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Source-Specific Molecular Signatures for Light-Absorbing Organic Aerosols

Amanda Susan Willoughby

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SOURCE-SPECIFIC MOLECULAR SIGNATURES FOR LIGHT-ABSORBING ORGANIC AEROSOLS

by

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ABSTRACT

SOURCE-SPECIFIC MOLECULAR SIGNATURES FOR LIGHT-ABSORBING ORGANIC AEROSOLS

Amanda Susan Willoughby
Old Dominion University, 2015
Director: Dr. Patrick G. Hatcher

Organic aerosols (OA) are universally regarded as an important component of the atmosphere based on quantitative significance as well as the far-reaching impact they have on global climate forcing and human health. Despite the acknowledged importance, OA amounts and impacts remain the largest uncertainties regarding radiative forcing estimates. Incomplete chemical characterization of aerosol organic matter (OM) and a lack of concrete source apportionment is a major source of this uncertainty. The primary focus of this study is to provide much needed molecular details regarding ambient OA from key emission sources, and establish links between molecular and optical properties.

Complete chemical characterization of OA has been a longstanding obstacle for the atmospheric community. In this thesis Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) was used to evaluate the molecular properties of OM extracted from ambient aerosols collected from marine, biomass burning, urban, and mixed sources. A method was developed to evaluate the water-insoluble OM in addition to the frequently analyzed water-soluble OM to provide a more complete evaluation of the molecular components that define each emission source. Molecular formulas facilitated by FTICR-MS reveal that water-insoluble OM contains numerous aliphatic and sulfur-containing compounds, and represent important anthropogenic components not previously recognized.
Principal component analysis reveals source-specific molecular characteristics for each of the emission sources. Aromatic nitrogen species are a distinguishing component for biomass burning aerosols, structurally diverse and highly processed aliphatic and oxygenated species are key components of urban aerosols, and marine aerosols contain a large number of biologically-derived organic compounds and organosulfates.

Atmospheric aging reactions including oligomerization and reactions with atmospherically-relevant inorganic species were explored using Kendrick mass defect analysis and evaluation of specific mass differences. Oligomerization of OM with isoprene-related compounds and reactions with inorganic species are apparent in each of the emission sources indicating widespread importance, and variations in extent of reaction indicate these urban and mixed source aerosols have undergone more atmospheric aging.

Finally, the link between molecular character and related fluorescence properties, specifically fluorescence, was explored by coupling FTICR-MS with excitation emission matrix spectroscopy (EEMs). Fluorescent signatures observed in each of the aerosols supports their widespread importance in the process of radiative forcing. Biomass burning aerosols display a unique feature associated with freshly-emitted OM, likely linked to the abundance of highly-aromatic nitrogen-containing compounds. The urban aerosols display unique diesel-like features likely associated with the PAH-like compounds identified in the mass spectra, highlighting their anthropogenic influence.

This study provides unique qualitative and analytical approaches for enhancing the understanding of the molecular properties, the atmospheric transformations, and associated optical properties of atmospheric OM necessary for ultimately eliminating the uncertainties associated with OA and their net global impacts.
This dissertation is dedicated to my family.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II.</td>
<td>A MOLECULAR-LEVEL APPROACH FOR CHARACTERIZING WATER-INSOLUBLE COMPONENTS OF AMBIENT ORGANIC AEROSOL PARTICULATES USING ULTRA-HIGH RESOLUTION MASS SPECTROMETRY</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>1. INTRODUCTION</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>2. METHODS</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>3. RESULTS AND DISCUSSION</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>4. SUMMARY AND IMPLICATIONS</td>
<td>46</td>
</tr>
<tr>
<td>III.</td>
<td>MOLECULAR SOURCE APPORTIONMENT OF AMBIENT AEROSOL ORGANIC MATTER USING ADVANCED ANALYTICAL TECHNIQUES AND STATISTICAL ANALYSES</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>1. INTRODUCTION</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>2. METHODS</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>3. RESULTS AND DISCUSSION</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>4. SUMMARY AND IMPLICATIONS</td>
<td>87</td>
</tr>
<tr>
<td>IV.</td>
<td>MOLECULAR CHARACTERIZATION OF AMBIENT AEROSOL ORGANIC MATTER USING KENDRICK MASS DEFECT ANALYSIS: A NEW APPROACH FOR ELUCIDATING MOLECULAR TRANSFORMATIONS IN THE ATMOSPHERE</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>1. INTRODUCTION</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>2. METHODS</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>3. RESULTS AND DISCUSSION</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>4. SUMMARY AND IMPLICATIONS</td>
<td>112</td>
</tr>
<tr>
<td>V.</td>
<td>FLUORESCENCE AND MOLECULAR PROPERTIES OF CHROMOPHORIC WATER-SOLUBLE ORGANIC MATTER IN ORGANIC AEROSOLS</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>1. INTRODUCTION</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>2. METHODS</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>3. RESULTS AND DISCUSSION</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>4. SUMMARY AND IMPLICATIONS</td>
<td>143</td>
</tr>
</tbody>
</table>
VI. CONCLUSIONS AND FUTURE WORK .................................................. 145
   1. CONCLUSIONS ........................................................................ 145
   2. FUTURE WORK ...................................................................... 150

REFERENCES .................................................................................. 152

APPENDICES .................................................................................. 171
   A. COPYRIGHT PERMISSIONS ..................................................... 171
   B. ABBREVIATIONS AND ACRONYMS ...................................... 172
   C. SUPPLEMENTARY TABLES AND FIGURES ....................... 175

