predicted outside of the 5$^{th}$ and 95$^{th}$ percentile boundaries were filtered prior to analysis, as most of these outlying values correspond to periods with low NH$_4$/SO$_4$/NO$_3$ loadings, where the assumptions mentioned above could result in significant uncertainties (e.g. if a small amount of Ca$^{2+}$
ions were present but remain undetected, this could greatly affect the ammonium balance for low loading periods).

3.2.2.5 Back-trajectory analysis

The NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model [Draxler and Hess, 1998; Rolph et al., 2014] was utilized to generate 24-hour air-mass back-trajectories (starting altitude 100 m) to analyze differences in PM$_1$ chemical characteristics for different near-surface air-masses for sampling periods at the Manvel and Conroe field sites, where more extensive measurements were performed (approximately 42 and 62 hours, respectively). Cluster analysis was then used to group back-trajectories in the GIS-based software package TrajStat [Wang et al., 2009].

The North America Model meteorological input data from NOAA with a spatial resolution of 12 x 12 km was used with a HYSPLIT model upper-limit of 10,000 m above ground level. These back-trajectories begin at the mid-point of hourly-averaged stationary AMS and trace gas measurements at both sites. The chosen 100-m AGL starting altitude was below typical mixing heights observed previously in the HGB area during the day (~500-1200 m) and at night (~100-300 m) [Bates et al., 2008]. Also, median boundary layer heights obtained during DISCOVER-AQ from a LIDAR (Ceilometer CL31; Vaisala, Vantaa, Finland) near the UH main campus ranged from 120 m at night to 1500 m during the day. Based on these data it was likely that PM$_1$ sampled by the MAQL at Manvel and Conroe was representative of the composition in the modeled air-masses. Additionally, HYSPLIT back-trajectories with starting altitudes of 50-m AGL were slightly noisier but similar to those presented here. The clustering of back-trajectories in TrajStat were based on the hierarchical method [Ward, 1963]. The
angle-distance method was chosen for this analysis [Sirois and Bottenheim, 1995], as it allows the grouping of back-trajectories by prioritizing the direction of travel as opposed to travel speed.

The clustering results of 24-hr back-trajectories are shown in Figure 10 (A & B). Additionally, 168-hr back-trajectories are produced to provide additional information on week-long travel paths of these air-masses (Figure 10 C & D). Most of these trajectories do not exhibit large deviations from the initial ~100-m AGL altitude throughout the 24-hr simulated travel path. Back-trajectory clusters #M1A and #M1B at Manvel were initially clustered as one based on 24-hr back-trajectories, but were separated based on large distinctions in aerosol composition and concentrations. Week-long back-trajectories in #M1A originated from the Gulf and the Atlantic, with brief contact with Florida (near Jacksonville); trajectories from cluster #M2 originated from the Gulf but spent considerable time (~3 days) on-land prior to arriving at Manvel from the North. Air-masses #M1B and #M3 arrived in Houston with rainfall on the nights of Sep 19 and 20, resulting in low PM$_1$ levels that were excluded from all other analyses in this paper.
Figure 10. Hourly HYSPLIT 100-m, 24-hr air-mass back-trajectories (colored by cluster number) and the derived trajectory cluster means (black lines labeled by cluster number) for Manvel (A) and Conroe (B) sites. One hundred sixty eight-hour back-trajectories were also generated at Manvel (C) and Conroe (D) to further distinguish air-mass origin.

3.2.2.4 Nitrate source apportionment

In this study, we explore two independent methods to apportion the AMS NO$_3^-$ signal (primarily from NO$^+$ and NO$_2^+$, or NO$_x^+$ ions) measured by the HR-AMS between inorganic and organic NO$_3^-$ functionalities. Aerosol mass spectrometer studies published prior to 2009-2010 typically assumed that all NO$_x^+$ signals measured by the AMS originated from inorganic NO$_3^-$ (in the form of neutralized NH$_4$NO$_3$ or acidic HNO$_3$) (e.g. Aiken et al. [2008]). Several chamber studies have since shown evidence of NO$_x^+$ detection from the ionization of ON-containing SOA[Bruns et al., 2010; Fry et al., 2009], and Farmer et al. [2010] documented very distinct NO$_2^+$ to NO$^+$ ratios in the AMS from
sampling inorganic NO$_3$ (NH$_4$NO$_3$) and ON laboratory standards. Farmer et al. [2010] proposed a method to estimate the relative fraction of the measured NO$_3$ signal originating from inorganic or organic NO$_3$ functionalities:

$$NO_{3,ON,frac,t} = \frac{[(R_{ambient,t} - R_{AN})(1 + R_{ON})]}{[(R_{ON} - R_{AN})(1 + R_{ambient,t})]}$$

Equation 3

where:

$NO_{3,ON,frac,t}$ = the fraction of NO$_3$ originating from organic functionalities (i.e. NO$_3$ functional groups in ON molecules) at each measurement time point ($t$)

$R = NO_2^+/NO^+$ ratio measured by the AMS, with subscripts “ambient”, “AN”, “ON” representing said ratios measured from ambient aerosols, pure NH$_4$NO$_3$ calibrants, and pure NO$_3$-containing ON particles respectively

The $NO_{3,ON,frac,t}$ determined from Equation 3 allows an estimate of the fraction of AMS NO$_3$ signal that belongs to ON functionalities at every measurement time point, with the remainder (1 - $NO_{3,ON,frac,t}$) assigned to inorganic NO$_3$. The NO$_2^+/NO^+$ ratio observed from our ambient measurements was defined as $R_{ambient,t}$, which varies depending on aerosol composition. The $R_{AN}$ ratio was a relatively constant value (0.381 ± 0.013) determined from the average of NO$_2^+/NO^+$ ratio from all six NH$_4$NO$_3$ standard calibrations during DISCOVER-AQ. Finally, the $R_{ON}$ value must be measured from laboratory ON standards that are representative of ambient ON, and can vary between individual AMS instruments [Farmer et al., 2010]. To overcome the challenging task of measuring $R_{ON}$ for every instrument for every field campaign, Fry et al. [2013] showed
that the ratio $R_{ON}/R_{AN}$ (“$X$” ratio) remains relatively constant between different AMS instruments. Based on calibration data in Farmer et al. [2010], this ratio was defined/calculated as:

$$X = \frac{R_{AN}}{R_{ON}} = 2.25 \pm 0.35$$

Equation 4

Using this $X$ ratio and our $R_{AN}$ values, we estimated $R_{ON}$ for our instrument during DISCOVER-AQ as $0.169 \pm 0.027$ (uncertainties were propagated from $X$ and $R_{AN}$). This ultimately allowed us to utilize Equation 3 to apportion measured AMS NO$_3$ at each time point into organic NO$_3$ (henceforth Org-NO$_3$) and inorganic NO$_3$ (Inorg-NO$_3$) functionalities. We define the use of $X = 2.25$ as the “central” estimate of Org-NO$_3$ and Inorg-NO$_3$ using the “empirical method” established and tested by Farmer et al. [2010] and Fry et al. [2013]. Essentially, the smaller $R_{ambient}$ is (or the closer it is to 0.169), the larger the fraction of NO$_3$ that is apportioned to Org-NO$_3$. According to the caveats stated in Farmer et al. [2010], this method is considered robust for our dataset because: 1) we obtained relatively constant $R_{AN}$ values during field measurements; 2) we observe ON-dominated NO$_3$ signal throughout this campaign as seen by predominantly low $R_{ambient}$ values (on average 0.194 in zone 1); 3) we expect little Inorg-NO$_3$ interference from other ambient species such as NaNO$_3$ or Ca(NO$_3$)$_2$ (known to have low $R$ ratios that could bias this method) since Na$^+$ and Ca$^+$ ions were not detected in our PILS measurements at Manvel. In addition, if these particles existed they were likely from larger particles and thus not relevant to the sampled PM$_1$. For most of the analyses in this thesis, Org-NO$_3$ data presented were calculated using the “central” estimate from the
“empirical” method (Equation 3) assuming $X = 2.25$ unless stated otherwise. The default NO$_3$ RIE value of 1.1 was used for organic NO$_3$ in this study due to existing debate on the true RIE for organic NO$_3$ functional groups quantified by the AMS. For instance, this method underestimates organic NO$_3$ by up to a factor of 2 when compared to an FTIR system [Liu et al., 2012].

In the analyses involving PMF data in week 4 (section 4.3.4), this “central” estimate was compared with “lower/upper” estimates from the same “empirical” approach and was also compared against “lower/upper” estimates from the PMF NO$_3$ apportionment approach. Details on these lower/upper estimates and PMF approach will be discussed in the remainder of this sub-section.

An important assumption for this “empirical” NO$_3$ apportionment approach is that the $X$ and $R_{ON}$ that were essentially determined from laboratory standards are on average representative of the measured ambient ON molecules [Farmer et al., 2010]. Xu et al. [2015b] reviewed a range of literature $X$ ratios that have been observed for ON formed from different precursor BVOCs involving both nighttime NO$_3$· radical chemistry or photochemistry and proposed 2.08 and 3.99 as lower/upper limits of $X$ ratios. This range of $X$ ratios was suggested specifically for the southeast US atmosphere. However, because Houston was similar in latitude and climate with the sites discussed, and because the range was predominantly selected based on the important SOA yields for isoprene ($X = 2.08$) and β-pinene ($X = 3.99$), it was likely that the suggested range of $X$ ratios provided good lower/upper bound estimates for ON contributions to AMS NO$_3$ signal in this dataset. Finally, the apportioned Org-NO$_3$ functionality can be used to predict the mass concentrations of the parent ON molecule prior to thermal or chemical
fragmentation in the AMS by mass-balance, assuming a representative molecular mass for the parent ON [Fry et al., 2013; Xu et al., 2015b]. Representative molecular weights for ON have been proposed by previous studies, and we use 232 g/mol [Fry et al., 2013] and 300 g/mol [Rollins et al., 2013] as our lower/upper bounds for OA with NO₃ functional groups (“ON₂₃₂” and “ON₃₀₀”) in this study. Based on both the lower/upper bounds for ON molecular mass assumptions and \( X \) ratios, we calculate lower/upper limits for ON concentrations (Table 9) for comparisons with PMF results during week 4 of this study. The “central” and “lower/upper bound” estimates of ON concentrations from the “empirical” method discussed here are presented in section 4.3.4.1, in comparison with the PMF NO₃ apportionment technique discussed next.

Table 9. Different scenarios used to account for the sensitivity of Org-NO₃ and ON estimates from the empirical method.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>( X ) ratio</th>
<th>( R_{ON} )</th>
<th>MW of ON molecule assumed (g/mol)</th>
<th>ON estimate “case”</th>
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<tbody>
<tr>
<td>1</td>
<td>2.08</td>
<td>0.183</td>
<td>232</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.08</td>
<td>0.183</td>
<td>300</td>
<td>Upper</td>
</tr>
<tr>
<td>3</td>
<td>3.99</td>
<td>0.095</td>
<td>232</td>
<td>Lower</td>
</tr>
<tr>
<td>4</td>
<td>3.99</td>
<td>0.095</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.25</td>
<td>0.169</td>
<td>232</td>
<td>Central</td>
</tr>
<tr>
<td>6</td>
<td>2.25</td>
<td>0.169</td>
<td>300</td>
<td>Central</td>
</tr>
</tbody>
</table>
3.3 Results and discussion

3.3.1 Spatiotemporal overview of PM$_1$ composition in Houston

As seen in Figure 6, the MAQL covered a large area in Houston while sampling near-surface non-refractory (NR) PM$_1$ chemical composition and mass loadings. Figure 9 shows the time series for five NR PM$_1$ species, PM$_1$ neutralization parameter (NH$_4$,measured/NH$_4$,predicted, defined subsequently), and O:C ratio measured by the AMS along with basic meteorological parameters (precipitation, temperature, and RH) for mobile and stationary measurements. The campaign-averaged NR PM$_1$ mass ($9.69 \pm 6.07$ µg/m$^3$) from stationary measurements was dominated by OA (64%), followed by SO$_4$ (26%), NH$_4$ (7%), NO$_3$ (3%), and Chl (0.2%). The mean and median NR PM$_1$ masses observed during September 2013 are ~20% lower than previously reported in Houston during the August/September period in 2000 [Jimenez et al., 2009] and 2006 [Cleveland et al., 2012] (primarily decreases in NH$_4$ and SO$_4$). The similar OA concentrations with past studies indicate the need for improved characterization of OA sources in order to further reduce ambient OA levels in Houston.

Using the empirical NO$_3$ apportionment method, the NO$_3$ signal was found to be primarily from organic NO$_3$ (on average 82%) during the Houston measurements, indicating significant presence of particulate ON in Houston. The predominance of organic NO$_3$ (defined as Org-NO$_3$) in AMS NO$_3$ signal was similarly observed by two other measurement platforms (Table 6) in Houston during this period. The low contribution of inorganic NO$_3$ (Inorg-NO$_3$) to total AMS NO$_3$ in this study (except rare episodes mentioned in Chapter 4) was consistent with below-detection levels of water-soluble PM$_1$ NO$_3$ sampled by the PILS-IC at the Manvel site (Table 6).
The PM$_1$ neutralization ratio $\text{NH}_4^{\text{measured}}/\text{NH}_4^{\text{predicted}}$ allows quantification of the “acidic” nature of PM [Zhang et al., 2005b]. Here $\text{NH}_4^{\text{predicted}}$ is defined as the sum of $\text{SO}_4^{2-}$ and $\text{Inorg-NO}_3^-$ in molar equivalents; Chl levels are mostly negligible and other PM$_1$ cations (e.g., metals) were below detection limits for off-line measurements of soluble PM$_1$ (Table 6) deployed at the Manvel site. “Acidic” particles in this context refers to NH$_4$-poor aerosol mixtures that imply the existence of ammonium bisulfates. Note that the acidity metric $\text{NH}_4^{\text{measured}}/\text{NH}_4^{\text{predicted}}$ may not correlate with aerosol pH under ambient conditions [Guo et al., 2015]. Given the uncertainties in the inorganic species, particles are considered slightly “acidic” if the $\text{NH}_4^{\text{measured}}/\text{NH}_4^{\text{predicted}}$ ratio is 0.75 or less; approximately 50% of SO$_4^{2-}$ likely exists as particulate bisulfate (HSO$_4^-$) at a ratio 0.75. The $\text{NH}_4^{\text{measured}}$ and $\text{NH}_4^{\text{predicted}}$ metrics were well correlated during stationary measurements ($R^2=0.93$, intercept=0), with several instances of less or more neutralized particles. The campaign-averaged $\text{NH}_4^{\text{measured}}/\text{NH}_4^{\text{predicted}}$ ratio was $0.75 \pm 0.13$ (median=0.73), indicating NH$_4$-poor particles and the existence of HSO$_4^-$. These results agree well with previous observations in Houston by Cleveland et al. [2012] and Bates et al. [2008] (both studies conducted in August/September 2006), indicating that particles in the HGB area are consistently more acidic than those observed in other major cities (e.g. Pittsburgh [Zhang et al., 2005b] and Mexico City [Aiken et al., 2009]). The high observed acidity of PM$_1$ coupled with high summer temperatures are not favorable for the formation of Inorg-NO$_3^-$ in the aerosol phase (except for two nighttime episodes discussed in Section 3.2.2), consistent with the predominance of Org-NO$_3^-$ signal discussed above and with observations reported previously for the Houston area [Gong et al., 2013b].
3.3.2 PM\textsubscript{1} pollution zones

Results of the cluster and outlier analyses indicate that two pollution zones (Silhouette measure of cohesion and separation 0.7 and ratio between cluster sizes 2.2) can be defined in the HGB area based on the investigated variables (i.e. PM\textsubscript{1} mass and concentration of PM\textsubscript{1} species) measured at the sixteen main stationary locations. The zones defined based on the concentration of OA, which showed to be the variable with the highest influence in the delineation of the clusters (predictor importance 0.7), are presented in (Figure 11). Each zone represents distinct source regions in the HGB area, as seen in the different PM\textsubscript{1} chemical composition and OA character in each zone. Zone 1 covers the forested sub-urban area northwest of Houston, while zone 2 encompasses the urbanized central Houston area and the Houston industrial region (HIR; defined as Texas City, La Porte and Baytown and industrial areas adjacent to the Houston Ship Channel).

Average NR PM\textsubscript{1} chemical composition measured by the AMS was qualitatively similar to those from similar instruments during DISCOVER-AQ (the UT ACSM at Conroe (zone 1) and the ARI mobile laboratory sampling in zone 2; Figure 11; see Table 6). The distribution of PM\textsubscript{1} and trace gas sampling time and the diurnal distribution of PM\textsubscript{1} sampling time in the defined pollution zones are summarized in Table 8 and Figure 12 respectively. To complement the spatial analyses presented in this study, spatial maps depicting average mass fractions of each PM\textsubscript{1} constituents are included in Figure 13. These spatial maps provide a way to determine ‘hot-spots’ or elevated average concentrations for particular PM\textsubscript{1} constituents, though data representativeness (or sampling time at each stationary site) must be considered when interpreting these spatial gradients. Table 10 summarizes stationary PM\textsubscript{1} mass loadings, elemental ratios, and trace
gas measurements in the pollution zones. Zone 1 exhibits substantially higher PM$_1$ (11.9 ± 5.7 µg/m$^3$) levels than those observed in zone 2 (4.4 ± 3.3 µg/m$^3$), primarily driven by elevated OA concentrations in zone 1 (on average 71% of PM$_1$ mass). Previous aircraft studies within the PBL in Houston have observed enhancement of PM$_1$ mass in industrial/ship channel plumes advected downwind of Houston [Bahreini et al., 2009; Brock et al., 2003], which may explain the large masses observed in zone 1 compared to zone 2. However, we show later that while industrial plumes can enhance downwind PM$_1$ mass, significant biogenic sources of SOA in zone 1 also could explain the large gradient of PM$_1$ between the two regions.
Figure 11. Two PM$_1$ pollution zones established by two-step cluster analysis of stationary MAQL PM$_1$ data. Campaign-average PM$_1$ mass loadings, O:C, H:C, OS$_c$, PM$_1$ composition (pie charts), and wind frequency plots are indicated for each zone. Wind frequency plots are also shown for Conroe and Manvel sites. Total OA mass was apportioned into POA and SOA using the CO-tracer method. Also shown are monthly averaged PM$_1$ compositions (pie charts) for two independent studies in zone 1 (UT ACSM) and in zone 2 (ARI SP-AMS) described in Table 6. All data presented here are calculated based on stationary data in each zone. Radial axes in wind frequency plots indicate the fractional wind occurrence from each direction and are colored based on wind speed.

Table 10. Averages and the associated 1σ standard deviations (sdev) for NR PM$_1$ species and trace gas mixing ratios observed at stationary sites within each zone.

|                | OA (µg/m$^3$) | sdev | SO$_4$ (µg/m$^3$) | sdev | Org. NO$_3$ (µg/m$^3$) | sdev | Inorg. NO$_3$ (µg/m$^3$) | sdev | NH$_4$ (µg/m$^3$) | sdev | Chl (µg/m$^3$) | sdev | OS$_c$ | sdev |
|----------------|---------------|------|-------------------|------|------------------------|------|------------------------|------|----------------|------|---------|------|-------|
| Zone 1         | 8.19          | 5.01 | 2.36              | 0.83 | 0.31                   | 0.21 | 0.04                   | 0.13 | 0.66          | 0.23 | 0.01    | 0.02 | -0.45  | 0.22 |
| Zone 2         | 2.48          | 1.81 | 1.53              | 1.28 | 0.08                   | 0.05 | 0.01                   | 0.01 | 0.45          | 0.36 | 0.01    | 0.01 | -0.30  | 0.26 |

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<thead>
<tr>
<th></th>
<th>O:C ratio</th>
<th>sdev</th>
<th>H:C ratio</th>
<th>sdev</th>
<th>OM:OC ratio</th>
<th>sdev</th>
<th>OA/ΔC O (µg/m$^3$) - ppbv</th>
<th>sdev</th>
<th>O$_3$ (ppbv)</th>
<th>sdev</th>
<th>NO$_x$ (ppbv)</th>
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<th>CO (ppbv)</th>
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<td>10.8</td>
<td>9.3</td>
<td>23.5</td>
<td>154</td>
<td>148</td>
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Figure 12. Diurnal distribution plots of PM$_1$ sampling time during DISCOVER-AQ 2013. Top plots are arranged according to stationary zones and the major site within each zone; bottom two plots include all stationary or mobile data collected in Houston. Trace gas sampling time distributions (not shown) follow similar trends as PM$_1$. 
Figure 13. Spatial distribution of POA, SOA and PM$_{1}$ constituents across the selected 16 stationary locations in the Houston area. The POA and SOA concentrations were estimated from the CO-tracer method.
Two major stationary sites were chosen for extended sampling in zone 1 (Conroe) and in zone 2 (Manvel). Conroe is situated near forest/sub-urban emissions in the north, and Manvel is south of the urban core and west of the HIR. These sites are at least 750 meters away from major roadways (TX-336 and TX-288 respectively) to avoid direct sampling of vehicle or point-source plumes. A large fraction of stationary sampling in zones 1 and 2 were conducted at these two sites (Table 8), and the sampling time at these sites was relatively well distributed diurnally (Figure 12). Manvel (zone 2) was defined here as a well-mixed urban background site due to the lack of direct influence from nearby sources, indicated by the comparatively strong correlation between CO and NO\(_x\) mixing ratios (Pearson R=0.775) observed at this site.

The OA/\(\Delta CO\) ratio serves as a surrogate for SOA formation [Aiken et al., 2009; Docherty et al., 2008; Takegawa et al., 2006], where \(\Delta CO\) represents measured CO less an urban background CO concentration of 100 ppbv. Additionally, \(\Delta CO\) allows an empirical estimate of the secondary fraction of sampled OA using the simplified CO-tracer method [Docherty et al., 2008; Takegawa et al., 2006]:

\[
POA = (POA/\Delta CO)_{\text{literature}} \times \Delta CO
\]

(E1)

\[
SOA = OA - POA
\]

(E2)

where primary organic aerosol (POA) (E1) was used to derive SOA fractions, assuming the absence of significant non-combustion POA sources. The POA/\(\Delta CO\) ratio of 0.008 \(\mu g/m^3\)-ppbv used here is the average of literature values derived from linear-regressions.
of ambient OA vs ΔCO in POA-dominated air-masses in urban environments (0.005-0.011 µg/m$^3$-ppbv) [Aiken et al., 2009; Docherty et al., 2008; Takegawa et al., 2006]. The CO-tracer approach compares well with other SOA estimation techniques [Docherty et al., 2008], while the SOA loadings estimated from the CO-tracer method agree well with the combined mass of SOA factors apportioned from positive matrix factorization (PMF) of OA mass spectra ($R^2=0.95$, slope=0.95) presented elsewhere [Leong et al., 2015b].