VITA ............................................................................................. 179
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Percent area contributions from the major proton regions in the $^1$H NMR spectra for the PSOM aerosol extracts</td>
<td>21</td>
</tr>
<tr>
<td>2. Molecular formula distributions for each solvent extract based on elemental composition with number average characteristics</td>
<td>31</td>
</tr>
<tr>
<td>3. Average TSP and TC concentrations and carbon percentages for each aerosol source type</td>
<td>60</td>
</tr>
<tr>
<td>4. Total formulas and average elemental properties for aerosol WSOM$_{PPL}$ and PSOM from each emission source determined using FTICR mass spectra</td>
<td>63</td>
</tr>
<tr>
<td>5. Total formulas and average elemental properties for molecular formulas identified by PCA</td>
<td>76</td>
</tr>
<tr>
<td>6. Average relative contributions of total spectral intensity for integrations of major proton regions in $^1$H NMR spectra for each of the aerosol sources</td>
<td>81</td>
</tr>
<tr>
<td>7. Average percentage and standard deviations of total molecular formulas that are part of a specific KMD series in each aerosol source</td>
<td>101</td>
</tr>
<tr>
<td>8. Number and percentage of formulas that represent potential CHO precursors and their products after reaction with NOx, NH$_3$, or SOx for each aerosol emission source</td>
<td>108</td>
</tr>
<tr>
<td>9. Molecular formula distributions for chromophoric formulas identified in FTICR mass spectra for aerosol WSOM$_{PPL}$</td>
<td>126</td>
</tr>
<tr>
<td>10. General molecular formulas corresponding to the homologous DBE series displayed in Fig. 16</td>
<td>127</td>
</tr>
<tr>
<td>11. Descriptions of peaks identified in EEMs for aerosol WSOM</td>
<td>136</td>
</tr>
<tr>
<td>12. Key characteristics of chromophoric molecular formulas suggested as important for classic fluorescence peaks in EEM spectra of aerosol WSOM</td>
<td>141</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Expanded $^1$H NMR spectra between 0-5 ppm for (a) WSOM and (b) PSOM for the aerosol particulate sample collected 25-26 June 2013.</td>
<td>26</td>
</tr>
<tr>
<td>2.</td>
<td>FTICR mass spectra expanded for $m/z$ at a nominal mass of 427 for (a) WSOM, (b) PSOM and (c) ASOM.</td>
<td>28</td>
</tr>
<tr>
<td>3.</td>
<td>The (a) Venn diagram showing the relative distributions of all molecular formulas (5106 total) present in any of the three solvents, and grey areas represent WIOM.</td>
<td>33</td>
</tr>
<tr>
<td>4.</td>
<td>Van Krevelen diagrams for molecular formulas assigned to the (a-d) WSOM, (e-h) WIOM$<em>{pyr}$, and (i-l) WIOM$</em>{acn}$ extracts.</td>
<td>36</td>
</tr>
<tr>
<td>5.</td>
<td>Representative full ESI(-) FTICR mass spectra for WSOM$_{PPL}$ extracts of (a) marine, (b) mixed source, (c) biomass burning, and (d) urban aerosols between 200 – 800 $m/z$.</td>
<td>62</td>
</tr>
<tr>
<td>6.</td>
<td>Van Krevelen diagrams for molecular formulas identified in the FTICR mass spectra for the marine, mixed source, biomass burning, and urban aerosols.</td>
<td>67</td>
</tr>
<tr>
<td>7.</td>
<td>PCA score plots for PC2 versus PC1 (left) and PC3 versus PC1 (right).</td>
<td>75</td>
</tr>
<tr>
<td>8.</td>
<td>Van Krevelen diagrams for molecular formulas identified by PCA for (a) marine, (b) mixed source, (c) biomass burning, and (d) urban aerosols.</td>
<td>77</td>
</tr>
<tr>
<td>9.</td>
<td>$^1$H NMR spectra for WSOM of mixed source, biomass burning, and urban aerosols, where each colored line represents a different sample spectrum.</td>
<td>80</td>
</tr>
<tr>
<td>10.</td>
<td>Aerosol WSOM (a) PC1 and PC2 scores for PCA of full $^1$H NMR spectra of marine, mixed source, biomass burning, and urban aerosols and (b) PC1 and PC2 scores for PCA omitting marine aerosols.</td>
<td>83</td>
</tr>
<tr>
<td>11.</td>
<td>Variable loadings plots for (a) PC1 and (b) PC2 resulting from PCA using full $^1$H NMR spectra of mixed source, biomass burning, and urban aerosol WSOM.</td>
<td>86</td>
</tr>
<tr>
<td>12.</td>
<td>Fractional contributions for KMD oligomer series of varying lengths for each aerosol source for (a) CH$_2$, (b) H$_2$, (c) CO$_2$, and (d) O$_2$.</td>
<td>100</td>
</tr>
</tbody>
</table>
13. Fractional contributions for KMD oligomer series of varying lengths for each aerosol source for (a) $\text{C}_2\text{H}_2\text{O}_2$ (glyoxal and isomers), (b) $\text{C}_3\text{H}_4\text{O}_2$ (methylglyoxal and isomers), and (c) $\text{C}_4\text{H}_6\text{O}$ (MVK/MACR and isomers) .......104

14. Average percentage of CHO formulas identified as precursors to a NOx, NH$_3$, and/or SOx product based on relative aromaticity.................................111

15. Venn diagram for the distribution of chromophoric molecular formulas identified in FTICR mass spectra for aerosol WSOM$_{PPL}$ ........................................124

16. H/C ratio versus carbon plot for chromophoric CHO and CHON formulas identified in FTICR mass spectra for aerosol WSOM$_{PPL}$ .................................129

17. Averaged EEMs contour plots for WSOM extracted from (a) mixed source, (b) biomass burning, and (c) urban aerosols.....................................................133
CHAPTER I
INTRODUCTION

There has been a considerable change to the chemical composition of the atmosphere and the magnitude of emissions from human activities since pre-industrial times, having a negative impact on human health (e.g., Dockery et al., 1993; Kaiser, 2005; Künzli et al., 2000; Pope et al., 2009) and contributing to a net global warming (IPCC, 2013; Myhre, 2009; Ramanathan et al., 2001). The Clean Air Act was implemented by the U.S. federal government in response to growing concerns about protecting the public from harmful emissions. The United States Environmental Protection Agency (US EPA) continues to create and enforce important air quality standards to reduce emissions of hazardous material for the overall improvement in the quality of human life with important ramifications for climate change.

The largest contributor to positive radiative forcing is undoubtedly carbon dioxide (CO$_2$) and an increased concentration of CO$_2$ in the atmosphere has led to global surface warming, ocean warming, sea level rise, and ocean acidification (IPCC, 2013). Radiative forcing describes the capacity of a substance to affect the global energy balance, where a positive value indicates a warming effect and a negative value describes a cooling affect. The amount of CO$_2$ and other well-mixed greenhouse gases such as methane (CH$_4$), nitrous oxide (N$_2$O), and halocarbons in the atmosphere is steadily increasing due to emission from human activities, such as fossil fuel combustion and industrial processes. All of the well-mixed greenhouse gases are responsible for much of the warming with an estimated radiative forcing of +2.22 to +3.78 W m$^{-2}$ (IPCC, 2013). Reduction of well-mixed
greenhouse gas emissions is widely sought, and necessary, to lessen their effect on global warming; however, their long atmospheric lifetimes (decades to centuries) and ubiquitous presence suggest that a substantial amount of time would be required for observable improvements. Aerosols, by contrast, have much shorter atmospheric lifetimes (typically days to weeks). Aerosol mixtures have light-scattering (cooling) and light-absorbing (warming) components with recent estimates indicating that total radiative forcing from aerosols is -1.9 to -0.1 W m\(^{-2}\), which includes estimates from cloud adjustments (IPCC, 2013). Although aerosols have a net cooling effect, there are components that are light-absorbing and mitigation of these species could present a means for reducing global climate forcing in the short term.

Aerosols are a major component of the atmosphere that largely impacts the total radiation budget, and they have been pinpointed as the component contributing to the largest uncertainty to the total radiative forcing estimate of the global radiation budget (IPCC, 2013). Aerosol components include organic matter (OM), black carbon (BC), inorganic species (e.g., nitrates and sulfates), and mineral dust. Aerosols can directly impact radiative forcing by scattering or absorbing solar radiation, or indirectly by acting as cloud condensation nuclei. The light-absorbing components of aerosol include BC and a subset of OM known as “brown carbon.” BC was thought to be the predominant form of aerosol light-absorbing carbon (LAC, Penner et al., 1993), but there is strong evidence to suggest that brown carbon also makes a significant contribution to LACs (Andreae and Gelencsér, 2006; Bond and Bergstrom, 2006; Bones et al., 2010; Krivacsy et al., 2000; Washenfelder et al., 2015). BC is defined by Bond et al. (2013) as refractory carbonaceous material that is formed during the combustion of carbon-based fuels, is water-insoluble, is
strongly light-absorbing, and exists as an aggregate of small spherules. However, this definition is highly inconsistent throughout the literature because the operational definitions used to define and measure BC vary with analytical technique. Additionally, recent discoveries suggest that BC present in DOM may come from sources other than combustion (Chen et al., 2014); however, the relevance of this process to the atmosphere has not yet been explored. Despite the inconsistencies, there is general agreement that BC is strongly light-absorbing and is highly aromatic among the various definitions (Andreae and Gelencsér, 2006; Bond and Bergstrom, 2006; Bond et al., 2013). Brown carbon refers to the light-absorbing constituent of aerosol OM that does not fall under the operational definitions of BC and is said to be composed of a network of aromatic compounds and humic-like substances (HULIS), which includes high molecular weight organic molecules comprised of aromatic rings, carboxyl, hydroxyl, and carbonyl groups (Andreae and Gelencsér, 2006; Chang and Thompson, 2010; Graber and Rudich, 2006; Miller et al., 2009; Mukai and Ambe, 1986). Here, the term LAC will collectively refer to all light-absorbing carbonaceous aerosols, specifically the BC and brown carbon components.