The background CO mixing ratio of 100 ppbv was derived from the linear regression between 5-minute averages of CO and NO$_x$ mixing ratios at the Manvel urban background site; a similar ‘clean’ background CO value was observed previously in Houston in 2006 (matching Northern Hemisphere background CO) [Lefer et al., 2010]. Filters were applied to total OA and ΔCO data used in the CO-tracer method to estimate POA and SOA contributions, as well as for computing OA/ΔCO ratios. ΔCO values above the 95$^{th}$ percentile (~500 ppb, 1-min averages) were filtered since these data points correspond to extreme plume events with non-representative OA/ΔCO ratios (e.g. in diesel-rich plumes). Rainy periods with low OA loading (<1 µg/m$^3$) also were excluded from this analysis because the relative uncertainties from the CO-tracer method would be largest, resulting in unfeasible results (e.g. POA > OA). Figure 14 illustrates the sensitivity of OA/ΔCO ratios and SOA fractions estimated from the CO-tracer method in each zone to varying background CO levels expected in Houston and to different literature POA/ΔCO ratios. As expected, the average SOA fraction increases with larger CO$_{\text{background}}$ and with smaller POA/ΔCO ratios. Average OA/ΔCO ratios and SOA fractions range from 0.085-0.156 µg/m$^3$-ppbv and 0.76-0.95 respectively, indicating the
predominance of SOA in measured OA mass in Houston and that the predicted ratios/fractions are not highly sensitive to variations in CO\textsubscript{background} and POA/ΔCO. Mainly, the CO-tracer method was relatively insensitive to changes in these parameters, indicating our central estimate (CO\textsubscript{background} = 100 ppb; POA/ΔCO = 0.008 µg/m\textsuperscript{3}-ppbv) as an appropriate estimate of SOA contributions in Houston.
Figure 14. Sensitivity of OA/ΔCO ratios (panel A) and SOA fractions estimated from the CO-tracer method (panel B) to varying background CO levels in Houston and to different literature POA/ΔCO ratios. Average SOA fractions are colored by zone and marker symbols represent different POA/ΔCO values obtained from literature. Cross (panel A) and square (panel B) markers at 100 ppbv CO_{background} represents the central estimate used in this study.

According to the CO-tracer approach, zones 1 and 2 exhibit high average SOA fraction (87% and 81% respectively), consistent with the high OA/ΔCO ratios (0.086 and 0.085 μg/m\(^3\)-ppbv respectively) that are representative of high SOA content. The CO-tracer estimated SOA accounts for ~90% of OA mass in zone 1 during an elevated OA period (OA=12.33 ± 4.70 μg/m\(^3\); September 23-27) and was highly correlated with the AMS Org-NO\(_3\) signal (Pearson R=0.90) during the day and at night. This is strong evidence of biogenic ON formation in the forested zone 1 that was particularly important during the elevated OA episode. A strong correlation between SOA mass and Org-NO\(_3\) still exists for the entire campaign in zone 1 (R=0.73) and in zone 2 (R=0.70) (Table 11), indicating strong mediation of SOA levels by ON processes in the entire Houston area including zone 2, which has slightly lower and less variable monoterpene mixing ratios (0.063 ± 0.087 ppbv in zone 2 compared to 0.074 ± 0.130 ppbv in zone 1). The higher average monoterpene concentrations in zone 1 are consistent with elevated SOA and Org-NO\(_3\) loadings (Figure 11 and Table 10), due to higher BVOC emissions in the north. These results are consistent with previous findings of enhanced ON processes in northern Houston from aircraft observations [Brown et al., 2013] and from model estimates [Russell and Allen, 2005]. Table 11 also shows varying but substantial correlation of AMS levoglucosan tracer ions for biomass burning OA (C\(_2\)H\(_4\)O\(_2^+\) and C\(_3\)H\(_5\)O\(_2^+\)) [Schneider et al., 2006] with both SOA mass and Org-NO\(_3\), indicating potential influence of biomass burning emissions on SOA/ON formation processes. This chapter provides an
overview of the importance of ON processes in each zone, but a detailed characterization of ON formation and biomass burning OA in Houston using positive matrix factorization are provided in chapter 4.

Table 11. Pearson R from correlation analysis of key indicators for biogenic SOA formation and biomass burning in each zone, using stationary data from sixteen main sites. Smoothing was applied to the 1-min data (5-point moving average) prior to regression analysis.

<table>
<thead>
<tr>
<th></th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 1 episode (9/23-9/27)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SOA mass</td>
<td>Org-NO(_3)</td>
<td>SOA mass</td>
</tr>
<tr>
<td>Org-NO(_3)</td>
<td>0.73</td>
<td>-</td>
<td>0.70</td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>-0.06</td>
<td>-0.06</td>
<td>-0.06</td>
</tr>
<tr>
<td>Isoprene</td>
<td>0.09</td>
<td>-0.11</td>
<td>-0.02</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>0.20</td>
<td>0.28</td>
<td>-0.01</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>0.79</td>
<td>0.44</td>
<td>0.94</td>
</tr>
<tr>
<td>tracer ions</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Finally, OS\(_c\) values were higher and more variable in zone 2, indicating on average more processed OA in the industrialized area and a mixture of freshly emitted and aged OA when compared to zone 1. The variations in OS\(_c\) for OA measured in different zones and air-masses are presented in the H:C vs O:C Van-Krevelen space [Heald et al., 2010] to describe aging/mixing processes in bulk OA (Figure 15). The OA elemental composition averaged by zones and by air-masses at Conroe and Manvel sites fall along the updated ambient OA fitted line in Van-Krevelen space [Chen et al., 2015], meaning bulk OA in
the HGB area generally follows mixing (decrease in OS\textsubscript{c}) and oxidation (increase in OS\textsubscript{c}) processes typically observed in bulk OA in other cities.

Figure 15. Van Krevelen “triangle” diagram of averaged elemental ratios (H:C and O:C) for sampled OA categorized by different zones (shape symbols) and by different trajectory clusters at the Manvel and Conroe site (e.g. text symbol M1A = Manvel cluster #1A). The Ng et al. [2011a] compiled ambient OA boundaries and the Chen et al. [2015] ambient OA fitted line (thick dashed black line) are updated with the Improved-Ambient elemental ratio calculations [Canagaratna et al., 2015]. From left to right, gray dashed slope lines correspond to increasing OS\textsubscript{c} values, while each gray solid line represents different functionalization processes in bulk OA [Heald et al., 2010]. The shaded circles represent average elemental ratios (± 1σ uncertainties) for fresh hydrocarbon-like OA (HOA), fresh semi-volatile oxygenated OA (SV-OOA), and aged/regional low-volatility oxygenated OA (LV-OOA) from AMS factor analyses [Canagaratna et al., 2015].
3.3.3 Diurnal and meteorological variations in PM$_1$ in each zone

The concentration of submicron aerosol species and OA oxidation metrics exhibited distinct diurnal trends in each of the defined pollution zones in Houston (Figure 16). The concentration of OA showed a moderate peak around 8:00 CDT in zone 1, with no particular enhancement in the H:C ratio, followed by continuous decrease during the day, and subsequent increase at nighttime. The concurrent increase in OA and Org-NO$_3$ concentrations during nighttime along with the diurnal trends observed for Org-NO$_3$ support the hypothesis of biogenic SOA production at night due to NO$_3$-driven oxidization of monoterpenes in zone 1 [Fry et al., 2013; Rollins et al., 2012; Rollins et al., 2013]. The daytime decrease in OA concentrations accompanied by an evident increase in the O:C ratio and OS$_c$ in zone 1 indicates strong photochemical processing and the prevalence of SOA potentially formed by photolysis-driven fragmentation [Henry and Donahue, 2012; Kroll et al., 2011] or by temperature-driven evaporation [Denjean et al., 2015] of biogenic SOA formed during nighttime.
Figure 16. Diurnal profiles of PM$_1$ species (in mass concentration units of µg/m$^3$) and oxidation metrics for submicron OA in zone 1 and zone 2 during DISCOVER-AQ. Bottom whisker, bottom box line, top box line and top whisker indicate the 5th, 25th, 75th and 95th percentile, respectively. Line inside the boxes and continuous solid line represent the hourly median and mean of the data, respectively.

In contrast, after evident enhancement in the oxidation state of OA during nighttime in zone 2, O:C ratio and OS$_c$ show a decreasing trend during the day accompanied by increasing H:C ratios, indicating important aging processes of OA at night, with a more reduced/primary character of OA during daytime and oxidation degrees that were
independent from photochemical processes. These observations are consistent with previous findings for industrial combustion/refining emissions of OA in the Houston area [Russell et al., 2009]. The concentration of OA in zone 2 peaks at 4:00 CDT and exhibits a continuous decrease during daytime and a marked increase at night. A peak in the H:C ratio was observed between 8:00-10:00 CDT, consistent with primary OA emissions during the morning rush hour, although minimal OA enhancement was observed at this hour. As observed in zone 1, Org-NO$_3$ in zone 2 shows a decrease in concentration during daytime followed by higher levels at night, indicating that nighttime ON formation, though lower in magnitude, likely occurs in zone 2. However, the less pronounced diurnal profile of Org-NO$_3$ as well as its higher variability (relative standard deviation ~62%) in zone 2 suggests that more variable sources of VOCs (compared with zone 1) with different Org-NO$_3$ yields could be involved in its formation in this region [Ayres et al., 2015; Rollins et al., 2012].

The diurnal trends of sulfate in zone 1 showed a relatively flat hourly profile with a first atypical peak at 9:00 CDT and a second less pronounced peak at 18:00 CDT, likely related with regional transport [Salcedo et al., 2006; Sun et al., 2011]. Sulfate concentrations in zone 2 exhibited a marked increase at nighttime and subsequent decrease during the day. As will be discussed in the following section, primary SO$_4$ detected in plumes sampled in zone 2 was expected to contribute to the elevated nighttime SO$_4$ levels in this industrialized area. Furthermore, the correspondence between the diurnal patterns of SO$_4$ and NH$_4$ in zone 1 and 2 indicates that NH$_4$ was predominantly associated with SO$_4$ in PM$_{1}$, given the low concentrations of Inorg-NO$_3$ during the campaign.
Median/mean wind polar plots for Conroe and Manvel sites (Figure 17) provide insight into the directional dependence of PM$_1$ sources influencing the Conroe and Manvel stationary sites. Secondary OA estimates at both sites show wind-direction dependence similar to total OA (not shown), indicating the predominance of SOA in all sampled air-masses. Secondary OA levels at the northwestern Conroe site were elevated from NW, N, NE, and E directions, with less SOA mass observed with winds from the urban/industrial directions. Both SOA and Org-NO$_3$ signals show similar wind patterns as NO$_x$, supporting previous observations of the influence of NO$_x$ on SOA and ON formation [Brown et al., 2013; Rollins et al., 2012]. In contrast, the sampled OA at Conroe appears to be more aged during southeasterly winds (based on OS$_c$ trends), indicating that OA from the urban core and HIR was likely more aged/processed than local or regional OA from other directions. The lack of wind-dependence in SO$_4$ levels at Conroe suggests that the SO$_4$ was predominantly regional (i.e. from long-range transport), though evidence of influence from primary SO$_4$ plumes from the HIR will be presented in the next section. Particle acidity (NH$_4$,measured/NH$_4$,predicted) does not exhibit wind-dependence at either site (not shown). This lack of wind-dependence and the absence of any correlation between acidity and SOA or OA levels in the stationary dataset rules out acid-catalyzed SOA formation mechanisms [Brock et al., 2003], consistent with the findings from a previous airborne study in Houston [Bahreini et al., 2009]. The directional dependence of aerosol parameters at the urban background Manvel site is discussed in the next section, because only four dominant air-mass types were observed when sampling here, two of which coincided with rainy periods.
Figure 17. Wind polar plots for stationary PM$_1$ and trace gas data collected at representative sites within zones 1 and 2, including organic NO$_3$ (dark blue) and inorganic NO$_3$ (light blue/cyan). At each location, measured parameters are divided by wind direction to compute the average (solid lines) and median (dashed lines) values for each parameter. Wind direction is presented in angular degrees from North. Shaded region denotes wind directions with at least 2% occurrence at the sampled location, shaded mean/median values have higher statistical relevance. Values at origin indicate insufficient data for the corresponding wind direction at each site.
3.3.4 Back-trajectory analysis at Manvel and Conroe sites

Because local wind variations can confound the directional analysis above, PM$_1$ has been classified by clustering HYSPLIT back-trajectories during sampling at the Conroe and Manvel field sites. The clustering algorithm identified four and six distinct back-trajectory clusters at Manvel and Conroe respectively. The 24-hr back-trajectories and cluster means corresponding to hourly stationary sampling at these sites are illustrated in Figure 10 and sampling periods for clusters are given in Table 12. Previous studies have identified significant enhancements in OA and SO$_4$ mass due to industrial/ship emissions in the HGB area [Bahreini et al., 2009; Brock et al., 2003; Wood et al., 2010], but have not focused on the influence of these emissions on OA composition (e.g. OS$_c$). The trajectory analysis presented here focuses on OA formation, aging, and mixing processes in air-masses influenced by industrial, urban, or biogenic emissions. Clusters are labeled based on #-site-number, e.g. clusters #2 from Manvel and #1 from Conroe are referred to as #M2 and #C1 respectively. Summaries of observed PM$_1$ and trace gas variables corresponding to each of these clusters are presented in Figure 18 (Manvel) and Figure 19 (Conroe). Gulf air-masses #M1B and #M3 coincided with a rainy period and aerosol washout (Figure 9).
Table 12. Details for clusters of back-trajectories sampled at Conroe and Manvel

<table>
<thead>
<tr>
<th>Cluster number</th>
<th>Site</th>
<th>Sampling period (CDT; local time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#M1A</td>
<td>Manvel</td>
<td>9/10 0:30 – 10:30</td>
</tr>
<tr>
<td>#M1B</td>
<td>Manvel</td>
<td>9/19 21:30 – 9/20 6:30</td>
</tr>
<tr>
<td>#M2</td>
<td>Manvel</td>
<td>9/21 7:30 – 19:30</td>
</tr>
<tr>
<td>#M3</td>
<td>Manvel</td>
<td>9/20 18:30 – 9/21 4:30</td>
</tr>
<tr>
<td>#C1</td>
<td>Conroe</td>
<td>9/6 4:30 – 14:30; 9/13 9:30 – 11:30</td>
</tr>
<tr>
<td>#C2</td>
<td>Conroe</td>
<td>9/11 10:30 – 9/12 8:30; 9/18 5:00 – 10:30</td>
</tr>
<tr>
<td>#C3</td>
<td>Conroe</td>
<td>9/24 14:30 – 9/25 11:30</td>
</tr>
<tr>
<td>#C4</td>
<td>Conroe</td>
<td>9/12 13:30 – 15:30; 9/23 5:30 – 10:30</td>
</tr>
<tr>
<td>#C5</td>
<td>Conroe</td>
<td>9/26 21:30 – 9/27 7:30</td>
</tr>
<tr>
<td>#C6</td>
<td>Conroe</td>
<td>9/26 1:30 – 11:30</td>
</tr>
</tbody>
</table>
Figure 18. Average values (solid diamond, color-coded) and box-and-whiskers plots of measured PM$_1$ parameters for three clusters of air-mass back-trajectories from the Manvel urban background site. The first plot on the top left also includes the total sampling time (hollow circles, in hours) that corresponds to each of the trajectory clusters. See Figure 10 for the SE (gulf, industrial), NE (inland), and S (gulf, mild traffic) trajectory clusters from Manvel. Missing box plots (SOA fraction, OS$_c$, and acidity parameter) indicate insufficient data for comparison.
Figure 19. Similar to the previous Figure 18, except values and statistics are for data obtained during six unique back-trajectory clusters at the northwest Conroe site.
The southerly Gulf cluster #M1A passed the Texas City industrial/port region before arriving at Manvel and was expected to have some degree of influence from the petrochemical and ship emissions expected from that area. The northerly cluster #M2 was expected to have regional influence from east Texas and the adjacent states, in addition to local sources in north/central Houston. [Bates et al., 2008] observed PM$_1$ concentrations from northerly flow twice as large as loadings from southerly flow when sampling on a cruise near the Houston Ship Channel. The opposite trend was observed at Manvel, with consistently higher OA and SO$_4$ mass in the southerly cluster #M1A when compared to the northerly cluster #M2. The OA sampled in cluster #M1A also exhibits higher OS$_e$ relative to continental #M2. Additionally, the elevated NO$_x$ concentrations in #M1A relative to other clusters also point to influence from local sources. These observations indicate significant sources of aged OA and SO$_4$ from Texas City.

A similar phenomenon of consistently elevated OS$_e$ was observed in cluster #C1 at Conroe, which was a southerly Gulf air-mass that also travelled near Texas City and outside of the urban core prior to arriving at the sampled at the Conroe site. Additionally, the OS$_e$ levels observed in the industrial clusters (#M1A and #C1) were equally enhanced at night. The direct emission of highly oxygenated OA from industrial/refining processes suggested previously in Houston [Russell et al., 2009] may explain these observations, though it was possible that nighttime oxidants were also responsible for the rapid aging of OA. The rapid SOA formation and aging observed in industrial plumes by aircraft measurements [Bahreini et al., 2009] due to elevated concentrations of OH and AVOCs supports this theory, though these measurements were conducted during the day. The nitrate radical can be formed rapidly at night in power plant plumes [Zaveri et al., 2010]
and is capable of oxidizing OA [Qi et al., 2012], making it a possible candidate (along with O₃) for nighttime aging of OA. The enhanced OSₑ values at night relative to daytime values in zone 2 (a trend not seen in zone 1) supports the theory of a nighttime OA aging process that potentially outweighs those during the day. Finally, it was unlikely that aged background OA from the Gulf contributed solely to the moderately elevated OA (~3.5-5.0 µg/m³) in zone 2 and high OSₑ (~0.3 to -0.1) levels observed in these air-masses, as previous factor analysis in the HIR attributed higher influence of aged/regional OA from northerly trajectories than Gulf trajectories [Russell et al., 2009]. This case study of enhanced OA oxidation states in clusters #M1A and #C1 suggest possible nighttime rapid aging of OA in industrial plumes from Texas City or the Ship Channel that was independent of photochemistry.

Several clusters in Conroe (#C3, #C5, and #C6) showed particularly enhanced SOA and Org-NO₃ signals, indicating strong biogenic episodes that coincided with highly correlated SOA and Org-NO₃ levels mentioned in Section 3.1. The elevated Org-NO₃ in the industrial clusters (#M1A and #C1) also supports the importance of the NO₃ radical in nighttime SOA aging/formation. These elevated ON events are discussed in detail in the separate manuscript focused on positive matrix factorization analysis [Leong et al., 2015b].

Cluster #M1A exhibits slight enhancement of SO₄ levels over the regional cluster #M2, suggesting possible primary SO₄ sources from Texas City. Elevated SO₄ levels also were observed in cluster #C5 (~3.5 µg/m³), which originated from the HIR and typically occurred at night. Considering transport times from potential sources in the HIR and the relatively slow conversion rate of SO₂ to SO₄, these plumes are probably caused by
primary emission. These observations are corroborated by several high-mass primary ammonium sulfate plumes observed during our mobile surveys in Texas City and the HIR, sampled directly downwind of petrochemical facilities (1-min averaged $\Delta$SO$_4$ enhancement = 3-30 µg/m$^3$; 200-300 nm size range; one such example shown in Figure 20).

![Figure 20. Time series and MS (inset) of a plume from a petrochemical facility in Texas City, TX near Houston.](image)

**3.2.5 PM$_1$ data inter-comparison and quality control**

In addition to the qualitative agreement between campaign-averaged PM$_1$ mass composition with the two independent measurement platforms (UT ACSM and ARI SP-AMS aboard a mobile laboratory) (Figure 11), we present here additional data comparisons for validation purposes. Note that the three PM$_1$ measurement systems of interest were operated independently without direct quantitative cross-calibrations and inlet loss comparisons. Due to project restrictions, there were limited co-located inter-comparison opportunities with the SP-AMS. The only co-located period with the ARI instrument (approximately 4 hours) was inconclusive due to potential contamination from
power generator emissions or the sampling of different airmasses. These data were
removed from our analyses due to the contamination. However, the MAQL was co-
located with the UT ACSM at Conroe during several sampling periods for comparison,
though the ACSM is an instrument intended for long-term, low-time-resolution PM\textsubscript{1}
characterization. Thus, the ACSM is expected to have lower sensitivity, and several
quantification issues were possible during DISCOVER-AQ (particularly involving SO\textsubscript{4}).
Given these issues, good correlation was observed between the AMS and ACSM 30-
minute averaged mass concentrations for OA, NO\textsubscript{3}, and SO\textsubscript{4} (with slopes of 1.2, 0.9, and
1.6, respectively).
Ammonium data was sparse for the UT ACSM, due to difficult quantification of NH\textsuperscript{+},
NH\textsubscript{2}\textsuperscript{+}, and NH\textsubscript{3}\textsuperscript{+} ions in the lower m/z-resolution MS from this instrument. As such, our
campaign-averaged acidity metric (NH\textsubscript{4,measured}/NH\textsubscript{4,predicted} = 0.75) was compared to that
measured by the SP-AMS (0.50). The lower acidity metric observed by ARI could be due
to two reasons: 1) inorganic RIE calibration disagreements between the HR-AMS and the
SP-AMS; and/or 2) the predominance of industrial plume sampling by the ARI mobile
laboratory (frequent sampling of primary acidic H\textsubscript{2}SO\textsubscript{4} particles). Regardless, both
instruments suggest the “acidic” or NH\textsubscript{4}-poor nature of particles sampled in Houston.
On the other hand, based on NO\textsuperscript{+}/NO\textsubscript{2}\textsuperscript{+} ratios observed by the UT ACSM (Conroe) and
the ARI SP-AMS (industrial area), the majority of NO\textsubscript{3} mass sampled during
DISCOVER-AQ also were associated with ON (\textit{personal communication}, Dr.
Hildebrandt from UT and Dr. Massoli from ARI). This provides validation for the ON-
dominated NO\textsubscript{3} signal observed by the MAQL throughout Houston and the importance of
biogenic SOA and ON formation processes discussed in chapters 3 and 4.
3.3.6 Summary of results

An extensive PM$_1$ mass spectral dataset was collected using an HR-ToF-AMS aboard the MAQL during DISCOVER-AQ 2013, allowing for spatial characterization of PM$_1$ chemical composition in the HGB area. Cluster analysis allowed the establishment of two distinct PM$_1$ pollution zones for the first time in Houston. The highest PM$_1$ mass concentrations were observed in the northern zone 1, dominated by SOA mass that was likely driven mostly by nighttime biogenic ON formation. Nitrate radical chemistry potentially drives a large portion of elevated OA mass in the north, highlighting the impacts of NO$_x$ emissions in the BVOC-rich sub-urban forested zone 1. Principal component analysis results further emphasize the importance of nighttime formation of ON in northwest Houston, and indicate the relevance of photochemical processes associated with daytime formation of secondary PM$_1$ in zone 2. Our analysis identified potentially short-lived but substantial emission of primary or secondary OA and SO$_4$ in zone 2 from industrial sources. Several back-trajectory case studies in zone 2 have identified potentially strong sources of highly oxidized OA from the Texas City industrial region, either through rapid day/night oxidant chemistry or direct emission of highly oxygenated OA.

The next chapter provides a more in-depth analysis of SOA and ON sources in Houston, by utilizing factor analysis and two NO$_3$ apportionment techniques. The roles of biomass burning and anthropogenic emissions on OA will be more clearly elucidated.

3.4 Chapter 3 appendix

The appendix to this chapter includes summaries of statistical data analysis efforts that were integral to the spatial overview of PM$_1$ presented above. These analyses include: 1)
a two-step cluster analysis on stationary data from DISCOVER-AQ; and 2) a principal component analysis on the combined trace gas and PM$_1$ data (mobile and stationary data). These statistical analyses were performed by Dr. Nancy P. Sanchez (Research Scientist from our research group), with whom I collaborated closely by providing accurate PM$_1$ and trace-gas data and by jointly interpreting the results of these analyses. The analyses presented in this chapter and appendices were combined to form the DISCOVER-AQ overview manuscript [Leong et al., 2015a]. Also included in this section are acknowledgements for our data originators and collaborators.

### 3.4.1 Cluster analysis for the establishment of PM$_1$ pollution zones

In order to better examine the spatial variation of PM$_1$ species in the HGB area and considering that different conditions present across the HGB (e.g. traffic activity, forested areas, levels of industrial activity, etc) could lead to large variability in the character of submicron aerosol, a two-step cluster analysis was performed to define distinct PM$_1$ pollution zones across Houston. Stationary data collected at sixteen main locations encompassing sampling times between 1 and 70 hours were used for the clustering task (SPSS 20.0, IBM Corp., Armonk, NY, USA). The number and quality of clusters established based on geographical coordinates and different variables including PM$_1$ total and speciated mass concentrations and elemental ratios were investigated. The optimum number of clusters in the dataset was determined based on the log-likelihood as the distance measure and the Schwarz’s Bayesian criterion as the clustering criterion. The variable having the largest influence (i.e. predictor importance) in the cluster definition was selected, and the Silhouette measure of cohesion and separation and the ratio between cluster sizes were examined in order to determine the adequacy of the defined
clusters. Potential spatial outliers were investigated based on the Anselin Local Moran’s I statistic using ArcMap 10.1 Spatial Statistics Tool (ESRI, Redlands, CA, USA).

### 3.4.2 Principal component analysis of combined PM$_1$ and trace gas data

The specific processes/sources influencing the pollution zones defined for the Houston area and their relative contribution to the observed variability in the measured PM$_1$ and trace gases in these, were investigated using principal component analysis [Hopke et al., 1976]. Correlation matrices of stationary and mobile datasets (sampling time distribution presented in Table 8) comprising 60-sec average concentration of PM$_1$ species (OA, SO$_4$, NH$_4$, NO$_3$ and Chl), trace gases (SO$_2$, NO, NO$_2$, CO and O$_3$), BVOCs (isoprene and monoterpenes) and meteorological parameters (temperature and RH) acquired in each pollution zone were analyzed by PCA using SPSS 20.0 (IBM Corp., Armonk, NY, USA). The Kaiser-Meyer-Olkin measure of sampling adequacy and the Bartlett’s test of sphericity were used to examine the appropriateness of each data set to be analyzed effectively by PCA. After examination of the scree plot, factors with eigenvalues above 1 and explaining at least 70% of the variability in each dataset were retained in the distinct zones. Varimax rotation was applied to the retained factors, and variables with loadings above 0.5 were used to establish the probable identity of the factors and the associated underlying processes/chemistry. The variability in the contribution of each factor along the zone-specific datasets was examined based on the standardized factor scores.

### 3.4.3 PCA results

Principal component analysis conducted independently in zones 1 and 2 indicated that four and five main factors explain over 80 and 74 % of the variance, respectively, of the combined datasets in each zone. These datasets include stationary and mobile trace gas,
PM$_1$, and BVOC concentrations, along with meteorological parameters. The loadings of the different variables in the retained factors after Varimax rotation are presented in Figure 21. Factor 1 in zone 1 (PC1$_{z1}$), which explains approximately 33% of the variance in the data set, has important positive loadings of Org-NO$_3$ and monoterpenes, significant negative loadings of O$_3$ and meteorological factors (i.e. temperature), and moderate loadings of OA. The diurnal variation of the standardized factor score for PC1$_{z1}$ (Figure 22) shows a marked increase during nighttime and lower levels during the day, resembling the trend observed for Org-NO$_3$ in zone 1. According to this, PC1$_{z1}$ is classified here as monoterpane-driven ON formation. Diurnal variation of this factor is similar to that exhibited by factor 3 in zone 2 (PC3$_{z2}$, explaining ~13% of the total variance in the zone 2 data set), which also shows high loadings of monoterpenes and Org-NO$_3$. The reduced contribution by PC3$_{z2}$ to the dataset variance in zone 2 points to the relatively reduced importance of biogenic SOA in zone 2 when compared to zone 1. Additionally, the less pronounced diurnal variation of PC3$_{z2}$ (Figure 22) compared with PC1$_{z1}$, suggests that more diverse sources of VOCs might be involved in the formation of Org-NO$_3$ in zone 2. The relevance of biogenic emissions in zone 1 is further demonstrated by the presence of a factor explaining approximately 9 % of the total variance in the specific dataset and with a predominant loading of isoprene (factor 4, PC4$_{z1}$). The hourly variation of PC4$_{z1}$ (Figure 22) resembles the diurnal profile of isoprene mixing ratios reported in previous studies [Ng et al., 2008]. Note that the OA loading is low in the PC4$_{z1}$ factor, indicating that monoterpane emissions were more important than isoprene for SOA formation in zone 1 (PC1$_{z1}$), consistent with findings from chapters 3 and 4.
Figure 21. Loadings of variables in rotated factors retained in zone 1 and 2 using principal component analysis (PCA).
Figure 22. Diurnal averaged variations of standardized factor scores retained after principal component analysis in zone 1 and 2.
Factor 2 in zone 1 (PC2\textsubscript{z1}), explaining ~22\% of the total variance in the data set, is dominated by SO\textsubscript{4}, NH\textsubscript{4} and Inorg-NO\textsubscript{3} and represents relevant secondary processes leading to the formation of inorganic aerosols (e.g. SO\textsubscript{2} oxidation to SO\textsubscript{4}). Factor 3 in zone 1 (PC3\textsubscript{z1}), reflecting traffic and industrial emissions (high loadings of NO, NO\textsubscript{2} and SO\textsubscript{2}) and explaining ~16\% of the variance in the dataset, exhibits a diurnal profile with a sharp peak between 6:00 and 10:00 CDT and a secondary peak between 18:00 and 20:00 CDT (Figure 22), corresponding to periods of important traffic activity. The morning peak in PC3\textsubscript{z1} concurs with the periods of marked increase observed in the hourly levels of PC2\textsubscript{z1}. Loadings in PC3\textsubscript{z1} closely resemble those observed in factor 2 in zone 2 (PC2\textsubscript{z2}), which explains ~16\% of the variance in the dataset and is classified here as an anthropogenic emissions-related factor. In contrast with PC3\textsubscript{z1}, no clear patterns are observed in the diurnal variation of PC2\textsubscript{z2}, likely reflecting the mixed nature of the distinct industrial and traffic sources present in zone 2.

While two of the factors identified in zone 1 and 2 (PC1\textsubscript{z1}/ PC3\textsubscript{z2} and PC3\textsubscript{z1}/ PC2\textsubscript{z2}) showed agreement (with different contributions to the variability in the respective datasets), PC2\textsubscript{z1} and PC4\textsubscript{z1} did not resemble any of the additional factors retained in zone 2 (Factor 1-PC1\textsubscript{z2}, 4- PC4\textsubscript{z2} and 5- PC5\textsubscript{z2}). PC1\textsubscript{z2} (~30\% of the total variance) has high loadings of SO\textsubscript{4} and NH\textsubscript{4} and more moderate loadings of OA, Org-NO\textsubscript{3} and O\textsubscript{3} (Figure 21). The hourly variation of this factor (Figure 22), which shows peak values during daytime, as well as the high loadings of aerosol species, indicates that PC1\textsubscript{z2} represents photochemically-driven processes related with the formation of secondary inorganic and organic PM\textsubscript{1} in zone 2 [Chan and Mozurkewich, 2007; Zhou et al., 2004]. Factor 4 (PC4\textsubscript{z2}) and 5 (PC5\textsubscript{z2}) in zone 2 have an aggregate explained variance of ~15\% (9 and 6\%
correspondingly), with predominant loadings of Inorg-NO$_3$ and chloride, respectively. Hourly variation of PC4$_{z2}$ shows a sharp peak occurring in the early afternoon that does not correspond to typical trends reported for Inorg-NO$_3$. The diurnal profile of PC5$_{z2}$ exhibits an early morning peak and continuous decreasing during the day, which agrees with observations previously reported for chloride [Sun et al., 2011]. Clusters of high levels of PC5$_{z2}$ (HH clusters based Anselin Local Moran’s I, see supplementary information) (Figure 23) were mostly concentrated in the Houston Ship Channel area and in a portion of central Houston, indicating that PC5$_{z2}$ likely represents chloride from industrial sources primarily centralized in the northeast part of zone 2.
Figure 23. Cluster analysis of PC5 standardized scores in zone 2. Cluster type established by Anselin Local Moran’s I statistic using ArcMap 10.1 Spatial Statistics Tool (ESRI, Redlands, CA, USA). HH and LL correspond to statistically significant ($p < 0.05$) clusters of high and low PC5 scores, respectively.

PCA results indicate marked differences in the dominant atmospheric processes/sources involved in each pollution zone and show that the relative importance of these zone-specific processes follows the order: biogenic SOA (monoterpene-derived Org-NO$_3$) >
secondary processes leading to inorganic PM$_1$ formation > traffic/industrial combustion emissions > BVOCs emissions (predominantly isoprene) in zone 1, and photochemical-driven processes > traffic/industrial combustion emissions > biogenic SOA (primarily monoterpane-derived Org-NO$_3$) > Inorg-NO$_3$ > chloride (likely from industrial processes) in zone 2. Note that the PCA results are likely to be modified and improved with updated CMAQ simulations of isoprene and monoterpenes, amines, and other potentially important parameters that have not yet been incorporated.

3.4.4 Trace gas and ancillary data originators

Trace gas and meteorology data recorded aboard the MAQL was processed and provided by members of the research group at University of Houston (PIs: Dr. Barry Lefer and Dr. James Flynn). Simulated BVOCs concentrations (isoprene and monoterpenes) from the CMAQ model were provided by Dr. Yunsoo Choi from University of Houston, a description of this model can be found in [Pan et al., 2015]. Finally, aerosol composition data for qualitative comparisons were provided by ARI and Dr. Lea Hildebrandt from University of Texas.
Chapter 4. Source Apportionment of Organic and Nitrate Aerosols using Factor Analysis of High Resolution Mass Spectrometry Data during DISCOVER-AQ 2013 Texas

4.1 Literature review

4.1.1 PMF source apportionment

The organic ensemble MS from the AMS can be deconvolved into different components to account for primary/secondary OA mass contributions and for source apportionment purposes [Aiken et al., 2009; Ulbrich et al., 2009; Zhang et al., 2011]. The custom principle component analysis (CPCA) method initially was used to analyze AMS OA data (consisting of real-time MS signals), yielding two factors/components of OA [Zhang et al., 2005a]. These factors are the chemically reduced hydrocarbon-like OA (HOA) that represents POA from urban sources and oxygenated OA (OOA) that represents SOA [Zhang et al., 2011]. An expanded version of this technique (multiple component analysis, MCA) was used to separate more than two factors from the OA. MCA was applied to 37 AMS datasets obtained from various field sites (ranging from urban to remote), and the main observation was that OOA dominated total observed OA mass, indicating the ubiquity of SOA in PM [Zhang et al., 2007].

Similar in concept to CPCA and MCA, PMF is a bilinear unmixing model that constrains the factor MS matrix to be positive (its main distinction and improvement compared with previous methods); PMF applies a weighted least-squares method when solving for factors [Paatero and Tapper, 1994; Ulbrich et al., 2009]. *A priori* information on the source profiles is not required by this statistical model, but PMF assumes that these source profiles remain constant with only the overall factor contributions to total OA
varying with time. PMF has been used extensively for factor analysis of AMS field data to resolve POA into components such as HOA, biomass burning OA (BBOA), wood burning OA (WBOA), and cooking OA (COA), while SOA factors commonly can be separated into low-volatility OOA (LV-OOA) and semi-volatile OOA (SV-OOA) factors [Crippa et al., 2013; Mohr et al., 2011; Ng et al., 2010; Ulbrich et al., 2009; Xu et al., 2015a; Zhang et al., 2011]. Coupled with measurements of tracers, meteorology, and aerosol properties (e.g. volatility, elemental ratios), the interpretation of the OA components has improved our understanding of the evolution and formation of ambient OA significantly [Jimenez et al., 2009; Ng et al., 2011a; Ng et al., 2010]. PMF has been applied to stationary [Xu et al., 2015a], mobile [Mohr et al., 2011], and aircraft AMS measurement data [DeCarlo et al., 2010].

The PMF OA factors mentioned above have been resolved at a large number of field sites in the northern hemisphere, and the OOA factors at different regions appear to become increasingly similar to each other chemically as they become highly aged/processed [Ng et al., 2010]. While PMF has been applied to factor analysis of other ambient measurements (e.g. VOCs and non-AMS measurements of PM species) [Buzcu and Fraser, 2006; Buzcu et al., 2003; Russell et al., 2009] in the HGB area, there are minimal studies applying PMF on high mass- and time-resolution ambient AMS data. Wood et al. [2010] discuss three factors (OOA, HOA, and BBOA) resolved by PMF using Q-AMS data at the La Porte industrial site in the eastern HGB and observed a correlation between OOA and odd oxygen (O\textsubscript{x} ~ O\textsubscript{3} + NO\textsubscript{2}) during TexAQS-2000. During TRAMP 2006, Cleveland et al. [2012] applied CPCA on Q-AMS data at Moody Tower (downtown) to resolve OA into HOA and OOA and found that OOA dominated (~2/3) OA mass in
Houston and are likely secondary but less regional in nature (i.e., less aged/processed). However, accurate O:C elemental ratios from a HR-AMS were not available for the factor analysis study by Cleveland et al. [2012]. Likewise, these previous studies were not able to separate OOA into SV-OOA (a common tracer for freshly produced SOA) and LV-OOA (a tracer for aged, regional SOA), which provide useful information on the local versus regional contribution of SOA in the HGB area. Wood et al. [2010] resolved a BBOA factor during TexAQs 2006, though biomass burning (BB) influence in Houston appears to be highly episodic and spatially dependent because BB marker concentrations were substantial in some studies [Wood et al., 2010; Yue and Fraser, 2004] but low/below-detection in others [Cleveland et al., 2012; Shakya et al., 2011].

Factor analysis using HR-AMS data provides better separation of factors (e.g., OOA into LV-OOA and SV-OOA) and allows for better characterization of chemical functionality and oxidation state (e.g., O:C) of these components [Aiken et al., 2009; Crippa et al., 2013; DeCarlo et al., 2010; Hao et al., 2014; Sun et al., 2012; Xu et al., 2015a]. For example, HOA components should have higher H:C and lower O:C when compared to the more oxidized OOA. Additionally, PMF studies using HR-AMS data have made significant progress recently by identifying new factors and generating new approaches to applying the model. By including inorganic AMS signals (SO$_4^{2-}$, NH$_4^+$, and NO$_3^-$) into the PMF input data matrix, Sun et al. [2012] identified eight total factors, though several factors were dominated by inorganic signals (i.e., inorganic factors); the accurate interpretation of such a large number of ‘true’ factors appears challenging. Conversely, Hao et al. [2014] included only the NO$_3^-$ signal in PMF and successfully split the NO$_3^-$ signal into three organic factors (HOA, SV-OOA, and LV-OOA) and a “nitrate inorganic
aerosol” (NIA) factor. This approach has strong implications as an alternative method to quantify the organic NO$_3$ functional groups found in organic nitrates (as discussed in Section 3.2.2.4 above) and was utilized in our PMF study. Of particular focus in this thesis are the correlations observed between the SV-OOA factor (less aged, locally produced SOA) and organic NO$_3$ groups, by Hao et al. [2014] in an urbanized boreal forest in Finland, and by Xu et al. [2015a] in a subtropical forested site in Southeast US. Both studies point to strong anthropogenic influence of NO$_x$ on nitrate-radical initiated, nighttime secondary formation of particulate ON, a phenomena that was likely very important in the forested area north of HGB [Brown et al., 2013] and was evaluated in detail at the surface in this study. Other PMF factors identified with HR-AMS data include marine OA (MOA) [Crippa et al., 2013], cooking OA (COA) [Sun et al., 2012], and isoprene OA (Isoprene-OA) [Xu et al., 2015a].

4.1.2 Biomass burning emissions

Biomass burning, particularly from large forest fires, contributes to significant primary and secondary gas/aerosol pollutants and has large impacts on local and regional air quality [Crutzen and Andreae, 1990; Kaufman et al., 1998]. Primary BB emissions have been characterized by experimental measurements (e.g. Akagi et al. [2011]) and secondary O$_3$ enhancement in BB plumes has been reliably modeled (e.g. Trentmann et al. [2003]). However, there remain significant uncertainties and uncharacterized reactions involving secondary PM formation (dominated by OA) in BB plumes. Several recent studies have investigated the aging and processing of BB smoke [Cubison et al., 2011; Hennigan et al., 2011; Jolley et al., 2015; Ortega et al., 2013], a process that can produce substantial SOA loadings downwind of BB sources. The AMS has been deployed to
characterize molecular markers from primary BBOA [Schneider et al., 2006] and SOA formation and growth from photooxidation of BB smoke [Ortega et al., 2013] in the laboratory as well as BBOA evolution in the ambient atmosphere [Cubison et al., 2011; Jolleys et al., 2015]. Since BBOA is mixed with other sources of OA, source apportionment techniques such as PMF have allowed improved characterization of the influence of BB plumes on OA levels [Aiken et al., 2009; Alfarra et al., 2007; Mohr et al., 2012; Xu et al., 2015b]. The BBOA factor has been correlated with brown carbon – a type of OA that absorbs solar energy at a wide range of wavelengths and has important climate implications [Washenfelder et al., 2015; Xu et al., 2015b]. The BBOA factor has been reported previously in Houston at the industrial La Porte site [Wood et al., 2010]. Biomass burning influence was observed during several nighttime aircraft surveys north of Houston, though the influence on local OA loadings and chemistry were unclear [Brown et al., 2013]. The relative importance of primary versus secondary OA mass in BBOA is variable and remains the focus of current BBOA studies.

4.1.3 Characterization of vehicular and industrial plume events

We have discussed the importance of industrial emissions of PM$_1$ and O$_3$ precursors, while several observations in chapter 3 suggest strong influence of industrial emissions on primary SO$_4$ in the HGB area. Aircraft measurements in Houston found that SO$_2$-rich industrial plumes resulted in enhanced SO$_4$ and OA aerosol volume/mass growth downwind of sources [Bahreini et al., 2009; Brock et al., 2003]. Industrial emissions from wastewater treatment and chemical plants were identified using the AMS as potential sources of organic amines in Ontario, Canada [McGuire et al., 2014], while industrial submicron Chl sources have been reported in Mexico City [Moffet et al., 2008]. The
characterization of the extent and chemical nature of industrial PM emissions near-source and at receptor locations in Houston (on-road or in housing areas) is important in terms of exposure risks and emissions control.

Vehicular emissions from gasoline and diesel engines are important sources of POA in urban areas, but the fate of POA upon emission remains poorly understood [Jimenez et al., 2009]. Diesel sources (usually in the form of heavy duty vehicles/trucks) have been identified as major PM emitters [Chirico et al., 2011; Fraser et al., 2003a]. The emitted POA can be in the form of unburned fuel or lubricant oil particles. Several studies have utilized mass spectral signatures from AMS (or similar) quantification of POA emitted from diesel engines and concluded that unburned lubricating oil contributes a large portion of the emitted POA mass [Canagaratna et al., 2004; Dallmann et al., 2014; Sakurai et al., 2003; Tobias et al., 2001]. There is also evidence of similar POA composition between diesel and gasoline sources [Dallmann et al., 2014], such that both types of POA showed large contributions from lubricating oil. Laboratory measurements of POA emissions under atmospherically relevant dilution ratios observed a negative correlation between O:C and POA mass loading [Collier et al., 2015]. The authors proposed that this correlation could be explained by the evaporation of more-volatile and reduced organics upon dilution, or by the fact that lubricant-derived particles were more dominant under high mass loading conditions. Because lubricating oil particles (and the co-emitted VOCs) are different in composition than fuel, the relative contribution of each component in vehicular emissions in Houston are thus highly important. For instance, we have shown in chapter 2 that VOCs from engine oil are capable of converting HNO₃ to
HONO. Such a reaction would likely be very important in Houston if the majority of
gas/particle emissions from vehicular sources were derived from lubricating oil.

4.2 Methodology for this study

4.2.1 PMF OA apportionment

As mentioned above, PMF is a bilinear unmixing model that assumes that the fitted AMS
time series (with \( i \) number of MS measured at each time step) is a linear combination of \( p \)
number of factors that has constant mass spectral profiles but varying relative
contributions to the total fitted MS signal [Ulbrich et al., 2009]. The assumption of
constant MS (with time) is key to this technique and this assumption will be evaluated in
this chapter. The PMF model is explained by the following equation:

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

Equation 5

where \( i \) and \( j \) refer to indices of rows (time stamps) and columns (m/z of fragments fitted
and chosen for PMF analysis) respectively; \( p \) refers to total number of factors in each
solution; \( x_{ij} \) is an element of the \( m \times n \) matrix \( X \); and matrix \( X \) consists of the \( m \times n \) (\( m =
m/z fitted in each MS; \( n = number of MS collected) data elements to be fit by PMF. The
data matrix \( X \) here can be modeled as the sum of \( f_{ip} \) (an element of the mass contribution
\( p \times n \) matrix \( F \) for each factor) multiplied by \( g_{ip} \) (an element of the factor time series \( m \times p \) matrix \( G \)), plus \( e_{ij} \) (an element of the residual \( m \times n \) matrix \( E \); residual refers to the MS
signals not fit by the model). Contrary to previous component analysis techniques, PMF
also constrains matrices \( G \) and \( F \) to be positive because negative MS signals in
factor/source profiles do not have real physical meaning. The model iteratively solves for matrices $G$ and $F$ with a weighted least-squares algorithm used to minimize $Q$ (quality of fit parameter), as given by:

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} (e_{ij}/\sigma_{ij})^2$$

Equation 6

where $\sigma_{ij}$ is an element of the $m \times n$ error matrix that corresponds to the 1-sigma estimated signal errors (uncertainties in the AMS ion count rate) of each element in matrix $X$. The PMF2 algorithm v.4.2 [Paatero and Tapper, 1994] was used to solve for matrices $G$ and $F$ assuming different number of factors ($p = 1$ to 10), while the PMF Evaluation Tool (PET, v2.06b) [Ulbrich et al., 2009] software was utilized for the selection of the optimized solution. An optimized solution entails the selection of the correct number of physically meaningful factors (e.g., factors with distinct time trends that correlate with internal/external tracers) that minimizes $Q/Q_{\text{expected}}$, where $Q_{\text{expected}}$ is calculated from the degrees of freedom of the data matrix $= mn - p(m+n)$ or $\sim mn$ since $mn >> p(m+n)$ in AMS datasets. Consecutively, different fPeak parameters in the PMF model were chosen for each model run to explore a subset of the rotational ambiguity of the chosen solutions [Paatero and Tapper, 1994; Ulbrich et al., 2009]. Selecting a non-zero fPeak parameter imposes distorted positive (fPeak > 0) or negative (fPeak < 0) rotations (or linear transformations) on the solution matrices and increases $Q/Q_{\text{expected}}$. A range of fPeak values were tested in PMF2 such that $Q/Q_{\text{expected}}$ increases by more than 10%, as recommended by Ulbrich et al. [2009]. To determine the qualitative uncertainties
in the chosen PMF solution, different starting pseudorandom values in the PMF2 algorithm [Paatero, 1997] known as SEED values were tested to rule out local minima in the optimized solution produced by the fitting algorithm (integer SEED values tested were 1 to 50). Bootstrapping analysis [Norris et al., 2008] (50 iterations) also was employed to determine quantitatively 1-σ statistical uncertainties in the factor MS and time series [Ulbrich et al., 2009].