Due to the shorter atmospheric lifetime of these LAC aerosols, it has been estimated that removing all aerosol OM and BC could eliminate 20-45% of the net warming within 3 – 5 years, while a removal of a third of present-day CO₂ would take 50 – 200 years to accomplish the same effect (Jacobson, 2002). Because reduction of these LACs may lessen the effects of warming on a shorter timescale, the US EPA has prioritized obtaining a better emissions inventory and characterization of emissions of in order to predict and assess the net benefits of mitigation policies on a global and local scale (US EPA, 2010).
The most recent (2000) total global emission of BC is estimated to be 7500 Gg C yr\(^{-1}\) with a total radiative forcing of approximately +1.1 W m\(^{-2}\) (Bond et al., 2013), without considering co-emissions. The largest global sources for BC include open burning of forests, solid fuel burning for cooking and heating, and diesel engines (Bond et al., 2013), where the estimated contributions are 70% biomass combustion-derived and 30% fossil fuel combustion-derived (Bond et al., 2004). The great deal of uncertainty associated with these estimates is due to the operational character of BC monitoring methods, where the inclusion of brown carbon in some analytical methods can sometimes interfere with BC concentration measurements. Due to the unclear nature of brown carbon, a world-wide inventory of its sources and concentrations has not been published.

While LACs are an important component of aerosol OM, there are light-scattering components that could potentially offset the warming effects of LACs. These aerosols can directly scatter incoming solar radiation or block it by acting as cloud condensation nuclei (CCN). It has been suggested that aerosol OC may play as important of a role as sulfate aerosol in determining climate impacts from cloud formation (Novakov and Penner, 1993). The ability of an aerosol to act as a CCN is related to its chemical properties, including hygroscopicity and water-solubility. Compounds such as organosulfates are ubiquitous and have been detected in ambient aerosols, cloud water, and fog water (e.g., LeClair et al., 2012; Pratt et al., 2013; Willoughby et al., 2014). Organosulfates are very polar in nature, and their presence may increase the ability of aerosol OM to act as CCN and therefore have an indirect radiative effect (Hallquist et al., 2009).

The individual structures of BC and OM compounds determine the effect each has on radiative forcing. Structures containing areas of unsaturation (double bonds and rings)
experience $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions that cause the compound to absorb ultraviolet (UV) or visible light (Andreae and Gelencsér, 2006; Robertson and O’Reilly, 1987) and warming effect is observed. Aliphatic structures do not undergo these electronic transitions and thus do not absorb light at wavelengths present in sunlight. LACs contain a large number of unsaturated moieties (C=C, C=O, aromatic rings), which are responsible for the light-absorbing nature and net warming caused by these substances (Andreae and Gelencsér, 2006). Thus, it is evident that the chemical composition of carbonaceous aerosols determines their radiative effect, and it is vital that carbonaceous aerosols from various sources (e.g., biomass burning and fossil fuel combustion) are characterized for their chemical composition in order to assess the efficacy of mitigation strategies.

BC and OM together account for 20-90% of total aerosol mass (Jacobson, 2000; Kanakidou et al., 2005; Murphy et al., 2006; Zhang et al., 2007). Aerosol OM is introduced to the atmosphere via direct emissions (primary organic aerosol) or is formed through the reactions of volatile organic compounds (secondary organic aerosol, SOA). BC is introduced to the atmosphere directly from combustion sources, and OM is co-emitted with BC from all of these sources (Bond et al., 2013). Both natural biomass-derived and fossil fuel combustion-derived materials contribute to these aerosol pools. Primary aerosol sources are estimated to account for 11% (Hallquist et al., 2009) to 57% (de Gouw et al., 2008) of these emissions, while the remaining 43-89% is understood to be SOAs forming in the atmosphere (de Gouw et al., 2008; Hallquist et al., 2009). Global organic aerosol budgets estimate fossil fuel sources to account for 13% (Bond et al., 2013; de Gouw et al., 2008; Hallquist et al., 2009) to 41% (Liousse et al., 1996) of organic aerosols, where anthropogenic SOAs are expected to account for more than half of fossil fuel organic
aerosols (de Gouw et al., 2008; Hallquist et al., 2009). While there has been considerable work done to chemically characterize aerosol OM from these sources, source-specific chemical signatures and their light absorption properties have not been fully characterized.

A suite of analytical techniques have determined that aerosol OM includes a multitude of compounds including both hydrocarbons and functionalized species with oxygen, sulfur and/or nitrogen atoms in their structure (Andreae et al., 1988; Decesari et al., 2001; Decesari et al., 2007; Duarte et al., 2005; Fuzzi et al., 2001; Hallquist et al., 2009; Heald et al., 2010; Jimenez et al., 2009; Mayol-Bracero et al., 2002; Narukawa et al., 1999; Reemtsma et al., 2006; Sannigrahi et al., 2006; Wang et al., 2006; Wozniak et al., 2008; Yamasoe et al., 2000). Concentrations of specific components have been evaluated by a number of principal quantitative techniques. Gas chromatography/mass spectrometry provides important structural information for component compounds, where many studies analyze single compound types (alkanes, alcohols, carboxylic acids, etc.) and others look at series of compounds (Alves et al., 2012; Andreae et al., 1988; Mayol-Bracero et al., 2002; Narukawa et al., 1999; Wang et al., 2006; Yamasoe et al., 2000). The high-volatility requirement for gas chromatography limits analytes to the small, low-molecular weight fraction (~10-20%) of aerosol OM. Fourier transform infrared and nuclear magnetic resonance (NMR) spectroscopy are able to characterize a broader range of analytes. They have been used to evaluate bulk molecular bond information for aerosol OM and have shown functional group (carbonyl, alcohol, aromatic rings, etc.) trends for water-soluble aerosols (Decesari et al., 2001; Decesari et al., 2007; Duarte et al., 2005; Sannigrahi et al., 2006). While these techniques have provided a wealth of quantitative information
regarding molecular and bulk properties, a significant fraction of aerosol OM remains uncharacterized.

Ultrahigh-resolution mass spectrometry (UHR-MS) techniques have significantly expanded the analytical window for aerosol OM. Fourier transform ion-cyclotron resonance mass spectrometry (FTICR-MS) has provided molecular formula information for thousands of individual compounds present in the water-soluble fraction of ambient aerosol samples, as well as laboratory-generated SOAs (Altieri et al., 2008a; Heaton et al., 2009; Mazzoleni et al., 2010; Reemtsma, 2010; Reimhardt et al., 2007; Wozniak et al., 2008). Orbitrap-MS, another UHR-MS instrument, has been successfully applied to characterizing aerosol OM. Most notably, it has been used to characterize laboratory-generated SOA samples and provide important information about the chemical nature of the aerosol OM formed through atmospheric aging processes with molecular-level detail (Bateman et al., 2010; Laskin et al., 2010; Nguyen et al., 2010). UHR-MS shows great promise for providing important BC and brown carbon molecular information at unprecedented resolutions. Pairing this molecular information with light absorption measurements provides reliable insight to the properties that define these LACs.

There is no unambiguous chemical definition for BC, consequently methods for preparing and quantifying BC from the rest of the aerosol pool are operational and rely on the measurement of thermal, optical, or molecular properties (Andreae and Gelencsér, 2006; Bond and Bergstrom, 2006; Bond et al., 2004; Hammes et al., 2007). Optical instruments, such as aethalometers, nephelometers, and particle soot absorption photometers, measure light absorption and use an empirical conversion factor to obtain a BC mass or concentration (Bond et al., 1999; Gundel et al., 1984; Hansen et al., 1984;
Heintzenberg, 1982; Hitzenberger et al., 1999). Thermal desorption techniques (e.g., chemothermal oxidation; CTO-375) involve the oxidation or evaporation of organic carbon with the remaining mass quantified as BC (Gustafsson et al., 2001; Gustafsson et al., 1997). This method relies on the thermal properties of BC, as a result does not include other LACs (Zencak et al., 2007). Although CTO-375 is more commonly measured for geochemical (soil and sediment) OM samples, this method has successfully been applied to atmospheric samples (Currie et al., 2002; Eglinton et al., 2002; Reddy et al., 2002; Zencak et al., 2007). While the techniques described are have great value, they have critical limitations and do not provide the specific chemical information that is required to consolidate LAC measurements and estimates.

Recently, excitation emission matrix spectroscopy (EEMs) has been used to determine the light-absorbing and fluorescence properties of aerosol OM. EEMs has the unique capability to simultaneously acquire a UV-visible spectrum and a fluorescence spectrum for a single sample. This method provides information about all of the LACs present within an NOM sample, and is not specific to an operationally-defined subset (e.g., BC). Therefore, the distinction between BC and other LACs does not need to be established in order to assess the properties that may have an impact on radiative forcing. EEMs has been used extensively to characterize dissolved OM (DOM), and has provided information regarding sources and biological and chemical reactivity (Fellman et al., 2010 and references within). Studies of aerosol OM with EEMs are surprisingly few, but have demonstrated seasonal and regional variations in fluorescent properties of urban aerosols (Duarte et al., 2005; Matos et al., 2015; Mladenov et al., 2011b), explored the effect of solar radiation on laboratory-generated brown carbon (Lee et al., 2014), and characterized
the chromophoric material in rainwater as indicators of storm origin (Kieber et al., 2006). The number of studies that use EEMs to characterize OA is surprisingly few given its demonstrated utility. The combination of FTICR-MS and EEMs analysis of ambient organic aerosols has the ability to provide detailed molecular information required to enhance LAC inventories.

The overall goal of this study is to employ the powerful characterization capabilities of ultrahigh-resolution mass spectrometry to field-collected carbonaceous aerosols from key emission sources and to correlate the detailed molecular composition to light-absorbing properties, determined by EEMs. Accordingly, I will test the hypothesis that the light-absorption characteristics of carbonaceous aerosols are closely linked to their physicochemical properties. Within this overarching hypothesis, I examine two specific sub-hypotheses: 1) aerosols containing substantial amounts of highly-aromatic organic compounds will correspond to stronger light-absorbing properties, and 2) there are source-dependent patterns of chemical structure that can provide a specific molecular signature for each key emission source. Ambient aerosols from an urban site, a biomass burning event, a mixed source site, and a marine site will be compared and key molecular properties for each emission source will be elucidated with the aid of multivariate statistical analyses.

Chapter II explores the molecular differences between water-soluble and water-insoluble aerosol OM collected in Gloucester Point, VA. Approximately 10-70% of aerosol OM is water-soluble (WSOM), which means that 30-90% of the OM water-insoluble (WIOM). Radiocarbon measurements have shown that WSOM is primarily comprised of biogenically-derived compounds and WIOM contains most of the fossil material (i.e., anthropogenically-derived; Wozniak et al., 2012a). The aerosol OM was extracted with
water (WSOM) and organic solvents (WIOM) and subsequently analyzed for their molecular and bulk properties using FTICR-MS and proton NMR (\( ^1 \text{H} \text{NMR} \)). This is the first time that aerosol WIOM has been characterized at the molecular level, and provides valuable information regarding the molecular composition of anthropogenically-derived aerosol OM. Anthropogenic aerosols play a huge role in the evolution of the chemical composition of the atmosphere, and this characterization is necessary to determine the environmental impact and fate aerosol OM has.

Chapter III describes the molecular differences between several aerosol emission sources using advanced analytical techniques and statistical analysis. Ambient total suspended particulate samples were collected from various locations throughout the eastern United States and Atlantic Ocean to represent urban aerosols (Philadelphia, PA), biomass burning aerosols (Great Dismal Swamp fire event), mixed source aerosols (Gloucester Point, VA), and marine aerosols (North Atlantic Ocean). The WSOM and WIOM for multiple samples from each key source were analyzed using FTICR-MS and \( ^1 \text{H} \text{NMR} \), and the important molecular differences were elucidated using principal component analysis (PCA). The marine, biomass burning, and urban aerosols contain molecular features that permit distinction from the other sources, and the mixed source aerosols share features with each of the key sources. Some of the disguising features include heteroatom content, aromaticity, and degree of oxidation. These molecular features provide clues to the formation and transformations that the OM experience in the atmosphere. Understanding the chemical features that define specific source types is critical in determining which emission sources may have the most harmful impacts on the surrounding environments.
Chapter IV presents new methods for extracting valuable information regarding the chemical transformations of atmospheric OM using molecular formulas identified in FTICR-MS datasets. The first of these methods uses Kendrick mass defect (KMD) analysis to evaluate the extent of OA processing due to oligomerization by important biogenic SOA species (isoprene derivatives) and carboxylation processes. The second method examines mass differences between CHO and CHON or CHOS formulas to investigate the extent of reactions due to the incorporation of inorganic ionic species. The KMD analysis has revealed that reactions with isoprene-related compounds are widespread amongst aerosols sources, but the oligomerization is more extensive in urban aerosols, which are presumably more aged. Additionally, reactions with inorganic species (NOx, NH3, and SOx) are also widespread among the sources, and reactions with NOx are important in altering OA in terrestrial environments than the marine. These data analysis techniques offer ways to extract important information on the relative importance of various atmospheric transformations in OA thereby enhancing the amount of qualitative information atmospheric chemists can obtain from extensive FTICR-MS datasets.

Chapter V focuses on the link between aerosol emission source and fluorescence properties using EEMs. While specific molecular features are revealed with FTICR-MS analysis, they do not provide direct evidence for the associated physicochemical properties. EEMs analysis provides evidence for the fluorescence properties of aerosol OM that are suggested by FTICR-MS. The fluorescence properties of these aerosols are distinct between the sources, including signatures for compounds associated with fossil fuels in the urban aerosols, and freshly emitted humic material in the biomass burning aerosols. Fluorophore intensities are an order of magnitude higher on a per carbon basis than the
other aerosols investigated, indicating they make a more significant contribution to aerosol LACs. These analyses provide the first link between aerosol emission sources, molecular characteristics, and associated fluorophoric nature.

Collectively, the findings from this research presents a more comprehensive accounting for component aerosol LACs and aerosol OM, based primarily on molecular character and fluorescence properties, providing a more thorough method for evaluating these atmospheric species, ultimately leading to a reduction in the uncertainties related to current climate modeling schemes. Determining the specific relationship between fluorescence character and chemical signatures helps to identify emission sources having a detrimental impact on the radiative budget, thus allowing environmental policy-makers to implement more effective mitigation strategies for carbonaceous aerosols.
CHAPTER II

A MOLECULAR-LEVEL APPROACH FOR CHARACTERIZING WATER-INSOLUBLE COMPONENTS OF AMBIENT ORGANIC AEROSOL PARTICULATES USING ULTRA-HIGH RESOLUTION MASS SPECTROMETRY

Preface

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1 Introduction

The introduction and improvement of advanced spectroscopic methods has provided a wealth of new chemical information regarding organic aerosols in the last few decades. Establishing the chemical identity of the individual components that make up organic aerosols has remained an important goal in order to understand the relationships between their sources, transport, molecular identities and transformations and their impacts and fates in the environment. The importance of organic aerosols to climate and biogeochemical cycling has been well documented (Andreae and Crutzen, 1997; Andreae and Gelencsér, 2006; Bond et al., 2013; Booth et al., 2012; Crutzen and Andreae, 1990; Jacobson, 2000; Ramanathan et al., 2001). The specific molecular nature of organic
aerosols directly influences the impact they have on the environment. For example, light absorption is caused by electronic transition associated with molecular double bonds and the number of double bonds and aromatic rings present within the structure has been linked to the ability of that molecule to absorb ultraviolet or visible light (Andreae and Gelencsér, 2006). Given the connections between chemical characteristics and environmental impact, establishing the relationship between aerosol organic matter (OM) source and associated chemical characteristics is important for modeling and predicting the net impact they have on environmental systems. To date, uncertainties in the molecular makeup of organic aerosols limit our ability to make these linkages between aerosol OM source, chemical characteristics, and environmental impact.