The HR dataset obtained from DISCOVER-AQ required additional processing to yield meaningful PMF results. Standard data pre-treatment and weighting procedures were used [Ulbrich et al., 2009; Zhang et al., 2011], and the appropriate diagnostic tools in addition to those mentioned above were used to choose the optimized PMF solution for this particular dataset. Briefly, the data and 1σ error matrices were produced from the PIKA software. A minimum error corresponding to the signal uncertainties from sampling a single ion during one sampling period in the AMS was calculated using PIKA and applied to the error matrix [Ulbrich et al., 2009]. Next, spiky time periods corresponding to bad MS sampling (e.g., due to electronic noise) were removed from these matrices. Certain ions (m/z) were removed or down-weighted from the data and error matrices when low signal-to-noise ratios (SNR) were observed [Ulbrich et al., 2009]. As recommended by Paatero and Hopke [2003], ions with SNR < 0.2 were considered bad and were removed entirely, while ions with SNR < 2 but larger than 0.2 were down-weighted by increasing their associated errors in the error matrix by a factor of 2. Several ions (e.g., CO+) in the HR spectrum were estimated based on proportionality with the CO2+ signal using a fragmentation table [Allan et al., 2004] and were down-weighted accordingly to avoid “over-weighting” the errors from the CO2+ ion. An error diagnostics
tool was used as supplement to the PIKA software to determine if errors for particular ions were underestimated; these were adjusted accordingly. Finally, by iterating several model runs using PMF, several additional data points in the time series were removed due to extreme plume events (likely POA) that were badly under-fit by the model.

Upon PMF analysis of the HR-AMS data, the resolved OA factors were compared to other co-located external tracer measurements as well as internal tracers (specific species or tracer ions measured by the AMS). This not only facilitates the identification of distinct factors (as HOA, BBOA, OOA, and etc.) but also ensures that the resolved factors represent physically real PM sources/types. The component MS for each factor have been compared to those from an online database of published studies, as component MS obtained from different locations are fairly similar and have matching characteristics (e.g., HOA factors show high signals of saturated alkane, alkene, and cycloalkane ions). Any differences observed in these MS would also be interesting.

In addition to being used as external tracers for comparison with OA components, the inorganic species and their fragments from HR-AMS data have been included in PMF to resolve more components of OA [Sun et al., 2012] because the inorganic portion can be internally mixed with OA and can provide additional information when included in the PMF analysis. In particular, Hao et al. [2014] and Xu et al. [2015b] successfully have included the AMS NO$_3^-$ signal (with mixed contributions from Org-NO$_3^-$ and Inorg-NO$_3^-$) into PMF analysis, resolving for certain datasets a nitrate inorganic aerosol (NIA) factor dominated by Inorg-NO$_3^-$ and simultaneously apportioning the remaining NO$_3^-$ into different PMF factors. Thus, in order to utilize PMF as an independent NO$_3^-$ source apportionment technique and to improve the characterization of the resolved PMF factors
in this study, two sets of AMS HR matrices (matrix $X_{\text{Org}}$ and matrix $X_{\text{Org}+\text{NO}_3}$) were analyzed using the PMF model. The first matrix consists only of organic fragments from m/z 1-120; the PMF analysis of this matrix will be referred to as PMF$_{\text{Org}}$. On the other hand, the second matrix contains NO$_x^+$ ions (NO$_2^+$ + NO$_3^+$) in addition to the same organic fragments; this PMF analysis will be referred to as PMF$_{\text{Org}+\text{NO}_3}$. Both PMF analyses follow the identical, standard analysis procedures outlined in Zhang et al. [2011], and the similarities/differences between these analyses are presented in section 4.3.

The presence of the aforementioned PMF factors in Houston were evaluated in our mobile/stationary dataset, along with the episodic BBOA that was found previously in Houston during TexAQS 2000 [Wood et al., 2010]. The PMF analysis was focused on the 4th week of September 2013, due to the elevated OA concentrations observed particularly in zone 1 during this period. The OA episodes during this period likely were influenced heavily by BB events (e.g., open fires) and strong biogenic emissions in the north.

Finally, an optimal 4-factor PMF$_{\text{Org}+\text{NO}_3}$ discussed later in this chapter was initially derived from a 5-factor solution (P=5, Figure 24A), whereby two of the factors (factor 2 and factor 3) were combined using a “mass-weighted combination” method established in Hao et al. [2014]. This approach was chosen because the P=5 solution clearly resolves a new factor – later identified as the important BBOA factor – which was mixed between all other factors in the P=3 and P=4 solutions. The original factors 2 and 3 had MS profiles and time series that indicated they were real and not “split” factors, but they did not correlate consistently with internal/external factors to allow identification as meaningful factors. Upon the mass-weighted combination (using Equation 7 below), the
combined factor is highly representative of the well-established SV-OOA factor for reasons described later in this chapter.
Figure 24. PMF diagnostics for the central 4-factor solution (PMF$_{\text{Org+NO}_3}$): (A) $Q/Q_{\text{expected}}$ (residual parameter) versus number of factors (optimized $P = 5$ indicated in gold); (B) $Q/Q_{\text{expected}}$ versus $f_{\text{Peak}}$ parameter indicating the range of $f_{\text{Peak}}$ parameters tested; (C) average mass fraction of each factor as a function of $f_{\text{Peak}}$; (D) Pearson R of time series and MS between each factor ($1_3$ indicates correlation between factors 1 and 3); (E) distribution of scaled residuals (residual/total signal) by m/z ratio (boxes and whiskers indicate 25th/75th and 5th/95th percentiles, respectively); (F) plot of PMF reconstructed/fitted time series and total OA and NO$_3$ signal; (G) time series of the sum of residuals not fit (top) and $Q/Q_{\text{expected}}$ contributions; (H) $Q/Q_{\text{expected}}$ contributions for individual fitted ions.

\[
m/z_{\text{combined}, j} = ((m/z_{\text{factor2}, j})^2 + (m/z_{\text{factor3}, j})^2) / (m/z_{\text{factor2}, j} + m/z_{\text{factor3}, j})
\]

Equation 7

The $m/z_{\text{factor}, j}$ variable in this equation refers to the scaled mass contributions at each m/z (column j) for each factor (combined, factor 2, or factor 3). The scaled mass contributions of the new, combined SV-OOA factor were then converted to the normalized MS profiles shown in Figure 25. The total mass loading (time series) for the combined SV-OOA factor was simply a linear combination of the mass loadings of factors 2 and 3. This method does not introduce additional residuals to the PMF solution and has been shown to produce physically meaningful combined factors (e.g., Hao et al. [2014]).
Figure 25. Component MS profiles for each factor from the 4-factor PMF$_{\text{Org+NO}_3}$ solution, colored by OA/NO$_3$ ion species ‘families’. The elemental ratios, OM:OC, and OS$_c$ for each factor are indicated along with the % contribution of each factor to the fitted Org-NO$_3$,PMF signal. The % NO$_x^+$ fraction of signal refers to the relative contribution of NO$_x^+$ ions to the total MS for each factor.
4.2.2 PMF nitrate apportionment and comparison with the empirical method

A second, independent approach to NO$_3^-$ apportionment was conducted for comparison with the empirical approach discussed above. The PMF NO$_3^-$ apportionment method utilizes the optimized solution from the PMF$_{\text{Org+NO}_3}$ analysis, which analyzes the combined OA and NO$_3^-$ matrix. The Org-NO$_3$,PMF signal was thus determined by summing up all NO$_x^+$ mass contributions to all organic factors in the optimized solution. Typically, the Inorg-NO$_3$,PMF signal would be determined based on the mass contribution of NO$_x^+$ in the inorganic NO$_3^-$-dominated NIA factor (e.g., Hao et al. [2014] and Xu et al. [2015b]). However, consistent with the inability of PMF to retrieve factors that are too low in concentration on average (<5% total fitted mass on average [Ulbrich et al., 2009]) accurately, we discuss later that a separate NIA factor cannot be retrieved in this dataset. As such, we explored the potential use of NO$_x^+$ residuals not fitted by the optimized PMF$_{\text{Org+NO}_3}$ solution to account for Inorg-NO$_3$,PMF, assuming that inorganic NO$_3$ was not correlated with any of the retrieved PMF factors (a valid assumption, as we show later, in this dataset).

4.2.3 Plume characterization

Emission plumes from vehicular, industrial, and BB sources were identified based on short, above-background enhancements of PM$_1$ (e.g., OA or SO$_4^-$) and of tracer species (e.g., CO and NO$_x$ for POA). These plumes were characterized by subtracting from the plume signal an averaged “background” signal prior to and after the plume of interest. This signal is referred to as plume enhancement (denoted by the Δ symbol), and the enhancement ratio between measured variables (such as OA-to-SO$_4^-$ enhancement ratios) were used to further characterize these plumes. The majority of plumes of interest in this
section were sampled in mobile mode, though several plumes were intercepted while sampling at a fixed, near-source location. Key plume characteristics were used to identify vehicular (spikes in reduced OA), industrial (spikes in SO$_4$), and BB (spikes in OA and levoglucosan tracers) plumes, and these plumes were compared with our source apportionment findings.

4.3 Results and Discussions

4.3.1 Overview of PMF source apportionment

For the dataset of interest (week 4 of DISCOVER-AQ), the PMF$_{\text{Org+NO}_3}$ 4-factor solution (P=5) was chosen as the best solution describing the combined OA and NO$_3$ dataset. The four factors resolved in this solution was identified as HOA, BBOA, SV-OOA, and LV-OOA, and was considered superior to the 3-factor (P=3) solution that only resolves HOA, SV-OOA, and LV-OOA (discussed in detail below). The component MS profiles used to distinguish these factors are shown in Figure 25, while the core PMF diagnostic plots for choosing this solution are given in Figure 24. First, in this section we describe the optimal choice of four factors, fPeak, and SEED values for the PMF$_{\text{Org+NO}_3}$ matrix. Second, we discuss why the inclusion of NO$_3$ in PMF was not only a robust approach but also highly beneficial for the analysis of this dataset. Finally, we provide an overview of the time and spatial trends of the four factors identified in the optimal solution and their correlation with internal and external tracers.

In addition to resolving the “fifth” BBOA factor, the P=5 solution from PMF$_{\text{Org+NO}_3}$ corresponds to the final point in the P solution space at which a large change in the Q/Q$_{\text{expected}}$ fit parameter was observed (Figure 24A). In other words, this P=5 solution minimizes the fit residuals for the PMF$_{\text{Org+NO}_3}$ dataset without adding additional factors
(P>5) that barely decrease Q/Q_{expected}. For P>5, “splitting” behavior [Ulbrich et al., 2009] was also observed, dividing existing factors into meaningless new factors that are identical to the “parent” factor and to each other in terms of MS and time series.

Although the combined SV-OOA factor from P=5 is similar in MS to “factor 2” from P=3 (Table 13), the time series are different between the two factors due to the mixed BBOA contribution in each factor in the P=3 solution. The aged LV-OOA factor in the central 4-factor solution was more aged (higher contribution of CO⁺ and CO₂⁺ signals) compared to that of the P=3 solution, which is to be expected due to the un-mixing of the less-aged BBOA signal in the 4-factor solution. Finally, the P=5 solution (the optimal 4-factor PMF_{Org+NO3} solution) shows substantially improved fit diagnostics (Table 14) compared to the alternative P=3 solution that does not resolve the BBOA factor. Upon choosing the ideal number of factors (P=5), rotational ambiguity of the dataset was also explored by varying the fPeak parameter from -3.0 to +3.0, following the convention of exploring fPeak values where at least 10% increase in Q/Q_{expected} values were observed (Figure 24B). This avoids choosing a ‘local minimum’ solution in the fPeak space; fPeak=0 was the solution with the lowest Q/Q_{expected}. By analyzing the MS and time series of individual factors (including the combined SV-OOA factor) resulting from different rotational fPeak values, we did not observe improved correlation with external tracers. Additionally, the BBOA factor was best resolved in solutions similar to fPeak=0, with minimal residual contributions in terms of its key fragments (m/z 60 and 73) to the other non-BBOA factors in the solution (observed before in Wood et al. [2010]). For the reasons outlined here, we chose fPeak=0 for the optimal solution presented. Next, SEED values representing pseudo-random starting points for the PMF algorithm (for each run),
ranging from 1 to 50 were tested for this dataset, with only minimal changes in the MS and time series for the P=5 (fPeak=0) solution. Hence, the default SEED=1 value was used for this solution. Overall, the quality of fits ($Q/Q_{expected} = 5.88$) for this solution was good, with two specific periods contributing to slightly higher residuals. The first period corresponded to two rare, but substantial inorganic NO$_3$ episodes (night of 9/25 and 9/26) that were not fit by the PMF model, the details of which will be discussed subsequently. The second period corresponds to a period of particularly high BBOA influence (night of 9/26), which was suspected to have contributed to elevated CO$_2(g)$ levels that were not completely accounted for by our daily filter CO$_2(g)$ interference corrections. Overall, the scaled residuals for all m/z fit by PMF showed reasonable distributions with no significant outliers (Figure 24E). The 4-factor PMF$_{Org+NO_3}$ solution accounts for 99% of the variability in the total OA + NO$_3$ mass loadings with a slope of 0.989 (Figure 26).

<table>
<thead>
<tr>
<th>PMF$<em>{Org+NO_3}$, P=5 vs. PMF$</em>{Org+NO_3}$, P=3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HR MS</strong></td>
</tr>
<tr>
<td>$R^2$</td>
</tr>
<tr>
<td>Slope</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>TS</strong></th>
<th><strong>HOA$<em>{p=4}$ vs. HOA$</em>{p=3}$</strong></th>
<th><strong>SV-OOA$<em>{p=4}$ vs. SV-OOA$</em>{p=3}$</strong></th>
<th><strong>BBOA$<em>{p=4}$ vs. BBOA$</em>{p=3}$</strong></th>
<th><strong>(SV-OOA + BBOA)$<em>{p=4}$ vs. BBOA$</em>{p=3}$</strong></th>
<th><strong>LV-OOA$<em>{p=4}$ vs. LV-OOA$</em>{p=3}$</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>0.889</td>
<td>0.869</td>
<td>0.571</td>
<td>0.940</td>
<td>0.793</td>
</tr>
<tr>
<td>Slope</td>
<td>0.870</td>
<td>0.686</td>
<td>0.532</td>
<td>1.219</td>
<td>0.537</td>
</tr>
</tbody>
</table>

Table 13. Least-squares fits of factor MS or time series for PMF$_{Org+NO_3}$ (4-factor or P=5) vs. PMF$_{Org+NO_3}$ (3-factor or P=3) solutions.
Table 14. Summary of PMF solutions and key fit parameters.

<table>
<thead>
<tr>
<th>PMF solution</th>
<th>Period</th>
<th>PMF input matrix</th>
<th>Fit parameter Q/Q&lt;sub&gt;exp&lt;/sub&gt;</th>
<th>fPeak chosen</th>
<th>Fitted vs Total (R&lt;sup&gt;2&lt;/sup&gt;; slope)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-factor</td>
<td>Week 4</td>
<td>HR Organics</td>
<td>6.79</td>
<td>0</td>
<td>0.963; 0.992</td>
</tr>
<tr>
<td>4-factor</td>
<td>Week 4</td>
<td>HR Organics</td>
<td>5.83</td>
<td>0</td>
<td>0.997; 0.987</td>
</tr>
<tr>
<td>3-factor</td>
<td>Week 4</td>
<td>HR Organics + NO&lt;sup&gt;+&lt;/sup&gt; + NO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>6.85</td>
<td>0</td>
<td>0.976; 0.985</td>
</tr>
<tr>
<td>4-factor</td>
<td>Week 4</td>
<td>HR Organics + NO&lt;sup&gt;+&lt;/sup&gt; + NO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>5.88</td>
<td>0</td>
<td>0.990; 0.989</td>
</tr>
</tbody>
</table>
Figure 26. Scatter plot of PMF$_{\text{Org+NO}_3}$ mass fit vs. total mass (1st plot) and between 4 PMF factors and their respective tracers.

As will be discussed later in the following PMF results sections, the inclusion of NO$_3$ signals (or NO$_x^+$ = NO$^+$ + NO$_2^+$) allows the comparison of NO$_3$ apportionment between two distinct techniques and also strengthens the source apportionment analysis of Org-NO$_3$ and ON from both biogenic and biomass burning origins. As seen in Table 14, the fit parameters are fairly similar between PMF$_{\text{Org+NO}_3}$ and PMF$_{\text{Org}}$ for the 4-factor solutions.
In fact, the organic HR MS and time series for the four resolved factors are nearly completely identical between PMF$_{\text{Org}+\text{NO}_3}$ and PMF$_{\text{Org}}$ (Table 15). The interpretation of the four factors and their correlation with external tracers remain largely the same for these two approaches. As such, the PMF$_{\text{Org}+\text{NO}_3}$ 4-factor solution was chosen to be the central, optimal solution presented in this section because it serves as an independent NO$_3$ source apportionment approach. Neither the PMF$_{\text{Org}+\text{NO}_3}$ or PMF$_{\text{Org}}$ solutions resolved any impact of cooking OA (COA, Crippa et al. [2013]), marine OA [Crippa et al., 2013] or isoprene OA factors [Xu et al., 2015a]. However, because this analysis involves data collected mostly north of Houston, it does not rule out the potential importance of these factors in other regions of the HGB area or during different periods of the year.
Table 15. Least-squares fits of factor HR MS or time series for PMF_{Org+NO3} vs. PMF_{Org} 4-factor solutions (i.e. with or without including NO\textsubscript{x}\textsuperscript{+} ions). Note that normalized MS were used here for both cases. In the case of PMF_{Org+NO3}, NO\textsubscript{x}\textsuperscript{+} ions were removed from factor MS and re-normalized prior to comparison with PMF\textsubscript{Org}, facilitating the comparison of organics-only fragments between each solution. The factor time series (TS) for PMF_{Org+NO3} include NO\textsubscript{x}\textsuperscript{+} mass, resulting in slopes larger than 1 for BBOA and SV-OOA.

<table>
<thead>
<tr>
<th></th>
<th>HOA</th>
<th>BBOA</th>
<th>SV-OOA</th>
<th>LV-OOA</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR MS, R\textsuperscript{2}</td>
<td>0.999</td>
<td>0.961</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>HR MS, Slope</td>
<td>0.986</td>
<td>0.916</td>
<td>0.983</td>
<td>0.991</td>
</tr>
<tr>
<td>TS, R\textsuperscript{2}</td>
<td>0.999</td>
<td>0.996</td>
<td>0.995</td>
<td>0.994</td>
</tr>
<tr>
<td>TS, Slope</td>
<td>1.010</td>
<td>1.050*</td>
<td>1.020*</td>
<td>0.998</td>
</tr>
</tbody>
</table>

*Corresponds to 6% (BBOA) and 2% (SV-OOA) of mass fractions NO\textsubscript{x}\textsuperscript{+} ions in PMF\textsubscript{Org+NO3} MS profile (see Fig 1)

The strong correlations between HOA and CO and NO\textsubscript{x}, BBOA and Δlevoglucosan (defined subsequently), SV-OOA and Org-NO\textsubscript{3,empirical}, and LV-OOA and SO\textsubscript{4} are key identifiers for these PMF factors (Figure 26 and Table 16). The aged LV-OOA factor also shows strong correlation with O\textsubscript{3} or O\textsubscript{x} during daytime, consistent with its highly oxidized/aged character. Unit-mass factor MS (normalized factor MS produced from summing the contributions of ions near an integer m/z for ease of comparisons with other studies) compared well to two other studies (Table 17) conducted at different locations (Mexico City, Mexico [Aiken et al., 2009] and Barcelona, Italy [Mohr et al., 2012]). Such a comparison indicates that the mass spectral patterns for factors identified in this study are quite similar to factors identified elsewhere. The BBOA factor in this study stands out...
due to slight differences compared to the unit-mass BBOA MS from the two mentioned studies, potentially due to different source characteristics (e.g., primary versus secondary contribution, fuel type, or burning conditions).

Table 16. Pearson R coefficients from correlation analysis between y-metrics (top row) and corresponding x-metrics, sorted by R values for week 4 data. All fitted data (including mobile/stationary) from week 4 were corrected by removing top 1\textsuperscript{st} percentile outliers and by applying 5-point box smoothing (MT = Monoterpenes from CMAQ; Wind S = wind speed; IN = inorganic NO\textsubscript{3}; \(j\text{NO}_2,\text{day}\) = NO\textsubscript{2} daytime photolysis rate; \(\Delta\text{Levog.}\) = excess signal for levoglucosan tracers at m/z 60 and 73; LWC = liquid water content from ISORROPIA). Parameters not listed as x-metrics are either not relevant or have low R values.