Between 10-90% of total aerosol mass is comprised of OM (Jimenez et al., 2009; Kanakidou et al., 2005), and 10-70% of that OM is water-soluble (Decesari et al., 2007; Kleefeld et al., 2002; Sullivan et al., 2004; Zappoli et al., 1999) depending on its physical and chemical composition. A suite of analytical techniques have provided bulk and specific chemical information about carbonaceous species present within fractions of atmospheric OM samples (Hallquist et al., 2009), including ambient aerosols, fog water and rainwater, and laboratory generated secondary organic aerosols (SOA). These efforts have shown aerosol OM to be made up of a highly diverse suite of oxygenated compounds that include aliphatic and conjugated functional groups (e.g., (Decesari et al., 2007; Jimenez et al., 2009; Mayol-Bracero et al., 2002; Wozniak et al., 2008), which influence the watersolubility as well as the light-absorbing capacity of the compounds (Andreae and Gelencsér, 2006; Robertson and O’Reilly, 1987). Recently, ultra-high resolution mass spectrometry has shown an extraordinary capacity for characterizing aerosol OM, and is
the only current technique able to provide elemental formula information for the thousands of compounds present within individual ambient aerosols (Lin et al., 2012; Mazzoleni et al., 2012; Reemtsma et al., 2006; Schmitt-Kopplin et al., 2010; Wozniak et al., 2008) and laboratory generated aerosols (Bateman et al., 2008; Heaton et al., 2009; Laskin et al., 2010; Reinhardt et al., 2007) without prior chromatographic separation. In addition to oxygenated compounds, many other functionalized species, including those containing nitrogen and sulfur, have been identified in ambient aerosols, fog water (LeClair et al., 2012; Mazzoleni et al., 2010) and rainwater (Altieri et al., 2012; Altieri et al., 2009; Mitra et al., 2013) from various sources.

Numerous publications characterize some fraction of aerosol OM using various solvent systems, ionization sources, and mass analyzers. To date, much of the work has focused on the water-soluble fraction, leaving little information regarding the water-insoluble fraction that comprises 30 - 90% of the OM (Decesari et al., 2007; Kleefeld et al., 2002; Sullivan et al., 2004; Zappoli et al., 1999). Radiocarbon data for organic aerosols collected in rural environments suggests that much of the water-insoluble carbon is fossil-derived and from anthropogenic sources, whereas the water-soluble carbon is contemporary and biogenically-derived (Szidat et al., 2004; Wozniak et al., 2012a; Wozniak et al., 2012b). Limiting molecular analysis to the water-soluble OM (WSOM) means that a quantitatively important component of organic aerosols is missing. Studies have examined the methanol-soluble and acetonitrile-soluble (Bateman et al., 2010; Heaton et al., 2009) fractions of SOAs and other laboratory generated aerosols. Studies of SOA, which are thought to be highly water-soluble, have shown that the water and acetonitrile extracted OM fractions are extremely similar at the molecular level (Bateman et al., 2010;
Heaton et al., 2009) However, Bateman et al. (2010) examined a laboratory-generated biomass burning aerosol and determined that the acetonitrile-soluble component of aerosol OM had characteristically lower oxygen to carbon (O/C) ratios than the water-soluble component, suggesting molecular differences between water-soluble and solvent-soluble components of some organic aerosols. These differences imply that the water-insoluble materials in aerosol OM have molecular characteristics distinct from water-soluble OM. However, the differences in water-insoluble and water-soluble aerosol OM have still not been extensively explored.

In the present study we evaluate the specific molecular composition of the water-insoluble fraction of ambient aerosol OM. We employ Fourier transform ion cyclotron resonance mass spectrometry with negative electrospray ionization (ESI-FTICR-MS) for molecular characterization and NMR spectroscopy for additional structural characterization. We select pyridine and acetonitrile, two solvents that exhibit different polarities than water, have different solvating characteristics, and are compatible with ESI-FTICR-MS and NMR.

Three ambient aerosol particulate samples were collected from a coastal Virginia (USA) site influenced by a mixture of anthropogenic and biogenic aerosol OM sources typical to the east coast of the United States. The suitability of pyridine and acetonitrile as solvents for characterizing aerosol water-insoluble organic matter (WIOM) by ESI-FTICR-MS was established by comparing the molecular formulas assigned to the pyridine-soluble organic matter (PSOM), acetonitrile-soluble organic matter (ASOM), and WSOM extracts of these ambient aerosol particulate samples.
2 Methods

2.1 Sample Collection

Three ambient aerosol total suspended particulate (TSP) samples were collected during the summer (16-17 August 2011; 24-25 June 2013; and 25-26 June 2013) at the Virginia Institute of Marine Science in Gloucester Point, VA (37.2482 N, 76.5005 W). Air was drawn through a pre-combusted (4 h, 475°C) quartz microfiber filter (Whatman QM/A, 20.3 x 25.4 cm, 419 cm² exposed area, 0.6 µm effective pore size) using a TSP high volume air sampler (Model GS2310, Thermo Andersen, Smyrna, GA) at an average flow rate of 0.81 m³ min⁻¹. Air particles were collected for 24 hours with total air volumes ranging between 1124-1169 m³, and are expected to have contributions from several nearby biogenic and anthropogenic sources (e.g., estuarine waters, natural vegetation, light vehicle traffic, oil refinery, coal-fired power plant) as is typical of the eastern United States. The samples were transferred to a pre-combusted foil pouch immediately after collection and stored at -8°C until analysis. A new and pre-combusted QM/A filter blank was stored under identical conditions as the sample, and was analyzed as a storage filter blank for the 2011 sample. A new and pre-combusted QM/A filter was attached to the air sampler immediately prior to the 2013 sampling (24 June 2013) and then stored under identical conditions as the samples, and was analyzed as a field filter blank for the 2013 samples.

2.2 Aerosol Mass and Carbon Measurements

The QM/A filters were weighed before and after sampling to determine the total aerosol mass (24.3 – 29.7 mg TSP) and concentration (20.8 - 26.2 µg/m³). Triplicate aerosol core plug (2.84 cm² area) samples were acidified to remove inorganic carbon by treating the plugs with 1M HCl followed by drying in an oven (4h, 80°C). Acidified filter
plugs were evaluated for total carbon (C = organic + elemental/black – inorganic carbonates) and nitrogen (N) content using a Flash EA 1112 elemental analyzer (ThermoFinnigan). Quantification was achieved using an aspartic acid standard calibration curve. Acidified blank QM/A filters were evaluated for blank subtraction; however, C and N quantities for all of the blank QM/A filter plugs were below the detection levels of the instrument.

2.3 Solvent Extractions

Replicate solvent extracts of the aerosols and the respective filter blank were obtained by combining three aerosol plugs or blank plugs (3 aerosol plugs contain between 0.116 and 0.147 mg C) with either 15 mL water (Millipore Synergy Ultrapure Water System), 5 mL pyridine (Acros, 99+%), or 5 mL acetonitrile (Fisher Optima, 99.9%) and thoroughly mixed on an orbital shaker table (150 RPM, 4h, 21°C). Insoluble particles were filtered out using a syringe filter with a pre-combusted glass fiber filter (0.7 μm pore size). The water extracts were then desalted in order to remove salts that can limit the ionization of OM by ESI and concentrated using an established procedure for PPL solid-phase extraction cartridges (Dittmar et al., 2008). PPL is expected to retain 60-75% of OM (Dittmar et al., 2008). Low molecular weight and exceptionally hydrophilic compounds are expected to be among the losses. Compounds with a low molecular weight (<200 Da) are not detected under the FTICR-MS conditions used here, so the negative effects of PPL extraction are expected to be minimal. The desalted sample was eluted in 5 mL of methanol (WSOM, Acros, 99.9%). The pyridine filtrate (PSOM) and acetonitrile filtrate (ASOM) did not require further manipulation, and all three extracts were thus prepared so that the final solutions had the same filter plug to solvent volume ratio (3 plugs in 5 mL of solvent).
Samples were stored at -8°C until FTICR-MS analysis, typically within 24 hours of preparation.