<table>
<thead>
<tr>
<th>y-metric:</th>
<th>HOA factor</th>
<th>BBOA factor</th>
<th>SV-OOA factor</th>
<th>LV-OOA factor</th>
<th>Organic NO\textsubscript{3}</th>
<th>Inorganic NO\textsubscript{3}</th>
<th>OS\textsubscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>x-metric R</td>
<td>x-metric R</td>
<td>x-metric R</td>
<td>x-metric R</td>
<td>x-metric R</td>
<td>x-metric R</td>
</tr>
<tr>
<td>Good (&gt;0.5)</td>
<td>NO\textsubscript{x}</td>
<td>0.778</td>
<td>(\Delta\text{Levog.})</td>
<td>0.925</td>
<td>Org. NO\textsubscript{3}</td>
<td>0.756</td>
<td>SO\textsubscript{4}</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>0.667</td>
<td>Org NO\textsubscript{3}</td>
<td>0.839</td>
<td>O\textsubscript{3,night}</td>
<td>-0.511</td>
<td>O\textsubscript{3,day}</td>
</tr>
<tr>
<td></td>
<td>PAH\textsubscript{soot}</td>
<td>0.656</td>
<td>Amines</td>
<td>0.533</td>
<td>O\textsubscript{x,day}</td>
<td>0.532</td>
<td>NH\textsubscript{4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SV-OOA</td>
<td>0.527</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mild (&lt;0.3; &lt;0.5)</td>
<td>SO\textsubscript{2}</td>
<td>0.366</td>
<td>T</td>
<td>-</td>
<td>(\Delta\text{Levog.})</td>
<td>0.434</td>
<td>(\Delta\text{Levog.})</td>
</tr>
<tr>
<td></td>
<td>Chl</td>
<td>0.332</td>
<td>RH</td>
<td>0.411</td>
<td>T</td>
<td>-0.404</td>
<td>T</td>
</tr>
<tr>
<td></td>
<td>SO\textsubscript{4}</td>
<td>0.394</td>
<td>RH</td>
<td>0.308</td>
<td>O\textsubscript{3,night}</td>
<td>0.342</td>
<td>NO\textsubscript{x,day}</td>
</tr>
<tr>
<td></td>
<td>Wind S</td>
<td>-</td>
<td>Wind S</td>
<td>-0.305</td>
<td>Wind S</td>
<td>-</td>
<td>0.350</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>-0.346</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weak (&lt;0.3)</td>
<td>SO\textsubscript{4}</td>
<td>0.262</td>
<td>CO</td>
<td>0.291</td>
<td>Amines</td>
<td>0.141</td>
<td>Wind S</td>
</tr>
<tr>
<td></td>
<td>Amines</td>
<td>0.155</td>
<td>Chl</td>
<td>0.230</td>
<td>MT</td>
<td>0.079</td>
<td>(j\text{NO}_2,\text{day})</td>
</tr>
<tr>
<td></td>
<td>BBOA</td>
<td>0.144</td>
<td>MT</td>
<td>-</td>
<td>NO\textsubscript{x,night}</td>
<td>-0.040</td>
<td>Amines</td>
</tr>
<tr>
<td></td>
<td>Wind S</td>
<td>0.010</td>
<td>NO\textsubscript{x}</td>
<td>0.027</td>
<td>Isoprene</td>
<td>-0.036</td>
<td>Org</td>
</tr>
<tr>
<td></td>
<td>PAH\textsubscript{soot}</td>
<td>0.004</td>
<td>LV-OOA</td>
<td>-0.009</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 17. Comparisons between unit-mass factor MS from the PMF_{Org+NO3} 4-factor solution in this study and from previously published PMF solutions. Literature factor MS were downloaded from the HR AMS Spectral Database (http://cires1.colorado.edu/jimenez-group/HRAMSsd/). Factor MS from this study (up to m/z 120) were adjusted and normalized to facilitate direct comparison with those from Aiken et al. [2009] (up to m/z 100) and Mohr et al. [2012] (up to m/z 115).

<table>
<thead>
<tr>
<th>PMF_{Org+NO3} (this study, NO_x^+ ions removed) vs. PMF_{Org} (literature)</th>
<th>HOA</th>
<th>BBOA</th>
<th>SV-OOA</th>
<th>LV-OOA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aiken et al. [2009], R^2</td>
<td>0.95</td>
<td>0.68</td>
<td>0.91</td>
<td>0.81</td>
</tr>
<tr>
<td>Mohr et al. [2012], R^2</td>
<td>0.82</td>
<td>0.61</td>
<td>0.81</td>
<td>0.93</td>
</tr>
</tbody>
</table>

In terms of overall oxidation state (best represented by OS_c), the factors follow a decreasing (OS_c) trend of LV-OOA (most oxygenated), SV-OOA, BBOA, and HOA (least oxygenated) (Figure 25). Contrary to bulk OA, the elemental ratios calculated for PMF_{Org-NO3} factors include NO_x^+ ions, resulting in slight increases in O:C or OS_c for all factors except BBOA compared to ratios calculated without NO_x^+ ions (Table 18), for which OS_c increased from -0.66 to -0.51 when including NO_x^+ ions due to the large fraction of NO_x^+ fragments in the BBOA spectrum. Next, the degree of oxidation of these factors (O:C and H:C) were plotted in Van Krevelen space (Figure 27) [Heald et al., 2010] for comparison with literature-averaged oxidation extents reported by [Canagaratna et al., 2015] (using the updated Improved-Ambient elemental calculations). Note that the Van Krevelen space (H:C versus O:C; with corresponding OS_c grid lines) tracks the evolution of bulk OA and OA factors, with ambient bulk OA oxidation/mixing processes generally following an updated slope of -0.6 [Chen et al., 2015]. Most factors generally show good agreement with literature-averaged PMF factors in the Van
Krevelen space and falls within typical ambient OA O:C/H:C boundaries [Ng et al., 2011a]. Again, BBOA stands out as significantly more oxidized than literature-averaged BBOA. This difference was only partially due to the NO$_x^+$ ions included in O:C estimates. The unique composition of BBOA identified in this study will be discussed in detail later in the BBOA section 4.3.5.

Table 18. Elemental ratios, OM:OC, OS$_c$, and NO$_2^+/NO^+$ ratios for each factor in the 4-factor solution for either PMF$_{Org}$ or PMF$_{Org+NO_3}$ (denoted by inclusion of NO$_x^+$). As appropriate, elemental calculations were performed with or without NO$^+$ and NO$_2^+$ signals in factor MS.

<table>
<thead>
<tr>
<th>PMF factor</th>
<th>NO$_x^+$ included</th>
<th>NO$_2^+/NO^+$ ratio</th>
<th>O:C</th>
<th>H:C</th>
<th>OS$_c$</th>
<th>OM:OC</th>
<th>N:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOA</td>
<td>Yes</td>
<td>0.178</td>
<td>0.18</td>
<td>1.92</td>
<td>-1.56</td>
<td>1.41</td>
<td>0.008</td>
</tr>
<tr>
<td>HOA</td>
<td>No</td>
<td>0.17</td>
<td>1.92</td>
<td>-1.58</td>
<td>1.39</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>BBOA</td>
<td>Yes</td>
<td>0.197</td>
<td>0.54</td>
<td>1.59</td>
<td>-0.51</td>
<td>1.89</td>
<td>0.037</td>
</tr>
<tr>
<td>BBOA</td>
<td>No</td>
<td>0.47</td>
<td>1.59</td>
<td>-0.66</td>
<td>1.77</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>SV-OOA</td>
<td>Yes</td>
<td>0.139</td>
<td>0.45</td>
<td>1.55</td>
<td>-0.65</td>
<td>1.74</td>
<td>0.010</td>
</tr>
<tr>
<td>SV-OOA</td>
<td>No</td>
<td>0.43</td>
<td>1.55</td>
<td>-0.69</td>
<td>1.70</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>LV-OOA</td>
<td>Yes</td>
<td>0.273</td>
<td>0.82</td>
<td>1.30</td>
<td>0.34</td>
<td>2.21</td>
<td>0.007</td>
</tr>
<tr>
<td>LV-OOA</td>
<td>No</td>
<td>0.81</td>
<td>1.30</td>
<td>0.32</td>
<td>2.19</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Ambient NO$_3$ zone 1</td>
<td></td>
<td>0.194</td>
<td>(average)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient NO$_3$ zone 2</td>
<td></td>
<td>0.149</td>
<td>(average)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$NO$_3$ calibration</td>
<td></td>
<td>0.381</td>
<td>(average)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 27. Elemental ratios (O:C and H:C) calculated for each factor MS using the Improved-Ambient method plotted in Van-Krevelen space for comparison with typical literature values. Elemental O:C and H:C ratios were calculated by including NO\textsubscript{x} fragments in factor MS.

The time trends for all factors exhibit relatively stable signal without added noise when switching between stationary (60 s) and mobile (20 s) sampling modes (frequencies) (Figure 28A-D). Downward spikes were minimal for non-HOA factors even when in primary plumes in excess of 10 µg/m\textsuperscript{3} of HOA, indicating that the PMF solution appropriately accounts for non-road OA (i.e. BBOA, SV-OOA, and LV-OOA) even
when sampling on-road HOA plumes. This provides justification for including both mobile and stationary data in correlation analyses and other zone-1-specific analyses presented below. The zone 1 aggregate analyses presented later (e.g., diurnal analyses including stationary/mobile data) were based on the assumption that the PM$_1$ variability observed across the spatial scales in zone 1 are on average smaller than the temporal variability observed in the entire zone. In part, this assumption was supported by the lack of large gradients in aged/regional species such as LV-OOA and SO$_4$ (Figure 28D) when the MAQL was driving from one stationary location to another within zone 1.
Figure 28. Week-4 time series of (A) HOA factor, (B) BBOA factor, (C), SV-OOA factor, and (D) LV-OOA factors from the 4-factor PMF\textsubscript{Org+NO\textsubscript{3}} solution, with their corresponding tracer species; (E) average OA mass and average OA mass fractions apportioned to each PMF factor in zones 1 and 2 during week 4; (F) diurnal average PMF mass fractions in zone 1 during week 4. Boxes at the top of (A) indicate data collected within zone 1 (red) and zone 2 (blue).
The apportioned SV-OOA, LV-OOA, and BBOA are shown in the following sections to be predominantly secondary in nature. Hence, these factors were summed to represent SOA mass apportioned from PMF, for comparison with the CO-tracer SOA estimates presented in chapter 3 (Figure 29). The two methods agreed well ($R^2=0.945$, slope=0.949), and uncertainties were highest for the CO-tracer method during periods of high HOA (POA) influence or high BBOA influence. This was due to variations in POA/ΔCO (from different POA sources) and BBOA/ΔCO (from varying BBOA plume age) ratios, discussed later. In short, the CO-tracer method is sufficient for a rough estimate of SOA fractions from OA and CO measurements, at least for this dataset, though this method should be used carefully when analyzing fresh POA plumes or when BBOA influence is high. Potential uncertainties in this method have been suggested, including variations in OA/ΔCO ratios in POA sources (diesel versus gasoline vehicles) or interferences from non-combustion POA that does not correlate with CO [Docherty et al., 2008]. Biomass burning plumes also have unresolved, highly variable OA/ΔCO ratios and likely confound the CO-tracer approach when applicable [Aiken et al., 2009].
Figure 29. Scatter plot and least-squares fit between SOA mass loadings derived from the CO-tracer method vs. SOA from PMF (SV-OOA + LV-OOA + BBOA, assuming predominantly secondary BBOA mass) for all stationary data during week 4. Data points are colored by HOA mass fraction (top) and BBOA mass fraction (bottom).
In zone 1 (where the majority of week 4 data was concentrated), SV-OOA accounts for 52% of OA mass, followed by BBOA (20%), LV-OOA (17%), and HOA (11%) (Figure 28E). Similar trends are observed in zone 2 (which has ~half OA mass compared to zone 1), except that BBOA was less important (8%) and SV-OOA was more important (68%). Because the majority of data during week 4 (9/21 – 9/27, 2013) was collected in zone 1 (mobile data and two major sites: Conroe and Spring Creek), the analyses presented in this section involving PMF data are focused on zone 1 data. In zone 1 during this period, diurnally averaged total OA mass concentration shows a steep increase beginning at 7-8pm, peaking around midnight (13.0 µg/m$^3$) with a smaller peak at 8-9pm (10.5 µg/m$^3$) before decreasing to daytime levels of ~6.0 µg/m$^3$ (Figure 28F). Qualitatively, the diurnal contribution of the SV-OOA factor to total OA mass in zone 1 remained relatively constant, with stark diurnal patterns in LV-OOA, BBOA, and HOA (Figure 28F), which will be discussed in detail in the following sections. It should be noted however, that SV-OOA and BBOA contributions were the highest at night (peaking at ~90% also at midnight) when OA levels were most elevated in this region, making these two factors the focus of the analyses presented here. Note that diurnal trends in meteorological factors are presented in Figure 30.
Figure 30. Diurnal profiles during week 4 in zone 1 for meteorological parameters (from top to bottom): temperature, relative humidity (RH), windspeed, and NO₂ photolysis rate measured aboard the MAQL in zone 1 during the study period (week 4). Lastly, the NO₃⁻ radical production rate ($P_{\text{NO}_3} = k(T)[O_3][\text{NO}_2]$) [Atkinson et al., 2004] was calculated (shaded region indicates night), though NO₃⁻ lifetimes during daytime are expected to be much lower due to photolysis.
Statistical uncertainties of this PMF solution derived from bootstrapping analysis are low for both factor MS profiles (Figure 31A) and factor mass loading time series (Figure 31B), indicating the robustness of the factor MS and time series presented here. The diurnal profiles for the four PMF factors, Org-NO$_3$,empirical, OS$_c$, monoterpenes and isoprene from CMAQ model calculations, O$_3$, and SO$_4$ are presented in Figure 32. The mobile/stationary sampling duration/frequency was well distributed diurnally for week 4 in zone 1 (Figure 33), because the MAQL was mostly sampling in zone 1 during this period of high OA pollution to the north of Houston (Table 19). It is important to note that the diurnal profiles in Figure 32 remain similar when normalized by CO (Figure 34), indicating that the diurnal trends were not driven solely by atmospheric dilution/accumulation effects.

Table 19. Distribution of sampling time during week 4 by zones/sites and under mobile/stationary modes.

<table>
<thead>
<tr>
<th>Category for PMF data</th>
<th>Sampling duration (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All data</td>
<td>100.5</td>
</tr>
<tr>
<td>All stationary</td>
<td>57.8</td>
</tr>
<tr>
<td>All mobile</td>
<td>42.7</td>
</tr>
<tr>
<td>Zone 1 all</td>
<td>68.6</td>
</tr>
<tr>
<td>Zone 1 stat</td>
<td>41.6</td>
</tr>
<tr>
<td>Zone 1 mobile</td>
<td>27</td>
</tr>
<tr>
<td>Conroe</td>
<td>28.3</td>
</tr>
<tr>
<td>Spring Creek</td>
<td>4.6</td>
</tr>
<tr>
<td>Zone 2 all</td>
<td>25.8</td>
</tr>
<tr>
<td>Zone 2 stat</td>
<td>13.1</td>
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<tr>
<td>Zone 2 mobile</td>
<td>12.7</td>
</tr>
<tr>
<td>Manvel</td>
<td>6.4</td>
</tr>
</tbody>
</table>
Figure 31. Statistical uncertainties for factor MS and time series obtained from bootstrapping analysis of the PMF\textsubscript{Org+NO$_3$} 4-factor solution.
Figure 32. Diurnal profiles for four PMF factors, Org-NO$_3$, empirical, OS$_c$, monoterpenes, (with sesquiterpenes) and isoprene from CMAQ model output, O$_3$, and SO$_4$ aerosol (with SO$_2$) for data collected in zone 1 during week 4. Box-and-whiskers plots show 5$^{th}$, 25$^{th}$, 50$^{th}$, 75$^{th}$, and 95$^{th}$ percentiles and solid lines and dots denote averages; only diurnal averages are shown for sesquiterpenes and SO$_2$.

Figure 33. Diurnal sampling time distribution for the PMF period of interest (zone 1, week 4).
Figure 34. Similar diurnal plots for PMF, Org-NO$_3$, and SO$_4$ as shown in Figure 32 (zone 1, week 4) but normalized by CO concentrations to remove atmospheric dilution or accumulation effects. Diurnal profiles are also shown for ΔCO (background CO = 100 ppbv) and NO$_x$ (average).
It should also be noted that the terms “semi-volatile” and “low-volatility” in SV-OOA and LV-OOA were based mostly on convention because recent ambient [Hildebrandt et al., 2010] and chamber [Xu et al., 2014] work has shown that SOA oxidation extent (O:C or OS_{c}) does not always correlate negatively with volatility. In the following sub-sections, the volatility and oxidation extent for each factor and their implications will be discussed. We present also a comparison of two independent NO_{3} apportionment techniques, followed by detailed interpretation of the individual OA factors: HOA, BBOA, SV-OOA, and LV-OOA retrieved from the PMF_{Org+NO_{3}} 4-factor solution.

### 4.3.2 Comparison of NO_{3} apportionment techniques

As mentioned earlier, the inclusion of AMS NO_{3} into PMF allows the apportionment of Org-NO_{3} between different OA factors that represent different sources [Hao et al., 2014; Xu et al., 2015b] and the determination of the NIA factor quantifying Inorg-NO_{3} formation for certain datasets. Based on these studies, the SV-OOA factor – a less-oxidized, semi-volatile factor representative of freshly produced SOA – has particularly strong association with Org-NO_{3}, typically accounting for most of the Org-NO_{3} mass fitted by PMF in these datasets. For the 4-factor solution in the DISCOVER-AQ dataset, the SV-OOA factor contributes on average 45% to Org-NO_{3,PMF}, followed by BBOA (39%), HOA (8%), and LV-OOA (7%). It is highly unlikely that the strong contributions of SV-OOA and BBOA to Org-NO_{3,PMF} were merely mathematical artifacts of the PMF model because each of these factors showed strong correlation with the independently calculated Org-NO_{3,empirical} (Table 16) in both zone 1 and zone 2 during week 4. These correlations also were observed diurnally, based on the similar nighttime enhancements of Org-NO_{3,empirical}, SV-OOA, and BBOA in zone 1 (Figure 32), even when factor
loadings were normalized by CO (Figure 34). The assignment of organic NO$_3$ signals to the BBOA factor has only been observed in a handful of datasets to date [Xu et al., 2015b] and to our knowledge this phenomenon has not been explained or studied in detail.

The Org-NO$_3$,$\text{empirical}$ estimates correlate well with Org-NO$_3$,$\text{PMF}$ for this dataset in week 4 ($R = 0.879$, slope $= 0.837$, Figure 35 top panel), with the PMF method mostly overestimating Org-NO$_3$, particularly during periods where Inorg-NO$_3$,$\text{empirical}$ signal was important (Figure 35 bottom panel). As alluded to earlier, an NIA factor was not retrieved from the current PMF$_{\text{Org+NO}_3}$ dataset, even when selecting more factors ($P>5$) to describe the combined data matrix. However, it was within expectations that the small, intermittent signal of inorganic NO$_3$ as predicted by the empirical method (peaking only occasionally at $\sim$7% of total OA) would not be retrieved reliably by PMF in this particular dataset, consistent with a recent study that did not resolve the NIA factor at sites with low inorganic NO$_3$ impact [Xu et al., 2015b]. However, a good correlation was observed between Inorg-NO$_3$,$\text{empirical}$ and the NO$_3$ residuals not fit by the PMF$_{\text{Org+NO}_3,P=4}$ solution ($R = 0.86$, slope $= 1.21$; Figure 35 bottom panel). This correlation provides a good explanation for NO$_3$ residuals in the PMF solution here, which peaks simultaneously with Inorg-NO$_3$,$\text{empirical}$ during the only sustained inorganic NO$_3$ episodes observed during DISCOVER-AQ (Figure 36). As discussed before, the Inorg-NO$_3$,$\text{empirical}$ was validated with below-detection inorganic NO$_3$ levels (PILS-IC) at the Manvel site throughout DISCOVER-AQ. Thus, these results support the potential use of PMF NO$_3$ residual as an estimate/indicator of Inorg-NO$_3$,$\text{PMF}$ in cases where an NIA factor cannot be retrieved. However, the focus in this section is on explaining the discrepancies between
Org-NO$_3$,empirical and Org-NO$_3$,PMF, while later discussions of inorganic NO$_3$ formation will be based on the established Inorg-NO$_3$,empirical estimate.

Figure 35. Time series comparisons and Pearson R for Org-NO$_3$ (top) and Inorg-NO$_3$ (bottom) estimates using the empirical method vs. PMF method during week 4. Inorg-NO$_3$,PMF is estimated from the NO$_3$ residual not fit by PMF$_{Org+NO3}$. 

\[ R = 0.88 \]
\[ \text{Slope} = 0.837 \]

\[ R = 0.86 \]
\[ \text{Slope} = 1.21 \]
Figure 36. (From top to bottom) Time series of RH and temperature, liquid water content (LWC) from ISORROPIA, PMF factors (aggregate mass loadings), \( \text{OS}_c \), \( \text{SO}_4 \), acidity metric (\( \text{NH}_4\text{measured}/\text{NH}_4\text{predicted} \)), \( \text{Org-NO}_3\text{empirical} \) and \( \text{Inorg-NO}_3\text{empirical} \), and AMS amines and chloride. The three BBOA episodes at the Conroe site are denoted in black boxes, with the corresponding dominant air-mass origins indicated. Data during this period was collected exclusively in zone 1.

As seen in Figure 35, periods of significant \( \text{Org-NO}_3\text{PMF} \) over-prediction (even when compared with upper-limit \( \text{Org-NO}_3\text{empirical} \) estimates using \( X = 2.08 \)) coincided with periods of \( \text{Inorg-NO}_3\text{PMF} \) under-prediction. This implies that PMF assigned some of the inorganic \( \text{NO}_3 \) signal to organic species in the PMF factors (i.e., \( \text{Org-NO}_3\text{PMF} \)) during these periods, due to a degree of covariance between organic and inorganic \( \text{NO}_3 \) (both increased at night). Uncertainties in the PMF apportionment of \( \text{NO}_3 \) signals have been observed before [Xu et al., 2015b] for certain sites in the southeast US. However, the minor disagreements between the two \( \text{NO}_3 \) apportionment methods are well explained in
this dataset. To our knowledge, this is the first reported temporal comparison between these two independent NO\textsubscript{3} apportionment methods. This comparison establishes these methods as robust and comparable techniques for NO\textsubscript{3} apportionment and we recommend that both methods be used simultaneously in future NO\textsubscript{3}-focused studies for validation purposes. Additionally, we recommend that the interpretation of PMF NO\textsubscript{3} apportionment be accompanied by an analysis of the NO\textsubscript{3} residuals in the PMF solution, whether or not an NIA factor is resolved.

Strong correlations were observed for Org-NO\textsubscript{3, empirical} (and by extension ON\textsubscript{232, empirical} and ON\textsubscript{306, empirical}) with SV-OOA (R = 0.76), BBOA (R = 0.84), and SV-OOA+BBOA (R = 0.90) (Table 16) for week 4 in both zones. These correlations indicate potentially strong contribution of ON processes to both SV-OOA and BBOA mass loadings in Houston. To quantify the true contribution of ON to SV-OOA and BBOA in zone 1, we present diurnal averages of lower, upper, and central ON estimates from the empirical method (assuming different parent ON molecular weights and X' ratios, Table 9) in Figure 37 (bottom panel). As expected, assuming a larger parent ON molecule (average = 300 g/mol) results in higher “central” estimates of ON contribution, amounting to a consistent ~25% of the sum of SV-OOA and BBOA loadings in zone 1 (Figure 37, top graph). The contribution of biogenic ON to SV-OOA have been reported in ambient studies [Hao et al., 2014; Xu et al., 2015a], but strong ON correlation with a BBOA factor has not been reported to our knowledge. These correlations are discussed in more detail in each factor’s respective sections.
Figure 37. (Top) Diurnal averages for SV-OOA and BBOA mass loadings and the sum of both (1σ shaded regions) and excess levoglucosan tracer signal; (Bottom) Diurnal averages for ON mass estimates from the empirical and PMF methods, assuming different $X$ ratios and ON average molecular masses. Diurnal plots were calculated from week 4 zone 1 data.
It should be noted that the upper and lower estimates (dashed lines) for the empirical ON estimates were intended to show the sensitivity of $\text{ON}_{232,\text{empirical}}$ and $\text{ON}_{306,\text{empirical}}$ estimates to variations in the assumed $X$ ratios. Assuming that PMF accurately captures the covariance of Org-NO$_3$ functional groups with SV-OOA and BBOA, we expect reasonable agreement between Org-NO$_3,\text{PMF}$ and Org-NO$_3,\text{empirical}$ (discussed above). The lower empirical estimate corresponding to $X = 3.99$ ($R_{\text{ON}} = 0.095$) appears to under-predict Org-NO$_3$ or ON when compared to the PMF method (Figure 37). Also, assuming $X = 3.99$ results in over-prediction of Inorg-NO$_3,\text{empirical}$ during periods when inorganic NO$_3$ was unlikely to exist (i.e., daytime with high temperatures). Based on these discussions, the $X$ ratios between 2.09 and 2.25 are likely more representative of ON molecules sampled in zone 1 during this period. In the previous paragraph, we discussed the over-prediction of Org-NO$_3,\text{PMF}$ during nighttime because PMF incorrectly assigned some inorganic NO$_3$ as organic NO$_3$. Here, we discuss the over-prediction of Org-NO$_3,\text{PMF}$ during daytime. The severe over-prediction of daytime ON$_{\text{PMF}}$ above upper-limit estimates of ON$_{\text{empirical}}$ (Figure 37) are likely caused by the changes in formation mechanisms for SV-OOA between daytime and nighttime. During daytime, SOA formed from NO$_3$· radical initiated processes are less important than from photochemical processes, making it likely that SV-OOA that persists during daytime has decreased organic NO$_3$ functionality. However, a key assumption in PMF is that factor MS remains constant with time, resulting in a best-fit Org-NO$_3$ content in SV-OOA that was likely biased high by the substantial ON processes at night, inevitably resulting in an over-estimate of daytime Org-NO$_3,\text{PMF}$. Additionally, this over-estimation of Org-NO$_3,\text{PMF}$ was likely not linked to the low daytime BBOA levels. In conclusion, we found that the base
case empirical approach is appropriate when describing ON processes in this region, and any discrepancies with the PMF NO$_3$ apportionment method are appropriately taken into account.

4.3.3 HOA factor

The HOA factor has been resolved in many studies through factor analysis of Q-AMS (e.g., Zhang et al. [2005c] and Mohr et al. [2011]) and HR-AMS (Aiken et al. [2009], Crippa et al. [2013]) datasets and was commonly resolved in OA datasets with some degree of urban influence. The HOA factor from this PMF$_{\text{Org+NO}_3}$ solution is in good agreement with previous studies (Table 17), with its distinctive spectra dominated by the C$_x$H$_y$ family of ions (Figure 25). The HOA spectrum also shows enhanced signals at m/z 43, 55, 57, identifying it as a proxy for reduced POA from vehicular emissions [Zhang et al., 2005c]. Its averaged diurnal character in the suburban zone 1 shows a marked morning rush hour (MRH) peak between 7:00-9:00 and less pronounced peaks in the afternoon (15:00) and late evening (20:00-22:00) (Figure 32), typical of periods with increased traffic emissions.

When normalized by CO to account for boundary layer effects (Figure 34), similar HOA peaks are observed with the additional enhancement as early as 4:00-6:00, indicative of early local traffic activity in the region with higher HOA/ΔCO emission ratios. This factor also shows higher variability during mobile measurements due to in-plume measurements of on-road exhaust emissions (Figure 28). These in-plume measurements also contributed to spikes in the PMF fit residuals, likely due to significant variations in POA MS profile depending on vehicle type, operating conditions, and vehicle age [Presto et al., 2014] that cannot be captured by an average, constant HOA MS profile.
The strong correlation of HOA with external tracers for vehicular emissions such as NO$_x$, CO, and PAHs on soot (PAH$_{soot}$, Table 6) in both zones (Table 16, Table 20) aided the identification of this POA factor. Additionally, the almost exclusive association of HOA with PAH$_{soot}$ (compared to the low correlation between BBOA and PAH$_{soot}$) suggests HOA or POA emissions as the main sources of soot-associated PAHs in the Houston area. Also, moderate correlation between HOA and SO$_2$, particularly in zone 1 (Table 20), points towards the importance of diesel-exhaust emissions in the region because SO$_2$ emission factors for diesel engines are orders of magnitude higher than for gasoline vehicles [Staehelin et al., 1998] (depending on fuel type). Industrial sources of SO$_2$ [Bahreini et al., 2009; Brock et al., 2003] co-emitted with POA were also potentially important during these measurements.
Table 20. Similar to Table 16, except using only data points from zone 1, to indicate correlations that are particularly strong/weak in this unique region. R values in bold refer to correlations that are substantially different from the previous Table 16.

<table>
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<tr>
<th>x-metric:</th>
<th>HOA factor</th>
<th>BBOA factor</th>
<th>SV-OOA factor</th>
<th>LV-OOA factor</th>
<th>Organic NO₃</th>
<th>Inorganic NO₃ OS₃</th>
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</thead>
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<td>NOₓ 0.051</td>
<td>Isoprene 0.068</td>
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<td>Amines 0.012</td>
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</table>

The low oxidation state (or OS₃) of HOA due to its reduced nature is typical of HOA factors and compares well with literature-averaged HOA oxidation metrics (Figure 27).
Although the HOA factor accounts for only 11% and 9% on average of total OA in zone 1 and zone 2, respectively, its contribution peaks at ~18% during MRH. Also, HOA showed the strongest correlation with the OS$_c$ of bulk OA among all factors, meaning that despite its small contribution, HOA could have a strong impact on the chemical characteristics (e.g., volatility and solubility) of bulk OA in Houston.

**4.3.4 SV-OOA factor**

The moderately oxidized (O:C = 0.45) SV-OOA factor has a strong correlation with central estimates of organic NO$_3$ functionalities (i.e., Org-NO$_3$,empirical) during week 4 (Table 16, Figure 26). Its organic unit-mass MS is similar to those observed at other locations (Table 17) and its MS consists of 2% mass contribution from NO$_x$+ fragments. This factor also accounted for 45% of the Org-NO$_3$,PMF signal apportioned by PMF, making it the factor with the highest organic NO$_3$ influence. On average, SV-OOA contributed a large fraction of total OA in zone 1 (52%) and zone 2 (68%) (Figure 28E), making it the most important and abundant OA factor in Houston. The SV-OOA factor had a diurnal profile (Figure 32) that averaged approximately 4 µg/m$^3$ during the afternoon and was elevated at night and in the morning (20:00-9:00), peaking at approximately 7 µg/m$^3$ around midnight. SV-OOA was the only factor that exhibited minor changes in its averaged diurnal pattern when normalized by CO (Figure 34), with its nighttime rise occurring later, around midnight and peaking around 2:00-6:00. These correlations, diurnal patterns, and the large contribution of SV-OOA to Org-NO$_3$,PMF suggest a strong association between SV-OOA and ON formation processes in Houston, as alluded to in section 4.3.2.
The fact that SV-OOA and organic NO$_3$ functionalities (a proxy for ON abundance) were elevated at night was likely because of 1) nighttime ON production from NO$_3$· reactions with BVOCs [Fry et al., 2009] occur more rapidly and have higher SOA yields compared to daytime photooxidation of AVOCs [Liu et al., 2012] and/or 2) a potential daytime ON sink (in addition to dilution effects accounted for by CO) that was driven by increased temperatures or photochemistry (Figure 30). However, it is important to note that SV-OOA maintained a relatively constant fractional contribution to total OA mass throughout the day in zone 1 (Figure 28F), in contrast to BBOA, which has trivial daytime signals during this period. Thus, a daytime photochemical source of SV-OOA is capable of maintaining approximately 4 µg/m$^3$ of SOA. As such, local daytime production of fresh SOA via different photooxidation pathways of either AVOCs or BVOCs likely contributed to the observed daytime SV-OOA levels. The contribution of NO$_3$· radical processes to daytime SV-OOA was likely low but cannot be completely ruled out, particularly below forest canopies with lower photolytic NO$_3$· losses and high BVOC concentrations [Spittler et al., 2006].

Because Org-NO$_3$,empirical exhibited correlations with both SV-OOA and BBOA (particularly with the sum of both, SV-OOA+BBOA), we discuss the relationship between biogenic ON processes and SV-OOA+BBOA in greater detail in the next section upon characterization of BBOA.

4.3.5 BBOA factor

4.3.5.1 Overview

The BBOA factor exhibited a mass spectral signature relatively similar to SV-OOA, with distinct, but small contributions (~1% of total signal) from levoglucosan tracers at m/z 60.
(C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}\textsuperscript{+}) and m/z 73 (C\textsubscript{3}H\textsubscript{5}O\textsubscript{2}\textsuperscript{+}) (the former ion was twice as large in signal) (Figure 25). These tracer ions were determined from laboratory AMS measurements of primary BBOA and were likely from levoglucosan produced from the decomposition of cellulose in biomass [Schneider et al., 2006]. In addition, Heringa et al. [2011] observed signals at these ions (C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}\textsuperscript{+} in particular) in SOA produced from the photooxidation of biomass burning smoke (this type of SOA shall be referred to as “secondary BBOA”). In other words, freshly formed secondary BBOA also retains its levoglucosan signal, though in smaller contributions compared to primary BBOA. However, because these levoglucosan tracer signals can be reduced significantly from further photooxidation and aging [Cubison et al., 2011; Hennigan et al., 2011], levoglucosan tracers in bulk OA should increase from the addition of primary BBOA and secondary BBOA (to a lesser extent) but decrease by photooxidation/processing of BBOA. Generally, as BBOA becomes aged and processed (through aging or addition of SOA mass), its signature levoglucosan ions become less important (but still apparent) and BBOA becomes more similar to aged SOA. The small contribution of C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}\textsuperscript{+} and C\textsubscript{3}H\textsubscript{5}O\textsubscript{2}\textsuperscript{+} ions (~1%) to the BBOA factor in this study coupled with its similarity to SV-OOA, suggest that this BBOA factor was representative of more processed and more secondary BBOA (i.e. only a small fraction of its signal was from fresh, primary BBOA).

The BBOA factor correlated well with an internal AMS tracer, Δlevoglucosan (or “excess levoglucosan”, Figure 26), which was calculated from the sum of C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}\textsuperscript{+} and C\textsubscript{3}H\textsubscript{5}O\textsubscript{2}\textsuperscript{+} ions less 0.2% of the measured OA signal to account for background signal of levoglucosan present in non-BBOA organics. The 0.2% background levoglucosan signal was determined from regression of OA vs C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}\textsuperscript{+} and C\textsubscript{3}H\textsubscript{5}O\textsubscript{2}\textsuperscript{+} signals and was slightly
smaller than the 0.3% background \((C_2H_4O_2^+ \text{ only})\) reported elsewhere (e.g. Aiken et al. [2009] and Cubison et al. [2011]). Subtracting 0.3% of the total OA from the levoglucosan signals in would result in substantial negative loadings in the tracer signal in this study; thus, a 0.2% background signal was used. The scatter plot of BBOA vs. Δlevoglucosan shows a much smaller intercept when compared to uncorrected levoglucosan signals (Figure 26). The good agreement between BBOA and excess levoglucosan tracer signals served as additional validation of this factor.

Based on the discussions thus far, it is worth emphasizing the evidence that rules out the possibility of BBOA as an artifact of “splitting” behavior in PMF suggested by the fact that BBOA and SV-OOA have similar MS profiles and were largely separated from the SV-OOA-like factor 2 in the 3-factor PMF\(_{\text{Org+NO}_3}\) solution. First, although both BBOA and SV-OOA exhibit strong nighttime enhancement in zone 1, their diurnal patterns were fairly distinct. Their time series (Figure 28B, C) also were unique, especially considering the omnipresence of SV-OOA throughout week 4 in both zones – a trend not seen in BBOA. Second, levoglucosan tracer ions at m/z 60 and 73 were only assigned to the BBOA factor, with minimal residual signals in other factors. Finally, BBOA shows exclusively strong correlation with Δlevoglucosan particularly in zone 1 (Table 20), when compared with HOA, SV-OOA, and LV-OOA.

### 4.3.5.2 BBOA processing and aging

The BBOA MS pattern exhibited a larger degree of difference from those from reference studies (Table 17) likely due to the more primary nature of BBOA sampled in the previous studies. As mentioned earlier in this section, the BBOA factor in Houston was significantly more oxidized \((O_S = -0.51)\) in Van Krevelen space compared to averaged
literature BBOA factors (Figure 27), even if NOx ions were not included in elemental calculations. However, it is not uncommon for factors to deviate from ‘standard’ factor regions in the Van Krevelen diagram due to differences in source/pollution characteristics at each location. A BBOA factor identified at an urban site in Atlanta during summer exhibited similar signs of higher oxidation (OSc ~ -0.3) than BBOA found at other sites in the southeast US [Xu et al., 2015b]. Based on BBOA OSc values and MS signatures reported in Xu et al. [2015b], BBOA factors identified with higher oxidation states appeared to have smaller contributions of m/z 60 and 73 to the total BBOA factor signal (or \( f_{60+73,\text{BBOA}} \), ~1%, similar to this study) at most sites with BBOA influence. Cubison et al. [2011] reported decreasing levoglucosan contribution in bulk OA \( (f_{60,\text{bulk OA}}) \) and increasing O:C with increasing plume age in biomass burning plumes, with \( f_{60,\text{bulk OA}} \) decreasing to about 1% in processed BB plumes, fairly consistent with \( f_{60+73,\text{BBOA}} \) in this study. Similarly, [Ortega et al., 2013] observed rapid decay of \( f_{60,\text{bulk OA}} \) during OH oxidation of BBOA. However, both studies indicate that the degradation of levoglucosan tracers levels off at a certain point, meaning that even highly processed BBOA does not completely lose its ‘levoglucosan’ character. Based on its high O:C and low \( f_{60+73,\text{BBOA}} \), it is highly likely that the BBOA factor identified in this study originated from BB sources and had underwent significant aging/processing.

The BBOA factor had significantly higher average contribution in zone 1 (20%) than in zone 2 (8%) (Figure 28E), indicating higher primary BBOA emissions or larger secondary mass growth in the forested zone 1. In zone 1, the relative importance of BBOA was low during daytime (~8%; from 10:00 to 19:00) but increased rapidly after sunset, peaking at 48% at midnight (Figure 28F). A similar nighttime increase in BBOA
and midnight peak was observed for the averaged BBOA diurnal profile (Figure 32), amounting to a substantial average nighttime enhancement of approximately 8 µg/m$^3$ during this period in zone 1. The diurnal pattern of BBOA remains similar when normalized by CO (Figure 34), indicating that most of these BBOA events were not accompanied by elevated CO that is typical of fresh BB plumes [Trentmann et al., 2003] and were not merely caused by boundary layer effects. Thus, it is likely that the burning occurred further upwind.

Several other metrics indicate the processed, secondary nature of the BBOA factor identified primarily in zone 1. The SOA metric OA/ΔCO for bulk OA in zone 1 remained relatively high (indicative of high SOA fraction) even during periods of high BBOA influence (Figure 38). When periods of high HOA influence (ΔCO > 250 ppbv; ~90% of stationary data in zone 1) and sharp BBOA spikes (likely fresh plumes) were excluded, the BBOA/ΔCO ratio averaged at 0.0425 µg/m$^3$-ppbv (Figure 39). This ratio was at least 10 times higher than the best-fit average HOA/ΔCO value. The large range of BBOA/ΔCO slopes that have been observed in literature [Aiken et al., 2009] show that biomass burning influenced OA has much higher variation depending on fuel, burning conditions, and plume age when compared to the relatively narrow ranges of observed OA/ΔCO ratios for HOA and OOA. In addition, HYSPLIT back-trajectories during major BBOA events at Conroe were compared with NASA MODIS active fire counts (https://earthdata.nasa.gov) near the HGB area (Figure 40B, C, and D). Generally, these BBOA events appear to result from open fires at locations at least several hours upwind (>80 kilometers); fire counts were usually monitored by MODIS in the late evenings (17:00-19:00), and the BBOA events were measured several hours later at Conroe.
Additionally, the average characteristics of near-source BBOA events at Spring Creek park (zone 1) were compared with an aged BB episode at Conroe (Figure 41), and similar trends of higher OS<sub>c</sub> and OA/ΔCO and lower <i>f_{60+73,OA}</i> were observed for the aged BB aerosol at Conroe. The fire and trajectory data, paired with higher BBOA/ΔCO ratio and low levoglucosan content in BBOA, indicate additionally that some of the observed BBOA is secondary in nature (from the addition of SOA mass as BB plumes are carried downwind). In short, given the high BBOA/ΔCO ratio, low levoglucosan content, and the oxidized nature of the BBOA factor, we conclude that the BBOA signal fitted by PMF has a strong (but not exclusively so) secondary and processed nature (with the exception of fresh BBOA spikes/plumes indicated in Figure 38 and Figure 39 discussed later).
Figure 38. Scatter plots of bulk OA vs. ΔCO with data points colored by HOA mass fraction (A), BBOA fraction (B). Only zone 1 stationary data points are shown here. Upper-bound BBOA/ΔCO (0.200 µg/m³) and HOA/ΔCO (0.0057 µg/m³) slopes from literature are shown as straight black lines, while HOA/ΔCO (0.0049 µg/m³, Figure 39) fit from this dataset is shown as a green line (A-E). Data points identified as fresh BBOA plumes were indicated by black circles.
Figure 39. Scatter plots and least-squares fits between PMF_{Org+NO3} factors, the sum of SV-OOA and LV-OOA (total OOA) vs. ΔCO (zone 1, week 4, stationary data). Gray circles were data points filtered due to significant primary plume influence that resulted in bad fits, with ΔCO values above 250 ppbv. Black solid data points indicating fresh BBOA plumes were also denoted in the BBOA vs. ΔCO plot. Literature BBOA/ΔCO and HOA/ΔCO fit lines as in Figure 38 are also included.
Figure 40. Maps of southeast Texas and HGB area, indicating MODIS fire counts that correspond with BBOA-influenced air-masses of interest: 9/12 PM in Spring Creek (A), 9/25 AM in Conroe (B), 9/25 PM in Conroe (C), and 9/26 PM in Conroe.
Figure 41. Scatter plots and least-squares fits of bulk OA vs. ΔCO for select BBOA plumes of interest: “Aged” 9/26 PM episode at Conroe (A), “fresh” 9/24 PM episode at Spring Creek (B), and “fresh” 9/12 PM episode at Spring Creek (C). Least-squares fits, average BBOA fraction, average $f_{60+73}$, and OS$_c$ for these plumes are shown. Literature BBOA/ΔCO and HOA/ΔCO fit lines as in Figure 38 are also included. Note that BBOA fraction for plot (C) was estimated by subtracting background OA from the BB plume.
4.3.5.3 Contribution of BVOCs and ON to BBOA mass

The influence of biogenic ON processes could have been responsible for the substantial nighttime enhancement of BBOA mass in zone 1. A number of studies have shown that BBOA plumes can result in substantial SOA growth from photooxidation [Hennigan et al., 2011; Heringa et al., 2011; Ortega et al., 2013], but to our knowledge there was no evidence of substantial nighttime growth of OA observed in biomass burning plumes attributable to NO$_3^-$ driven reactions. As mentioned previously, the BBOA factor correlated strongly with Org-NO$_3$,empirical and moderately with SV-OOA in both zones (Table 16 and Table 20), indicating covariance with ON and SV-OOA. The BBOA factor follows a stark diurnal profile that is in better agreement with those for Org-NO$_3$,empirical and ON estimates when compared to that for SV-OOA (Figure 32 and Figure 37). Additionally, NO$_x^+$ signals contribute 6% of the BBOA factor MS, and BBOA on average contributes to 39% of the PMF apportioned NO$_3$ signal (Figure 25). Further, in the month-long DISCOVER-AQ dataset, Org-NO$_3$,empirical correlated well with $\Delta$levoglucosan (Figure 42; with the exception of fresh BB plumes identified), confirming the relationship between ON and BBOA tracers in Houston. The agreement between BBOA and Org-NO$_3$,empirical diurnal profiles, the substantial PMF assignment of NO$_3$ signals to the BBOA factor, and the correlation between ON and BBOA tracers strongly suggest the enhancement of BBOA mass by nighttime NO$_3^-$ driven ON formation in zone 1. Although it is also possible that nighttime aging/processing of existing BBOA mass (whether primary or secondary) by the NO$_3^-$ radical resulted in changes in BBOA composition (higher O:C and higher NO$_3$ content), the aging process does not explain the
addition of OA mass and the temporal correlation between BBOA mass and Org-NO$_3$\textsubscript{empirical}.

Figure 42. Scatter plot of Org-NO$_3$\textsubscript{empirical} vs. Δlevoglucosan tracer mass (m/z 60 + 73) for the entire DISCOVER-AQ campaign and the gray, excluded data points corresponding to “fresh” BB spikes in levoglucosan.

It is unclear if secondary BBOA formed from NO$_3$· oxidation of BVOCs or of a different set of VOC precursors, potentially VOCs that were co-emitted with BBOA plumes [Ortega et al., 2013] that were capable of producing SOA from photooxidation. A multi-phase NO$_3$· radical mass transfer and reaction kinetics study observed rapid degradation
of levoglucosan by NO$_3^-$ under high humidity conditions [Shiraiwa et al., 2012], potentially explaining the low $f_{60+73, BBOA}$ in this study as a result of not only photochemical, but also nighttime NO$_3^-$ processing. However, because only pure tracer substrates were used (levoglucosan and abietic acid), the study does not provide data for direct comparison with ambient BBOA oxidation by NO$_3^-$ radicals. With the processed nature of BBOA and the strong correlation of ON processes to BBOA, we conclude that PMF analysis of this dataset provides first evidence of nighttime NO$_3^-$ radical driven oxidation and growth of BBOA plumes in the forested region of Houston. To our knowledge, there is no published study characterizing SOA formation from NO$_3^-$ oxidation of BB smoke; thus it is unclear if NO$_3^-$ oxidation of BVOCs alone contributed to the BBOA mass. Due to the potential for significant SOA formation downwind of BBOA plumes observed in this forested region, future chamber or field work would be needed to constrain the importance of NO$_3^-$ radical oxidation of BB smoke in similar environments.