### 2.4 Extraction efficiency determinations

The filtrates from the water-extracts were evaluated for non-purgeable organic carbon using a Shimadzu TOC-VCPH analyzer to determine water soluble organic carbon (WSOC) content (Wozniak et al., 2008; Wozniak et al., 2012a) The WSOC content was then compared with the total aerosol organic carbon content to find that 54 – 60% of the total aerosol organic carbon was WSOC.

An important aspect of choosing a suitable solvent for WIOM characterization is its extraction efficiency which could not be accurately determined for acetonitrile and pyridine using standard TOC analysis. Upon evaporation of solvent extracts, these organic solvents adhere to natural organic matter artificially inflating the carbon content in acetonitrile and pyridine extracts. Therefore, a method was developed based on $^1$H NMR using glucose (98%, Acros Organics) as a standard, which is 100% soluble in pyridine at low concentrations (<1mg/mL). Acetonitrile interferes with our $^1$H NMR quantification strategy due to a strong signal from acetonitrile hydrogen (occurring at ~2 ppm) that overlap with the signal from OM (occurring between 0.1-4.4 ppm). This overlapping signal impedes our ability to determine the amount of proton signal derived from the sample and precludes a reliable calculation of extraction efficiency for acetonitrile. A known mass of glucose was dissolved into pyridine-D$_5$ (100% atom D, Acros Organics) providing known carbon and hydrogen concentrations to compare to $^1$H NMR spectra. Aerosol plugs of known OC masses were each dissolved into pyridine-D$_5$ and water. The WSOM and PSOM samples were then subjected to $^1$H NMR spectroscopy using a Bruker Daltonics 400 MHz
NMR with a BBI probe. WSOM samples were diluted using D$_2$O (100% atom D, Acros Organics) at a ratio of 90:10 WSOM:D$_2$O. PSOM samples were analyzed in a solvent system of 100% pyridine-D$_5$. All samples were analyzed for 4000 scans using a standard Bruker water-suppression pulse program, where the 90° pulse and the transmitter offset were optimized individually for each sample.

The signals obtained from $^1$H NMR spectra were integrated over the range of 0.1 to 4.4 ppm to get a total signal response, and also integrated over three ranges of chemical shifts to determine contributions from the major proton types (Moretti et al., 2008; Shakya et al., 2012) aliphatic, unsaturated alkyl, and oxygenated aliphatics. Aliphatic hydrogen (H-C, 0.6-1.8 ppm for WSOM and 0.7-1.95 ppm for PSOM), unsaturated alkyl or hydrogen α to unsaturated carbons (H-C-C═, 1.8-3.2 ppm for WSOM and 1.95-3.2 ppm for PSOM), and oxygenated aliphatic hydrogen including alcohol, ether, and ester function groups (H-C-O, 3.2-4.4 ppm in WSOM and PSOM). Though aromatic protons (6.5-8.2 ppm) are used in other studies, we omit them from analysis due to the interference of exchanged protons in the pyridine-D$_5$ solvent. The region of 0.1-4.4 ppm is appropriate for this study because it is free of signals from the solvent and contains the majority of signal for these types of samples. The signal response for each proton region was normalized to the total signal response between 0.1-4.4 to establish the percent contribution for each proton type. These percentages were used to calculate the average H/C ratio for each sample to be used to convert hydrogen to carbon content (see Table 1). An H/C ratio of 2 is used for the aliphatic hydrogen and unsaturated alkyl hydrogen, and an H/C ratio of 1.1 is used for the oxygenated aliphatics (Decesari et al., 2007; Moretti et al., 2008; Shakya et al., 2012).
Table 1. Percent area contributions from the major proton regions in the $^1$H NMR spectra for the PSOM aerosol extracts.

<table>
<thead>
<tr>
<th>Functional Group Region</th>
<th>Chemical Shift (ppm)</th>
<th>% $^1$H NMR spectral area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16-17 August 2011</td>
<td>24-25 June 2013</td>
</tr>
<tr>
<td>H-C-O</td>
<td>3.2 – 4.4</td>
<td>2.5</td>
</tr>
<tr>
<td>H-C-C=</td>
<td>1.95 – 3.2</td>
<td>18.3</td>
</tr>
<tr>
<td>H-C</td>
<td>0.7 – 1.95</td>
<td>78.8</td>
</tr>
<tr>
<td>Calculated H/C</td>
<td>1.98</td>
<td>1.98</td>
</tr>
</tbody>
</table>

The signal obtained for glucose protons dissolved in pyridine-D$_5$ were used to establish a glucose response factor (area per mass unit hydrogen). The total area between 0.1-4.4 ppm in each sample was converted into a mass of dissolved hydrogen using the glucose response factor. The dissolved hydrogen mass was converted to dissolved carbon mass using the calculated average H/C ratio (1.94-1.98). Comparison of the calculated dissolved carbon amount to the starting mass of carbon gives a relative percentage of extractable organic matter.

2.5 ESI-FTICR-MS

Immediately prior to analysis, the WSOM replicates (in methanol) and filter blank extract were diluted by 2 using LC/MS grade water with a small amount (<0.1% total volume) of ammonium hydroxide to enhance ionization efficiency. The PSOM, ASOM, and respective filter blank extracts were diluted by 2 using methanol with a small amount (<0.1% total volume) of ammonium hydroxide. Prior to sample analysis, the instrument was externally calibrated using a polyethylene glycol standard. Each of the samples was introduced to an Apollo II electrospray ionization source (negative ion mode) at a flow rate of 120 nL/min on a Bruker Daltonics 12 Tesla Apex Qe FTICR-MS housed at the College of Sciences Major Instrumentation Cluster at Old Dominion University. Spray voltages...
were optimized for each sample. Ions were accumulated in the hexapole for 0.5-2.0 seconds before transfer into the ICR cell, where exactly 300 transients were co-added. Experimental duplicates were evaluated for each aerosol sample and solvent mixture to ensure good experimental and instrumental reproducibility.

### 2.6 Data Processing

Each spectrum was calibrated internally using naturally occurring molecules (fatty acids, dicarboxylic acids, and other homologous series with only carbon, hydrogen, and oxygen in the molecular formula) within the sample (Sleighter et al., 2008). Salt peaks (mass defect 0.4-0.98 for \( m/z < 400 \), and mass defect 0.6-0.97 for \( m/z > 400 \)), blank peaks (those present in the respective QM/A filter blank), and \(^{13}\)C isotopologue peaks were removed from each mass list prior to formula assignments. Additionally, each set of duplicates was evaluated for common \( m/z \), where only common \( m/z \) were used for molecular formula assignments. Each set of duplicates was threshold-corrected for peaks that were below the S/N 3 threshold, but above S/N 2.5 (for example, if a peak was present at S/N 3.1 in one sample, and S/N 2.9 in the second sample, then it was considered common; Sleighter et al., 2012). This corrects for minor differences in peak magnitude that may cause a peak to go undetected, when it is present at a magnitude slightly below the method detection limit. Each set of duplicates had more than 67\% of the peaks (300-600 \( m/z \)) in common, indicating good instrumental and experimental reproducibility (Sleighter et al., 2012).

Molecular formulas were assigned to \( m/z \) common to duplicates using an in-house MatLab (The Math Works, Inc., Natick, MA) code according to the criteria \(^{12}\)C\(_{5-50}\), \(^1\)H\(_{5-100}\), \(^{14}\)N\(_{0-5}\), \(^{16}\)O\(_{1-30}\), \(^{32}\)S\(_{0-2}\), and \(^{31}\)P\(_{0-2}\), where the subscripts indicate the range of atoms allowed
in a formula. The assigned formulas were screened to eliminate any chemically unreasonable formulas for naturally occurring organic compounds. The criteria for formula assignments are consistent with published procedures (Stubbins et al., 2010; Wozniak et al., 2008). Most (79%-96%) of the common peaks between 200-800 m/z could be assigned a formula. A large majority (>90%) of the formulas are within 0.5 ppm agreement of the measured m/z, and all formulas are within 1 ppm error.

3 Results and Discussion

3.1 NMR spectroscopy

One of the initial concerns for this comparison was to determine whether the organic solvents chosen were as effective as water for removing OM from aerosol particulates. We resorted to 1H NMR spectroscopy to evaluate the relative proportion of OM extracted by water and pyridine. Pyridine has been demonstrated to extract significant quantities of macromolecular OM from natural samples that have distinctly low water-solubility (e.g., coals, soils, kerogen, etc.; (McKee and Hatcher, 2010; Salmon et al., 2011; Wu et al., 2003). Extracts of pyridine lend themselves well to recovery estimates using 1H NMR. By integrating the peaks in the main resonance absorption region of the spectrum of aerosol PSOM, between 0.1 and 4.4 ppm, we determined the area response from the sample and used the glucose response factor (area per mass unit of hydrogen) to determine the amount of carbon present in the PSOM. The starting mass of carbon for each aerosol is known, and the percent of extractable carbon, and therefore extractable OM, could be determined. We determined that 31 – 59% of the aerosol OM is soluble in pyridine, which is comparable to what is found for WSOM (54 – 60%). We recognize that assumptions were made in order to determine these values, and that OM solubility in pyridine will vary
with sample type; however, we are confident in these values due to the matched signal response in both PSOM and WSOM samples.

Acetonitrile has been used in the characterization of laboratory-generated aerosol OM in previous studies (Bateman et al., 2010; Bateman et al., 2008; Heaton et al., 2009; Laskin et al., 2010; Reinhardt et al., 2007) and is examined by FTICR-MS in this study for this reason. We did not evaluate the acetonitrile extraction efficiency by NMR because this solvent displays its main signal in the 0.1 to 4.4 ppm region and a comparison like the one made with pyridine was not feasible. However, we can speculate that the efficiency is comparable to that of water and pyridine, considering its relative polarity as a solvent.

While the primary motivation for obtaining $^1$H NMR spectra was to evaluate extraction efficiencies, the information contained therein is valuable for bulk characterization. A more detailed structure characterization is beyond the scope of this manuscript but will be the subject of future work. Figure 1 shows the $^1$H NMR spectra for the WSOM and PSOM fractions for one of the aerosol samples (collected 25-26 June 2013) and the table inset gives the chemical shifts and average relative intensities (for all three aerosol samples) and standard deviations. Both spectra are dominated by aliphatic signals if one does not consider the strong resonances in the aromatic region of the PSOM spectrum assigned to pyridine protons. The peak positions are different for PSOM giving the impression that functionalized structures in WSOM are different from those of PSOM. For example, the methylenic peak (CH$_2$) in WSOM spectrum falls between 1.1-1.2 ppm, and is between 1.2-1.5 in the PSOM spectrum. However, it is likely that we are observing peak shifts due to solvent interactions (Sanders and Hunter, 1993) and some of the peaks in the PSOM spectrum are shifted downfield with respect to the WSOM spectrum. A majority of
the signal is due to aliphatic hydrogen in both spectra. However, this group is proportionally of greater intensity (73.9% of spectral intensity) in the PSOM spectrum relative to all other resonances. Methyl protons (CH$_3$ at 0.7-0.8 ppm for WSOM and 0.8-0.9 ppm for PSOM) are nearly in the same relative proportions to methylenic (CH$_2$ at 1.1-1.2 ppm for WSOM and 1.2-1.5 ppm for PSOM) protons in both extracts (a CH$_2$/CH$_3$ ratio of 4 for both WSOM and PSOM). This suggests aliphatic structures of similar chain lengths.

Additional differences between the WSOM and PSOM spectra are found in the regions downfield of 1.7 ppm, regions typically associated with protons near electron withdrawing functional groups (e.g., hydroxyl, carboxyl, carbonyl, and amino groups). The WSOM extract shows higher relative peak areas in this region, evidence for a greater relative abundance of these types of resonances. Protons found in this region make up 41.8% of the spectral area for WSOM and 25.4% of the spectral area for PSOM. The peaks between 2.0 and 2.8 ppm in both spectra are characteristic of hydrogen attached to a carbon alpha to an unsaturated carbon (H-C-C=), which represent alkenes and carbonyl groups. The relative abundance is higher in the WSOM than PSOM (33.5% and 21.6%, respectively), suggesting that WSOM is more selective for unsaturated compounds, which absorb light (Andreae and Gelencsér, 2006), and WSOM may contribute more light absorption on a per carbon basis than PSOM. The broad peak between 3.2 and 4.0 ppm in the WSOM spectrum is attributed to hydrogen attached to carbon adjacent to oxygen or nitrogen could represent polyols, carbohydrate-like materials, or peptide-like materials. Their relative abundance in the PSOM spectrum is less than in the WSOM spectrum (3.8% versus 8.3% spectral intensity) demonstrating that the two solvents extract chemically
Figure 1. Expanded $^1$H NMR spectra between 0-5 ppm for (a) WSOM and (b) PSOM for the aerosol particulate sample collected 25-26 June 2013. The table insets give the chemical shifts and average relative intensities (normalized to total intensity between 0 and 4.4 ppm) and standard deviations for the three aerosol samples in the major proton regions, including aliphatic (H-C), unsaturated (H-C-C=), and oxygenated aliphatics (H-C-O).

distinct portions of aerosol OM. The NMR spectral information thus shows a greater preponderance of signals from protons near functionalized structures and unsaturated carbons in the WSOM and a higher relative signal for aliphatic protons in the PSOM.

3.2 Mass spectra and molecular formula characteristics

The ESI-FTICR mass spectra for ambient aerosol WSOM are comparable to previously published FTICR-MS spectra of aerosol WSOM extracts (Lin et al., 2012;
Mazzoleni et al., 2012; Schmitt-Kopplin et al., 2010; Wozniak et al., 2008) averaging thousands of peaks across a broad range of 200-800 \( m/z \); the PSOM and ASOM also contained thousands of peaks across the same mass range. There are clear spectral differences between the WSOM and the solvent extracts (i.e., PSOM and ASOM), including differences in the presence of some peaks, as well as the relative magnitudes of common peaks (Fig. 2).

Figure 2 shows a WSOM, PSOM, and ASOM spectra for one of the aerosol samples (collected August 16-17, 2011) expanded at a single nominal mass (\( m/z=427 \)). This distribution of peak intensities is representative of odd nominal masses across the spectral range. Each of the peaks with S/N of at least 3 is labeled with colored shapes to denote the elemental makeup of the assigned molecular formula. There are a few peaks that were not assigned a molecular formula because no chemically reasonable formula was possible using the given criteria suggesting these molecular formulas contain elements other than C, H, N, O, S, and/or P. A Kendrick mass defect plot for formulas differing by a CH\(_2\) group (Fig. S1, Appendix C) shows that the formulas identified in Fig. 2 are involved in Kendrick mass defect series that span nearly the entire mass range (200-800 \( m/z \)). One of the striking differences is the presence of more peaks at the low mass defect region (below 427.1 \( m/z \)) in the PSOM (Fig. 2b). PSOM has the most peaks in this low mass defect region (masses having a decimal less than 0.1) throughout the entire spectrum when compared to WSOM and ASOM (Fig. S2, Appendix C). Peaks with low mass defect are either deficient in hydrogen or rich in oxygen, which suggests that PSOM contains either more unsaturated formulas or more highly oxygenated species than does the WSOM. Those specific peaks at 427.05294 \( m/z \) and 427.05518 \( m/z \) represent CHOS compounds with high O/C ratios.
Figure 2. FTICR mass spectra expanded for m/z at a nominal mass of 427 for (a) WSOM, (b) PSOM and (c) ASOM. Peaks with S/N ≥3 have a colored shape above the peak to indicate the elemental makeup of the assigned molecular formula. Blue circles represent CHO formulas, green triangles represent CHOS formulas, orange diamonds represent CHON formulas, red squares represent CHONS formulas, and a black “x” denotes m/z that did not have a formula assigned under the chosen criteria.