**4.3.5.4 BBOA impact on inorganic NO$_3$, Chl, and amines**

Another important feature of the elevated OA episode (9/24 - 9/27) in zone 1 was the enhancement of AMS Chl, Inorg-NO$_3$,empirical, and tracer signals for amines (sum of CH$_4$N$^+$ and C$_2$H$_4$N$^+$; Sun et al. [2012]) as shown in Figure 36. The Chl signal was intermittent and more elevated during southeasterly flow from the Houston Ship Channel and Gulf of Mexico, indicating either marine or industrial sources. Garbage burning and forest fires also are potential sources of trace-level Chl [Akagi et al., 2011]. This was also the only period with sustained Inorg-NO$_3$,empirical signals throughout the campaign and was characterized by low temperatures and high humidity. The correlations for Inorg-
NO$_3$$_{\text{empirical}}$ with temperature or RH (mild), and with LWC (strong) (Table 20) in zone 1 indicate that decreasing temperatures and increasing aerosol LWC favored gas-to-particle partitioning of inorganic NO$_3$ (as NH$_4$NO$_3$). In addition, the co-enhancement of Inorg-NO$_3$$_{\text{empirical}}$ (and good correlation) with BBOA (and not SV-OOA) suggest potential impact of BB on NH$_4$NO$_3$ formation in the aerosol phase, since HNO$_3$ and NH$_3$ levels were likely enhanced in these BB-influenced episodes [LeBel et al., 1988; Trentmann et al., 2003]. The influence of BB on these inorganic NO$_3$ episodes was likely strong because relatively low temperature, high RH, and high LWC conditions were not exclusive to these inorganic NO$_3$ episodes during DISCOVER-AQ.

The elevated amine tracer signals in PM$_1$ during the BB events can be explained by a combination of amine reactions and gas-to-particle partitioning. You et al. [2014] observed enhanced amines signals (C1-C6) from long-range transported BB plumes at a forested site in the southeast US and frequent ammonia/amines local plumes in Kent, Ohio. The authors observed a greater fraction of amines in the particle phase at night at the forested site, likely due to gas-to-particle partitioning at lower temperatures. Nitrate radical oxidation of tertiary amines produced significant SOA formation in the laboratory and in ambient measurements [Silva et al., 2008]. Based on these studies, the moderate correlation observed for BBOA and amines (Table 20) and mild correlation between amines and Org-NO$_3$$_{\text{empirical}}$ suggests that elevated gas-phase amines from BB fires [LeBel et al., 1988] could have contributed to the secondary BBOA mass growth observed during these periods (Figure 36). However, BBOA tracers (i.e. Δlevoglucosan) only correlated with amines during this specific period (week 4), while smaller amines spikes were frequently observed during DISCOVER-AQ, indicating local sources. Other
potential amines sources include agriculture and dairy farms [Silva et al., 2008] that were located near Conroe and around Houston, as well as amines that were potentially co-emitted with NH$_3$ from power plants and industrial processes [Gong et al., 2011; Gong et al., 2013a]. These sources of amines were likely important during the BB episodes mentioned because particulate amines were specifically enhanced in BBOA events with southwesterly (city outskirts, Parish power plant) and southeasterly (urban/industrial areas) flow. These particulate amines events also occurred at night and at relatively low temperatures, consistent with gas-to-particle partitioning of C1-C3 amines as observed by You et al. [2014].

It should be noted that the formation of semi-volatile aminium salts from amines and inorganic NO$_3$ also was possible during these events because Inorg-NO$_3$,empirical correlated mildly with amines (Table 20), as observed previously between low-molecular-weight amines and inorganic NO$_3$ [Paglione et al., 2014b]. Specifically during these elevated amines/BBOA periods (9/25-9/27 nighttime), the acidity parameter correlated with amines tracers (R = -0.56) but not with other inorganic PM$_1$ signals, indicating the presence of some aminium neutralizing the acids in place of NH$_4$ (amines were not accounted for by the acidity formulations, hence the apparent increase in “acidity” when aminium was present). Biogenic marine sources of amines were unlikely because AMS tracers for marine biogenic emissions (i.e., methanesulfonic acid) [Crippa et al., 2013; Paglione et al., 2014b] were not detected during these episodes. We conclude that a combination of temperature/humidity-driven partitioning effects, enrichment of precursor gases from BB or local sources, and potentially NO$_3$· radical chemistry contributed to the enhancement of NH$_4$NO$_3$ and particulate amines signals during these BB events.
4.3.5.5 BBOA, SV-OOA, and ON formation

In this section, we have discussed the processed, secondary nature of the observed BBOA as well as the strong link between organic NO$_3$ functionalities and BBOA. Because ON processes were clearly related to both SV-OOA and BBOA, it makes sense to sum the two OA factors for ON analysis. The central ON$_{232}$ or ON$_{300}$ empirical estimates (assuming an average ON molecule weight of 232 or 300 g/mol) correlated strongly with the sum of SV-OOA and BBOA time trends (SV-OOA + BBOA; R=0.90), with slopes that indicate 17 or 25%, respectively, of the SV-OOA+BBOA mass was made up of compounds with NO$_3$ functionalities. Additionally, chemically-resolved, averaged size distributions during these overnight OA enhancement periods (9/24-9/27) showed internally mixed OA and NO$_3$ particles, with a slight shift towards larger particles for SO$_4$ and NH$_4$ (Figure 43). Because NO$_3$ radical initiated reactions can form SOA through pathways that do not result in the molecular retention of a NO$_3$ group [Brown et al., 2013; Rollins et al., 2012], it is also possible that the importance of ON processes was higher than predicted here.
As mentioned above in section 4.3.2, due to the fact that the PMF method overestimated daytime organic NO$_3$ levels (i.e., incorrect assignment of too much NO$_3$ signal to SV-OOA during daytime), it is likely that SV-OOA during the day has less organic NO$_3$ content compared to nighttime SV-OOA. This is true based on the diurnal profile of the ratio of Org-NO$_3$,empirical/OA (Figure 44, top), which showed obvious enhancement during nighttime, similar to previous observations by Rollins et al. [2012] in Bakersfield, CA. The ratio of Org-NO$_3$,empirical/(SV-OOA+BBOA) had a less pronounced diurnal character but still exhibited enhanced ON content at night for these ON-influenced factors (Figure 44, bottom). These trends imply that daytime ON formation processes are less important than “typical” photochemical SOA pathways (in which NO$_3$-containing groups do not appear) and that nighttime ON formation processes are more important than during the
day. Also, NO$_3^-$ radicals were likely the dominant reactants at night and NO$_3^-$-initiated SOA formation pathways resulted in bulk SOA with higher ON content.

Figure 44. Diurnal profile for ratios of Org-NO$_3$,empirical/OA (top) and Org-NO$_3$,empirical/(SV-OOA+BBOA) (bottom).

SV-OOA, BBOA, and SV-OOA+BBOA were not correlated with simulated mixing ratios of monoterpenes, isoprene, or sesquiterpenes (in 1-min intervals, Table 16 or diurnally, Figure 32). Spatiotemporal uncertainties in the model could have contributed to this observation, though it is more likely that BVOCs were not the limiting factor for ON production during the day or at night. In fact, Rollins et al. [2012] reported that primary
BVOCs likely suppress ON formation due to consumption of the NO$_3^-$ radical and production of more volatile 1$^{\text{st}}$-generation oxidation products. Under low-NO$_3^-$ radical concentrations, these BVOCs do not proceed to 2$^{\text{nd}}$- or higher generation products that are required to yield significant particulate ON [Rollins et al., 2012]. Similarly, this theory may explain the early evening peak (19:00-22:00) in NO$_3^-$ production rates (Figure 30; dominant nighttime pathway, $P_{\text{NO3}} = k(T)[O_3][NO_2]$ [Atkinson et al., 2004]; $k(T)$ is the temperature-dependent rate constant) while ON did not peak until later at night. Despite the large NO$_3^-$ source during this period, high NO$_3^-$ reactivity with BVOCs (mainly isoprene, which peaks during this period) likely resulted in low NO$_3^-$ levels and predominantly 1$^{\text{st}}$-generation oxidation products that did not partition into the aerosol phase.

It is also interesting that both of the ON/OA ratios (Org-$\text{NO}_3^-$,$\text{empirical}$/OA; Org-$\text{NO}_3^-$,$\text{empirical}$/(SV-OOA+BBOA)) were lowest during 16:00-19:00, the period that corresponded with a slight rise in SV-OOA levels without an increase in Org-$\text{NO}_3^-$,$\text{empirical}$. This was likely due to a decrease in daytime ON production due to low photooxidant levels and low NO$_3^-$ concentrations due to photolysis and/or high reactivity with isoprene, consistent with the arguments above. The slight rise in SV-OOA despite lower photooxidation could be explained by the decreasing temperatures and gas/particle partitioning of existing SOA precursors.

In short, we have shown that nighttime NO$_3^-$ reactions with biogenic VOCs can result in significant SOA mass growth in the forested area north of Houston, with significantly enhanced SOA formation when mixed with BB plumes originating upwind. These BB episodes also likely contributed to elevated inorganic NO$_3$ and particulate amines due to
BB enrichment of precursor gases. Assuming BBOA, Inorg-NO$_3$\textsubscript{empirical}, and amines signals were all attributable to BB sources, BB has the potential to produce up to approximately 12 µg/m$^3$ of PM$_1$ in the forested region. To our knowledge, we have provided the first evidence of nighttime NO$_3^-$ radical processing and enhancement of BBOA (and potentially particulate amines) in an ambient, forested sub-urban environment.

### 4.3.6 LV-OOA factor

The LV-OOA factor MS is characterized by the predominance of C$_x$H$_y$O$_z$ family of ions and its high m/z 44 to m/z 43 ratio (Figure 25). These characteristics, along with its high OS$_c$ (0.34) and O:C (0.82), are representative of aged or processed OA from multiple sources. The LV-OOA factor on average contributed 17% and 15% to total OA in zone 1 and zone 2, respectively (Figure 28E), during this period, indicating its ubiquity in Houston. Broadly, the proposed sources of similar, aged LV-OOA factors observed by AMS studies include long-range transport of regional and highly processed/aged OA from upwind sources [Jimenez et al., 2009; Ng et al., 2010] and ambient humic-like substances (HULIS) due to similar chemical composition and oxidation extent [Ng et al., 2010; Paglione et al., 2014a]. Extensive ambient processing of OA usually results in aged OOA with increasingly similar chemical composition, regardless of the original source of OA [Jimenez et al., 2009]. This LV-OOA (recently named as more-oxidized OOA, “MO-OOA”) factor was identified in most PMF studies at sites around the world [Jimenez et al., 2009; Ng et al., 2010]. As expected, the LV-OOA factor (a proxy for highly processed OA) retrieved in this dataset is similar in MS to those observed at other sites (Table 17). This also makes it highly difficult to apportion the true sources of LV-OOA,
though we discuss here the different possible sources of LV-OOA in Houston based on the time trends of LV-OOA and its correlations with other tracers.

The diurnal profiles of LV-OOA mass fractions (Figure 28F), loadings (Figure 32), and CO-normalized concentrations (Figure 34) in zone 1 provide some information on the local versus regional sources of LV-OOA in the suburban area. The stark increase in LV-OOA mass fraction (of total OA) from nighttime (on average 9%) to daytime (on average 25%) levels shows how LV-OOA contribution to OA mass became increasingly important as night progressed into day. Although the increased daytime LV-OOA mass fractions during daytime were due in part to the decrease of other factors, the LV-OOA factor mass loadings did show consistently higher levels during daytime, with a broad daytime peak around 10:00 to 15:00 (approximately 2.2 µg/m$^3$) and a smaller and narrower nighttime peak at 1:00 to 2:00 (approximately 1.7 µg/m$^3$). When normalized by CO, the daytime peak broadened to 10:00-20:00, but the nighttime peak remains similar. These diurnal trends suggest 1) a regional background level of LV-OOA (approximately 9% of total OA) that is present at night and during day time; 2) significant daytime enhancement of LV-OOA due to higher temperatures or photochemistry; and 3) potential early morning production of LV-OOA indicated by the consistent sharp peak between 1:00-2:00 due to nighttime NO$_3^-$ radical processing of OA. Combined with the analysis of air-mass origins discussed below, the diurnal profiles of LV-OOA suggest that a significant daytime portion of this factor is produced locally or at most several hours upwind of Houston, which stresses the potential of the highly reactive Houston atmosphere for rapid local aging/processing of OA. The observations here are qualitatively consistent to the intense aging of OA (i.e. increase of LV-OOA fraction or
bulk O:C) over the polluted Mexico City atmosphere, observed on an aircraft [DeCarlo et al., 2008] approximately 6 hrs downwind of the urban area.

Strong correlations between LV-OOA and SO$_4$, O$_3$, and O$_x$ were observed during daytime in Houston (Table 16). The correlation with SO$_4$ indicates regional/transported LV-OOA, while correlations with O$_3$ and O$_x$ indicate photochemical production on similar timescales as O$_3$ (i.e., less than 12 hours) [Wood et al., 2010]. In addition to regional and local photochemical sources of LV-OOA, we discuss other possibilities based on recent findings of SOA oxidation and aging processes.

Previous studies have suggested the association of LV-OOA retrieval with diurnal temperature fluctuations [Lanz et al., 2007; Ng et al., 2010; Ulbrich et al., 2009]. Meanwhile, Wood et al. [2010] attributed daytime losses of SV-OOA in Mexico City to evaporative sinks but did not discuss the impact this had on LV-OOA production, which was attributed to photochemical sources due to strong daytime correlations with O$_x$ (R~0.78). A recent chamber study proposed ‘apparent’ oxidation of OA that is almost exclusively driven by temperature-induced evaporation of biogenic SOA [Denjean et al., 2015]. In this study, we observe LV-OOA daytime increases that are concurrent with decreases in both SV-OOA and BBOA signals in zone 1 (Figure 32). Because photochemistry (indicated by O$_x$ levels) and temperature follow similar daytime patterns, it is possible that the strong correlations previously observed between LV-OOA and O$_x$ (e.g. Wood et al. [2010] and Lanz et al. [2007]) were partially artifacts of this temperature-induced oxidation. The mild correlations of LV-OOA (positive), SV-OOA (negative), and BBOA (negative) with temperature in both zones (Table 16 and Table 20) and the fact that both SV-OOA and BBOA were highly influenced by biogenic
precursors (discussed above) also corroborate this theory of LV-OOA production from partial evaporation of volatile compounds from biogenic SOA. To be precise, biogenic SOA could potentially be converted to LV-OOA by evaporation of less-oxidized compounds in the outer layer of heterogeneous particles, leaving behind an oxidized core similar to LV-OOA. This temperature-induced “aging” mechanism was first proposed by Denjean et al. [2015] and is supported by this dataset. Due to moderate correlation between LV-OOA and daytime O\textsubscript{x} (Table 16), we do not rule out photochemistry as a source of LV-OOA, though temperature-induced evaporation of biogenic SOA may have also contributed to the observed LV-OOA during DISCOVER-AQ.

The PMF factors identified in this study generally followed a Van Krevelen oxidation slope of about -1 (Figure 27), contrary to bulk OA slope of ~-0.5 mentioned above. Assuming that OA aging/processing in Houston progresses from the less oxidized HOA, BBOA, or SV-OOA factors to LV-OOA, this slope is indicative of bulk OA aging processes that involved increasingly important relative contribution from carboxylic acid functionalities (e.g., through the evaporation of less functionalized OA proposed above). This slope also suggests less fragmentation reactions and/or peroxide/alcohol formation (with slopes > -0.5) that would otherwise be expected in bulk photochemical oxidation processes. In other words, the production of the observed LV-OOA could be partially driven by evaporation of less functionalized compounds in addition to typical ambient photochemical functionalization processes. Such a trend would have otherwise been missed without the application of PMF analysis because bulk OA in Houston appears to follow a typical slope of approximately -0.6 (Figure 15).
By qualitatively comparing the three distinct air masses observed at Conroe during nighttime (Figure 36), we do not observe the expected elevated LV-OOA signals from the northern and southwesterly airmasses, which originated from the continental US. In fact, the southeasterly Gulf of Mexico airmass during the night of 9/26 at Conroe showed the highest levels of LV-OOA (in absolute or fractional mass) along with overnight increases in SO$_4$ levels. Such an observation suggests the potential for the high oxidative capacity of the nighttime Houston urban/industrial atmosphere to rapidly oxidize/process local OA, producing the aged OOA contributing to the LV-OOA signal.

A mix of primary or secondary SO$_4$ (potential SO$_2$ oxidation from nighttime oxidants) could explain the elevated SO$_4$ levels in these industrial airmasses, based on industrial plume data in section 4.3.7. The rapid aging of OA in industrial plumes has been reported by previous studies in Houston during daytime [Bahreini et al., 2009; Brock et al., 2003], but not during nighttime. However, Zaveri et al. [2010] documented potential nighttime SOA production in power plant plumes due to the high NO$_3$· radical concentrations possibly found in these plumes. Qi et al. [2012] showed that NO$_3$· radical is capable of increasing the O:C of biogenic SOA (i.e., aging by NO$_3$·) under nighttime conditions. Thus, it is possible that NO$_3$· radical driven oxidation at night was responsible for the nighttime enhancement of SV-OOA/BBOA (discussed above) as well as LV-OOA on the night of 9/26 at Conroe.

The potential SOA production/aging from industrial plumes was discussed previously based on back-trajectory analysis of bulk OS$_e$ levels at the Manvel site (section 3.3.4). While the trends observed in the handful of distinct trajectories here do not suggest that these proposed sources of LV-OOA are representative of Houston in general, it does
support the theorized impact of nighttime industrial/Houston Ship Channel plumes on SOA formation (SV-OOA/BBOA) and aging (LV-OOA). A recent chamber study showed that extremely low-volatility VOCs (ELVOCs) that form from an ozonolysis pathway (daytime or nighttime) of α-pinene, helped explain most of the SOA mass formed from this monoterpene [Ehn et al., 2014]. Most interestingly, due to the low volatility and high oxygen content of these precursor ELVOCs, the resultant SOA is highly aged (O:C = 0.7). This is a potential pathway by which biogenic processes could have contributed to LV-OOA in Houston, due to the abundance of BVOCs and the oxidative capacity of the Houston atmosphere.

Another pathway by which aged OA can form is from photooxidation of AVOCs co-emitted with primary HOA, which was characterized in recent chamber experiments [Presto et al., 2014]. This pathway is potentially important due to large vehicular exhaust emission rates in Houston, though SOA formed from these AVOCs did not progress to the point of heavily aged OA (such as LV-OOA) within the chamber photooxidation time frames (~3 hrs) [Presto et al., 2014]. Additionally, an AMS source apportionment study coupled with radiocarbon analysis in Los Angeles showed that despite heavy influence from traffic emissions, more than 69% of the OC in LV-OOA (termed “LV-OOC”) is of non-fossil origin (i.e., from biogenic SOA, COA, or BBOA) [Zotter et al., 2014]. The findings by Zotter et al. [2014] support the importance of LV-OOA production from the evaporation/photooxidation of SV-OOA or BBOA in Houston though such radiocarbon analysis has not been performed previously in Houston. One of our collaborators, Dr. Sheesley from Baylor University has recently shared radiocarbon, total organic carbon, and levoglucosan tracer (for BBOA analysis) data collected during DISCOVER-AQ at
Conroe. Future work utilizing this dataset for radiocarbon analysis will be conducted to determine the relative contributions of fossil and non-fossil OA to aged LV-OOA.

4.3.7 Characterization of primary PM$_1$ emissions

4.3.7.1 BBOA plumes

In addition to the BBOA factor and fresh BB plumes identified at the Conroe and Spring Creek sites above, fourteen other BB plumes were identified based on above background enhancements of OA (\(\Delta\text{OA}\); 1.5–48.7 $\mu$g/m$^3$) and levoglucosan tracers (\(\Delta(m/z60 + m/z73)\)) (Table 21). Ten “fresh” BB plumes were identified based on exceeding the levoglucosan enhancement ratio (\(\Delta f_{60+73} = \Delta(m/z60 + m/z73) / \Delta\text{OA}\)) threshold of 1%. This threshold was chosen based on $f_{60,\text{bulk OA}}$ of ~1% observed in processed BB plumes [Cubison et al., 2011] discussed above. Note that \(\Delta f_{60+73}\) enhancements calculated from these plumes are different from the $f_{60+73}$ described previously, which was used to describe levoglucosan content of the bulk OA signal. These fresh BB plumes exhibited \(\Delta f_{60+73}\) in the range of 1.2–3.9 % and the averaged, background-subtracted MS for these fresh BB plumes is shown in Figure 45. This fresh, mostly primary BBOA is significantly less aged when compared to the PMF BBOA factor identified during week 4, with a higher $f_{60+73}$ (1.7%) compared to the BBOA factor (1.0%). These characteristics of fresh BBOA with higher levoglucosan content ($f_{60+73}$) and lower oxidation states are in agreement with the discussions above about primary versus secondary BBOA. The \(\Delta\text{OA}\) values were also significant for “other” BB plumes with \(\Delta f_{60+73} < 1\%\), indicative of strong enhancements in OA mass in aged/processed BB plumes.
Figure 45. Background-subtracted, averaged, and normalized mass spectrum of fresh BBOA plumes listed in Table 21.
Table 21. Aerosol enhancements from biomass burning (BB) plumes identified in Houston. All enhancements (Δ) are in units of µg/m³. Empty entries indicate no detectable enhancement. Fresh BB plumes were characterized based on $\Delta f_{60+73} > 1\%$ (ratio of m/z 60 and 73 enhancements to ΔOA).

<table>
<thead>
<tr>
<th>Event ID</th>
<th>Time start (CDT)</th>
<th>Plume duration (s)</th>
<th>Region/ location</th>
<th>ΔOA</th>
<th>$\Delta$(m/z60+m/z73)</th>
<th>$\Delta f_{60+73}$</th>
<th>ΔAmines</th>
<th>$\Delta$Inorg-NO$_3$</th>
<th>$\Delta$Org-NO$_3$</th>
<th>ΔChl</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
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<tr>
<td>Fresh plumes ($\Delta f_{60+73} &gt; 1%$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>9/18/2013 8:57</td>
<td>100</td>
<td>Dyess Park, Tomball, TX I-10/TX-8, Channelview, TX</td>
<td>1.45</td>
<td>0.03</td>
<td>2.2%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>30.039</td>
<td>-95.674</td>
</tr>
<tr>
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<td>FM-2920, Tomball, TX Residential, NW Houston</td>
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<td>0.17</td>
<td>3.9%</td>
<td>-</td>
<td>-</td>
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<td>0.14</td>
<td>29.770</td>
<td>-95.159</td>
</tr>
<tr>
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<td>FM-2920, Tomball, TX Residential, NW Houston</td>
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<td>1.7%</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>30.079</td>
<td>-95.763</td>
</tr>
<tr>
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<td>Residential, NW Houston</td>
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<td>0.15</td>
<td>1.8%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>30.136</td>
<td>-95.804</td>
</tr>
<tr>
<td>5</td>
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<td>60</td>
<td>Tomball, TX</td>
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<td>0.18</td>
<td>2.1%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30.134</td>
<td>-95.653</td>
</tr>
<tr>
<td>6</td>
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<td>16.67</td>
<td>0.31</td>
<td>1.8%</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-95.581</td>
</tr>
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<td>0.27</td>
<td>1.3%</td>
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<td>-</td>
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<td>-</td>
<td>30.230</td>
<td>-95.507</td>
</tr>
<tr>
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<td>0.33</td>
<td>1.2%</td>
<td>0.12</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>30.229</td>
<td>-95.513</td>
</tr>
<tr>
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<td>0.43</td>
<td>1.2%</td>
<td>0.22</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
<td>30.133</td>
<td>-95.738</td>
</tr>
<tr>
<td>Other plumes ($\Delta f_{60+73} &lt; 1%$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9/22/2013 10:41</td>
<td>20</td>
<td>I-45, League City, TX Residential, NW Houston</td>
<td>3.99</td>
<td>0.02</td>
<td>0.5%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>29.507</td>
<td>-95.117</td>
</tr>
<tr>
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<td>9/24/2013 20:55</td>
<td>60</td>
<td>Residential, NW Houston Residential, NW Houston</td>
<td>35.13</td>
<td>0.28</td>
<td>0.8%</td>
<td>0.18</td>
<td>0.26</td>
<td>-</td>
<td>0.71</td>
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<tr>
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<td>20</td>
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<td>0.14</td>
<td>0.8%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.41</td>
<td>30.132</td>
<td>-95.736</td>
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<tr>
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<td>0.40</td>
<td>0.8%</td>
<td>-</td>
<td>0.24</td>
<td>-</td>
<td>4.66</td>
<td>30.171</td>
<td>-95.610</td>
</tr>
</tbody>
</table>
These BB plumes were concurrent with elevated amines, inorganic/organic NO₃, and Chl signals (Table 21), though the contribution of BB to these particulate species was fairly variable. These observations support the abovementioned contribution of BB activity to these trace PM₁ species. In short, the analysis of individual BB plume events provided validation for the previous PMF BBOA discussions and also elucidated the role of BB activity in enhancing PM₁ concentrations in various neighborhoods around Houston.

4.3.7.2 Industrial plumes

A large number (N = 21) of SO₄-dominated plumes were observed in industrial areas within the HGB area (Table 22), and most were attributed to industrial sources (petrochemical or power generation). Other important PM₁ constituents found in these industrial plumes are NH₄ produced from the neutralization of primary/secondary SO₄ and amines tracers (CH₄N⁺ and C₂H₄N⁺). For most of these plumes, the measured spikes in SO₄ mass did not result in a change in the background acidity parameter (NH₄,measured/NH₄,predicted ~0.75), indicating relatively neutralized or slightly acidic SO₄ aerosol. In several non-neutralized or highly acidic SO₄ plumes (Table 22), the particles could have existed as pure H₂SO₄ or were neutralized by amines (as aminium) or compounds not detected by the AMS. Sulfate-only enhancements in these plumes (ΔSO₄) varied from 0.5 to 24.3 μg/m³ (Table 23), which are substantial especially when considering the frequent, concurrent enhancements in OA (ΔOA/ΔSO₄ = 0.1 – 3.93) and NH₄.
Table 22. PM<sub>1</sub> enhancements and enhancement ratios for industrial and ship plumes identified from measurements near petrochemical facilities and refineries in the Houston Industrial Area. All enhancements (Δ) are in units of µg/m<sup>3</sup>. Empty entries indicate no detectable enhancement. Event ID 12* represents a possible ship emission plume in the ship channel.

<table>
<thead>
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<th>Event ID</th>
<th>Time start (CDT)</th>
<th>Plume duration (s)</th>
<th>Region /location</th>
<th>ΔSO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>ΔNH&lt;sub&gt;4&lt;/sub&gt;</th>
<th>ΔNH&lt;sub&gt;4&lt;/sub&gt;/ΔSO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>ΔSO&lt;sub&gt;2(g)&lt;/sub&gt;/ΔSO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>ΔOA</th>
<th>ΔOA/ΔSO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>ΔAmines</th>
<th>ΔAmines/ΔOA</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Neutralized</th>
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<td>0.26</td>
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<td>-</td>
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<td>-95.032</td>
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<td>60 I-10 Fwy, N of Pasadena, TX</td>
<td>2.12</td>
<td>0.71</td>
<td>0.34</td>
<td>14.08</td>
<td>0.87</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>29.771</td>
<td>-95.194</td>
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<td>0.31</td>
<td>1.92</td>
<td>0.28</td>
<td>1.30</td>
<td>0.38</td>
<td>0.09</td>
<td>0.07</td>
<td>29.380</td>
<td>-94.919</td>
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<td>0.07</td>
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Table 23. Summary statistics for enhancement ratios from industrial and ship plumes listed in the previous Table 22. All enhancements (Δ) are in units of µg/m³.

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<th></th>
<th>Date</th>
<th>Time</th>
<th>Location</th>
<th>ΔSO₄</th>
<th>ΔNH₄/ΔSO₄</th>
<th>ΔSO₂(g)/ΔSO₂(g)+ΔSO₄</th>
<th>ΔOA/ΔSO₄</th>
<th>ΔAmines/ΔOA</th>
</tr>
</thead>
<tbody>
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<td>0.25</td>
<td>0.79</td>
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</tr>
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<td>9/22/201</td>
<td>3:32</td>
<td>Texas City, TX</td>
<td>2.61</td>
<td>0.46</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>9/22/201</td>
<td>3:46</td>
<td>Texas City, TX</td>
<td>2.00</td>
<td>0.54</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>9/22/201</td>
<td>3:52</td>
<td>Texas City, TX</td>
<td>3.15</td>
<td>0.64</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 23 summarizes the statistics for ΔSO₄ and other important enhancement ratios for the observed industrial plumes. The enhancement ratios of amines tracers to OA in these industrial plumes can be significant (0.01-0.28; Table 23), especially considering that the amines tracer ions represent only fragments of the parent amine molecules. These findings indicate that industrial sources are potentially important sources of gas- and/or particle-phase amines in Houston, even in air masses transported downwind to sub-urban sites such as Conroe (as discussed in section 4.3.5). The large ΔSO₂(g)/(ΔSO₂(g)+ΔSO₄) ratios often observed for these plumes indicate relatively fresh plumes that exhibited minimal SO₂ conversion to SO₄, though these processes would have likely proceeded further downwind [Bates et al., 2008; Brock et al., 2003]. Several plumes that exhibited low ΔSO₂(g)/(ΔSO₂(g)+ΔSO₄) ratios were likely more primary ((NH₄)₂SO₄) in nature, because SO₂ conversion to SO₄ could not have proceeded so rapidly given the high ΔSO₄ observed near-source (e.g., event ID 8, Table 22). In short, the industrial plumes with substantial PM₁ mass enhancements observed throughout the HGB area elucidate the importance of industrial sources of SO₄, OA, and amines. Control of primary PM₁ (directly emitted sulfuric acid particles), SO₂ and other PM₁ precursor emissions should continue to be a priority in the HGB area for improvements in regional air quality and compliance.

4.3.7.3 POA plumes

Due to the relatively low time- and spatial- resolution (20 s; 0.25 miles) employed for mobile PM₁ measurements during this study (for higher sensitivity and improved chemical characterization), on-road PM emission ratios or emission factors could not be
reliably obtained. Such estimates require fast (1 s) time resolution PM$_1$ data to capture individual vehicle plumes and to compute accurate emission ratios/factors [Dallmann et al., 2012; Dallmann et al., 2014] when paired with our fast trace gas instrumentation (e.g. CO, NO$_x$, and CO$_2$). To address this, fast MS mode data (1 s) was acquired using the AMS during a recent on-road study in March/April 2015 (HACHE project), which allowed improved identification of narrow POA plumes (down to 1 s) when compared with the current V-mode dataset (Figure 46) and can be utilized for emission ratio calculations. Fast trace gas and aromatic VOC data (1 s) also were collected by the MAQL during these measurements (on-road or road-side) and are currently undergoing quality control and processing. Fuel-based and mileage-based emission factors for PM$_1$ and trace gas species measured by the MAQL will then be developed for the vehicle fleet in Houston, for comparison with emissions models (e.g. EPA MOBILE) and existing emissions inventories.
Figure 46. Comparison of a current DISCOVER-AQ plume (top) with higher time resolution fast MS mode plumes (data from HACHE 2015).

Because of the lack of temporal resolution, we focus on the chemical characterization of twenty extreme POA plume events (20-40 s) that were identified above background OA signals (background POA and SOA) from on-road or off-road measurements. The goal is to characterize the chemical nature of these POA plumes and provide a comparison with the HOA factor identified from PMF analysis.

These plume events resulted in enhancements of 6 to 38 µg/m$^3$ in the AMS OA signal and the averaged, background-subtracted MS is shown in Figure 47. This “POA MS”
correlated and compared well with the HOA MS ($R^2 = 0.88$), with slightly higher contribution of reduced ions ($C_xH_y$) and lower contribution of oxygenated ions ($C_xH_yO_z$). These differences were also consistent with the more reduced character of this averaged POA MS (lower O:C and higher H:C ratios), when compared with the HOA factor.

Figure 47. Background-subtracted, averaged, and normalized mass spectrum of HOA/POA plumes listed in Table 22.

There are several explanations for the higher oxidation state of HOA factor relative to these POA plume events: 1) the HOA factor represents a constant, “averaged” MS for POA from all sources observed during week 4 and was likely skewed by more oxidized/processed POA particles measured further away from sources; 2) these twenty extreme POA events/spikes were identified close to the respective sources and are more reduced; 3) the transport and dilution of POA away from sources results in the evaporation of more reduced and volatile compounds while more oxygenated (less
volatile) species remain in the POA phase. This increase in O:C due to partitioning has been proposed by laboratory characterization of vehicular POA emissions using the AMS under atmospherically-relevant dilution conditions [Collier et al., 2015].

Another important feature of POA observed in Houston is the predominance of POA mass resulting from direct emissions of lubricating oil. These findings were based on the premise that different ratios between ions derived from saturated alkanes ($C_nH_{2n+1}$) and those from cycloalkanes or unsaturated hydrocarbons ($C_nH_{2n-1}$) are expected from lubricating oil or unburned fuel particles, due to differences in oil and fuel composition. In particular, the ion ratios m/z 69-to-71 and m/z 83-to-85 are good indicators for the relative contribution of lubricating oil in sampled OA particles. Sakurai et al. [2003] concluded that these ratios were larger than unity for diesel POA mixtures dominated by lubricating oil. Dallmann et al. [2014] showed additionally that on-road POA from gasoline and diesel emissions were very similar in chemical composition and that both types of POA showed large contributions from lubricating oil. The average ion ratios of m/z 69-to-71 and m/z 83-to-85 in the twenty background-subtracted POA plumes were $1.45 \pm 0.16$ and $1.62 \pm 0.14$, respectively (with one excluded outlier at 2.95 and 3.70, respectively). Similar ratios were observed for the averaged POA MS (Figure 47) and for the HOA factor (Figure 25; 1.48 and 1.58 respectively). These findings strongly support the predominance of lubricating oil in POA sampled from on-road or off-road locations in Houston. This importance of lubricating oil emissions from the vehicle fleet in Houston is consistent with POA emissions obtained from a tunnel study in California [Dallmann et al., 2014] and from laboratory measurements of gasoline and diesel vehicle
emissions [Collier et al., 2015]. Additionally, our HONO production studies (Chapter 2) provide an example of reactive VOCs from engine oil vapors that participate in the recycling of reactive nitrogen and OH radicals, hence influencing ozone and SOA formation. In short, based on characterization of plumes and factor analysis, vehicular POA emissions in Houston were on average composed primarily of lubricant oil constituents, which could have significant implications compared to fuel-rich emissions scenarios.

4.3.8 Summary of source apportionment findings

Positive matrix factorization of the combined OA and NO\textsubscript{3} data matrix during week 4 of DISCOVER-AQ resolved four OA factors: HOA, SV-OOA, BBOA, and LV-OOA. The majority of the NO\textsubscript{3} signal (likely organic) was apportioned to the SV-OOA and BBOA factors, and the PMF NO\textsubscript{3} apportionment technique agreed well with the established “empirical” approach. The results summarized here focus on zone 1 due to less sampling time in zone 2.

The HOA factor correlated with vehicle combustion tracers and was important during early morning, morning, and evening rush hour periods. This POA factor drives the variability in bulk OA oxidation state despite its relatively small contribution to total OA mass.

Next, the SV-OOA factor represents locally produced SOA and dominates OA mass in both zones. This secondary factor was likely strongly influenced at night by NO\textsubscript{3}· oxidation of BVOCs and the subsequent partitioning of the resulting oxidation products into the aerosol phase. Daytime sources of SV-OOA were weaker, though photochemical
formation pathways involving NO\textsubscript{x} still likely contributed to both SV-OOA and ON mass during the day.

The resolved BBOA factor represented a mix of primary, secondary, and aged BBOA due to its chemical and temporal behavior. This factor likely originated from BB events further upwind of sampling locations, and the associated material had undergone significant processing through SOA mass addition from biogenic sources; the aerosol was chemically different than freshly emitted BBOA. The impact of nighttime radical (NO\textsubscript{3}·) processes on the aging of and SOA mass addition to this factor was apparent in the data. Both SV-OOA and BBOA contributed to large overnight enhancements of SOA mass in zone 1, likely with substantial influence from nocturnal reactions between NO\textsubscript{3}· and BVOCs.

Finally, the LV-OOA factor was omnipresent in Houston OA and was highly oxidized/processed. This factor is relatively complex and may have originated from a mixture of anthropogenic and biogenic OA (i.e., POA, SV-OOA, or BBOA) that underwent temperature-induced, photochemical, or nighttime oxidation processes.
Chapter 5. Conclusions

The gas-phase conversion of HNO$_3$ to HONO by VOCs discussed in chapter 2 has significant atmospheric implications due to the “renoxification” of less reactive HNO$_3$ into more reactive HONO. Results from chapter 4 also showed that PM (and by extension, VOCs) from engine oil was likely a main constituent of vehicular emissions of PM$_1$, suggesting the potential importance of this reaction in urban areas similar to Houston.

The premise that HNO$_3$ serves as a sink of reactive nitrogen may need to be reconsidered, particularly in areas influenced by vehicular emissions. This HONO source has been parameterized with a “best estimate” rate constant for use in regional modeling efforts (Gall et al. [2015], in revision for *Atmospheric Environment*), and it appears that the mechanism is most important very close to emission sources. However, future experiments paired with full VOC speciation will be required to fully characterize the reaction mechanism and to derive rate constants that can be used to improve existing O$_3$ and PM prediction models.

The sampling approach outlined in chapter 3 successfully identified PM$_1$ ‘hot zones’ in Houston and could facilitate the development of appropriate PM control strategies that are tailored to each zone. These observations also highlight the potential roles of reactive nitrogen, BVOCs, and AVOCs in regulating the formation, evolution, and aging of SOA in the HGB area. These observations underscore the need for continued NO$_x$ and AVOCs reduction efforts in the populated HGB area (though NO$_x$ reductions under certain conditions may worsen O$_3$ pollution), as well as the need for additional work characterizing the complex and spatially variable chemistry. The results from the PCA
analysis agreed spatially and temporally with the analyses presented in this section.

Finally, we recognize that the short term observations at multiple stationary sites in the expansive HGB region presented here may not be fully representative of PM$_1$ trends in September 2013. To address this, the MAQL has since been systematically deployed for extended 1-2 month sampling at multiple locations (from 2013-2015) for continued analysis of spatial, weekly, monthly, and seasonal trends of PM$_1$ composition in the HGB area.

Inclusion of the AMS NO$_3$ signal in the PMF OA matrix in chapter 4 provided additional validation of empirical NO$_3$ source apportionment techniques and also strengthened the association of ON with two PMF factors (SV-OOA and BBOA). As such, we recommend the use of the PMF NO$_3$ apportionment technique as a standard validation procedure in future NO$_3$ and OA apportionment studies, particularly at sites where ON processes are important.

We have shown that the NO$_3^\cdot$ radical and BVOCs play a profound role in regulating OA mass in Houston, particularly in the north where substantial SOA mass can be produced overnight. Much of the overnight SOA production episodes were likely influenced by BB plumes that grew in mass and were aged due to the NO$_3^\cdot$ radical. These findings implicate the strong impact of BB activity and NO$_x$ emissions (impacting NO$_3^\cdot$ levels) on air quality, particularly in regions such as northern Houston with substantial nighttime sources of BVOCs.

While forest fires are difficult to mitigate, stricter regulations of open burning and residential wood burning facilities (e.g., requiring high-efficiency burners) would be
helpful in reducing BB impacts during summertime (e.g., camping, waste disposal) and other seasons (e.g., home heating). It is unclear if household wood burning in winter months in Houston would have a comparable impact on air quality, thus we recommend future work quantifying the effects of household or forest burning on PM₁ pollution in the region during winter (the additional data collected during 2013-2015 may address this). Additionally, future mobile efforts are required to track the chemical evolution and mass addition of OA in BB plumes and to resolve the remaining questions on daytime/nighttime BBOA emission, SOA mass addition, and processing. These efforts should focus on mobile transects of ground level BB plumes from near-source to downwind locations.

On the other hand, the reduction of anthropogenic emissions of NOₓ and O₃ precursors in the region should help reduce NO₃⁻ radicals (from the main NO₂ + O₃ source) and its detrimental effects on air quality. However, the effect of NOₓ reductions on SOA and O₃ formation are highly non-linear. Thus, extensive field and modeling data would be required to direct NOₓ reduction strategies in this region to avoid worsening O₃ pollution (note that O₃ is a key oxidant and a source of NO₃⁻), which could occur under particular atmospheric conditions (e.g., under high NOₓ, low VOC conditions).

The aged LV-OOA was omnipresent in Houston and likely was derived from many different sources/pathways. This type of OA is highly oxidized and low in volatility and could have strong radiative (due to water uptake) and health (due to its chemical properties and lifetime) impacts. Thus, it is important to characterize its sources in the complex urban/industrial/forested Houston atmosphere. In the near term, we will expand
this analysis by utilizing radiocarbon data from our collaborators to determine the relative contributions of fossil and non-fossil OA to bulk OA and LV-OOA during DISCOVER-AQ. Although much information was retrieved from OA and NO$_3$ source apportionment in week 4 of DISCOVER-AQ, it is worth noting that future long term studies in Conroe (at least one month in each season) with expanded gas phase instrumentation (e.g., concentrations of AVOCs, BVOCs, and NO$_3^-$ radicals) is required to fully characterize the myriad of OA sources and their seasonal variability.

Chemical analysis of POA in Houston (from both PMF and in-plume characterization) found the predominance of engine oil-derived POA mass from vehicular sources, also implying that VOCs from engine oil were likely important in the gas-phase exhaust emissions. In addition to implications for the HONO reaction mentioned above, the relative importance of oil versus fuel emissions in the local vehicle fleet impacts ambient VOC composition and needs to be characterized in future efforts to improve the accuracy of atmospheric models (because VOC reactivity varies by species). Emission ratios/factors for POA could not be reliably retrieved given the time resolution of mobile measurements in the current dataset; thus, future work in Houston must focus on high-time-resolution chemical characterization of POA and VOC emissions under real-world driving, cold-start, and idling conditions. Such a dataset has already been collected using the MAQL with improved instrumentation in Houston (March-May 2015) and is under preliminary processing.

Industrial processes play an important role in air pollution in Houston, and the MAQL successfully intercepted several industrial plumes with large enhancements in SO$_2$, SO$_4$,
NH₄, OA, organic amines, and Chl. Future studies and air monitoring efforts should focus on quantifying emission rates of these and other pollutants at the fence-line instead of relying solely on emissions inventories that could be biased by issues such as reporting errors, fugitive emissions, and pollutant transformations upon release. New EPA requirements for fence line monitoring of fugitive emissions of benzene by refineries (September, 2015) will likely improve the tracking and reduction of benzene (a toxic and reactive AVOC).
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Appendix

A.1 Research manuscripts from doctoral research

A manuscript describing the HONO sensitivity experiments described in chapter 2 has been accepted for publication in *Atmospheric Pollution Research* (APR) [Leong et al., 2015b]. A co-authored paper preceding this analysis was also published in *Atmospheric Environment* (AE) [Rutter et al., 2014].

The DISCOVER-AQ PM$_1$ spatiotemporal overview study in chapter 3 is currently in the later stages of its preparation for submission to the *Journal of Air and Waste Management Association* (JAWMA) [Leong et al., 2015a].

The PMF OA and NO$_3$ source apportionment study described in chapter 4 is currently in preparation for submission to the journal *Environmental Science and Technology* (ES&T) [Leong et al., 2015b]. The sections covering BBOA and its interactions with ON processes may be included as a separate manuscript for AE.

The emissions characterization study described in chapter 4 is in early preparation, requiring additional data processing of on-road and road-side emissions data collected in Spring 2015 (HACHE campaign) and potential collaboration with an emissions modeling research group.

Finally, during my 4 months as a visiting research scholar at University of Eastern Finland (Primary Investigator: Professor Annele Virtanen), I was tasked with analyzing AMS aerosol composition data shared from multiple collaborating research groups in support of two particle hygroscopicity (water uptake) studies at three ambient sites in the
U.S., Finland, and Italy. Co-authorship is expected from the two manuscripts that describe these analyses (in preparation).

A.2 Relevant research presentations made as first author

Y. J. Leong, N. P. Sanchez, H. W. Wallace, B. Karakurt Cevik, J. H. Flynn, Y. Han, P. Massoli, C. Floerchinger, E. Fortner, S. Herndon, B. Lefer, R. J. Griffin,
Overview of Surface Measurements of Submicron Particulate Matter in the Greater Houston Area during the DISCOVER-AQ 2013 Field Campaign,
American Association for Aerosol Research Annual Conference, Minneapolis, MN, October 2015. (Presentation)

Y.J. Leong, N. P. Sanchez, W.H. Wallace, A.T. Bui, Y. Han, B.L. Lefer, J.H. Flynn, and R.J. Griffin, Overview of Surface Measurements and Spatial Characterization of Particulate Matter during the 2013 DISCOVER-AQ Campaign in Houston, TX, Texas Air Quality Symposium, Austin, TX, April 2015. (Poster)


Y.J. Leong, L. Gong, C. Gutierrez, B. Lefer, J. Flynn, and R.J. Griffin, Measurement of Aerosol Number Concentrations in Houston, TX, American Association for Aerosol Research Annual Conference, Minneapolis, MN, October 2012. (Poster)