indicating that the selectivity is likely due to the compounds being more highly oxygenated rather than hydrogen deficient. In addition to peak presence and absence, there is a
difference in the peak intensity distributions between the three solvents. The most intense peak in the WSOM (Fig. 2a) is in the center of all peaks for that nominal mass at 427.19723 \( m/z \), and has been assigned as a formula containing only CHO (C\(_{21}\)H\(_{32}\)O\(_9\)). This peak is present in both ASOM and PSOM, but the relative intensity is considerably lower. The most intense peak (427.09168 \( m/z \)) in the ASOM and PSOM is a CHOS formula (C\(_{15}\)H\(_{24}\)O\(_{12}\)S) located at a lower mass defect than the most intense peak in the WSOM spectrum. This peak is also present in WSOM, but at a much lower relative intensity. These differences in relative magnitude of peaks and the presence or absence of some peaks reflect the differences in the ability of these three solvents to extract and detect certain compounds. Recently, the relative magnitude of peaks for compounds detected using ESI-FTICR-MS have been shown to be quantitatively significant and reproducible in a consistent solvent system (Kamga et al., 2014) and have also been used to highlight the differences in sample composition in ESI-FTICR-MS studies of aerosol OM (e.g., Mazzoleni et al., 2012). However, differences in solvent composition have not been evaluated to determine how the solvent affects ESI efficiency, so the remainder of the discussion of the data focuses on differences in presence and absence of peaks in water, pyridine and acetonitrile extracts to provide a qualitative view of WIOM components detected by ESI-FTICR-MS.

A majority of the detected peaks in each extract were assigned molecular formulas within 0.5 ppm error. All of the assigned formulas present in any of the three aerosol samples were combined for each of the three solvents to generate master lists containing every molecular formula assigned to each WSOM, PSOM, and ASOM. Additionally, the master lists for the three solvents were combined to evaluate the molecular properties of
the aerosol sample as a whole. The master lists for each solvent were compared for distinct molecular characteristics. The molecular characteristics for each solvent are arranged by their elemental makeup (e.g., number and percentage of CHO formulas) and numerical averages for O/C, H/C and a modified aromaticity index (AI_{mod}, Eq. 1), shown in Table 2. For simplicity and due to low number frequency, all formulas containing phosphorus (CHOP, CHONP, and CHOSP) have been grouped together and reported as CHOP(N,S).

AI_{mod} is a metric established by Koch and Dittmar (2006) that estimates the degree of aromaticity of an organic compound using only its molecular formula. AI_{mod} is calculated using Eq. 1:

$$AI_{mod} = \frac{(1 + C - 0.5O - S - 0.5H)/(C - 0.5O - S - N - P)}{1}$$

(1)

for any molecular formula comprised of C, H, N, O, S, and P. AI_{mod} is similar to other aromaticity metrics, such as carbon normalized double bond equivalent (Hockaday et al., 2006), and it includes heteroatoms as points of unsaturation and conservatively assumes that half of all O participate in a double bond, such as that of a carbonyl group. A low AI_{mod} indicates a low degree of aromaticity where a value of zero is an aliphatic compound, a value between 0-0.5 is representative of olefinic compounds (containing at least one double bond) and includes alicyclic molecules. A high AI_{mod} indicates a higher degree of aromaticity where a compound having a value above 0.5 is aromatic, and a value of 0.67 or higher indicates condensed aromatic compounds (fused aromatic rings; Koch and Dittmar, 2006). Aromatic and condensed aromatic compounds play an important role in the light-absorbing ability of organic aerosols (Andreae and Gelencsér, 2006).

Before analyzing the molecular properties of the individual solvents, every molecular formula (5106 formulas total) assigned to any of the three solvents was
Table 2. Molecular formula distributions for each solvent extract based on elemental composition with number average characteristics. The values for PSOM and ASOM do not include formulas common with WSOM, thus represent characteristics for WIOM.

<table>
<thead>
<tr>
<th>Solvent Extract</th>
<th>Elemental Composition</th>
<th># of Formulas</th>
<th>% of Formulas</th>
<th># of Formulas</th>
<th>% of Formulas</th>
<th>Number Averages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O/C</td>
<td>H/C</td>
<td>AI\textsubscript{mod}</td>
</tr>
<tr>
<td>WSOM</td>
<td>CHO</td>
<td>1563</td>
<td>46%</td>
<td>0.43 ± 0.15</td>
<td>1.43 ± 0.24</td>
<td>0.17 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>CHON</td>
<td>671</td>
<td>20%</td>
<td>0.47 ± 0.23</td>
<td>1.41 ± 0.20</td>
<td>0.16 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>CHONS</td>
<td>214</td>
<td>6.3%</td>
<td>0.71 ± 0.21</td>
<td>1.65 ± 0.20</td>
<td>0.02 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>CHOS</td>
<td>868</td>
<td>26%</td>
<td>0.47 ± 0.23</td>
<td>1.46 ± 0.35</td>
<td>0.15 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>CHOP(N,S)</td>
<td>80</td>
<td>2.4%</td>
<td>0.39 ± 0.09</td>
<td>1.54 ± 0.14</td>
<td>0.09 ± 0.10</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>3396</td>
<td>100%</td>
<td>0.46 ± 0.19</td>
<td>1.45 ± 0.27</td>
<td>0.15 ± 0.17</td>
</tr>
<tr>
<td>WIOM\textsubscript{pyr}</td>
<td>CHO</td>
<td>155</td>
<td>15%</td>
<td>0.29 ± 0.20</td>
<td>1.59 ± 0.36</td>
<td>0.13 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>CHON</td>
<td>101</td>
<td>9.8%</td>
<td>0.54 ± 0.32</td>
<td>1.53 ± 0.42</td>
<td>0.19 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>CHONS</td>
<td>311</td>
<td>30%</td>
<td>0.64 ± 0.23</td>
<td>1.52 ± 0.28</td>
<td>0.07 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>CHOS</td>
<td>442</td>
<td>43%</td>
<td>0.49 ± 0.31</td>
<td>1.54 ± 0.38</td>
<td>0.10 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>CHOP(N,S)</td>
<td>21</td>
<td>2.0%</td>
<td>0.49 ± 0.18</td>
<td>1.43 ± 0.50</td>
<td>0.23 ± 0.29</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1030</td>
<td>100%</td>
<td>0.51 ± 0.29</td>
<td>1.54 ± 0.35</td>
<td>0.11 ± 0.18</td>
</tr>
<tr>
<td>WIOM\textsubscript{acn}</td>
<td>CHO</td>
<td>428</td>
<td>40%</td>
<td>0.25 ± 0.16</td>
<td>1.67 ± 0.24</td>
<td>0.10 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>CHON</td>
<td>101</td>
<td>9.4%</td>
<td>0.48 ± 0.35</td>
<td>1.66 ± 0.42</td>
<td>0.12 ± 0.22</td>
</tr>
<tr>
<td></td>
<td>CHONS</td>
<td>136</td>
<td>13%</td>
<td>0.45 ± 0.25</td>
<td>1.27 ± 0.29</td>
<td>0.25 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>CHOS</td>
<td>387</td>
<td>36%</td>
<td>0.49 ± 0.32</td>
<td>1.42 ± 0.36</td>
<td>0.16 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>CHOP(N,S)</td>
<td>28</td>
<td>2.6%</td>
<td>0.42 ± 0.20</td>
<td>1.49 ± 0.25</td>
<td>0.14 ± 0.19</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1080</td>
<td>100%</td>
<td>0.39 ± 0.28</td>
<td>1.53 ± 0.35</td>
<td>0.15 ± 0.19</td>
</tr>
</tbody>
</table>

combined to evaluate the aerosol samples as a whole. The Venn diagram shown in Fig. 3a shows the percentage of the total formulas unique to each of the solvents, and the ones found in one or more of the solvents. Of all the formulas, WSOM analyzes the largest fraction (3396, 67%). There are 3152 formulas (62%) identified in ASOM, and 2397 formulas (47%) found in PSOM. Many formulas are common between WSOM and the organic solvent extracts, where 1077 formulas (21%) are found in all three solvents, 1367 (27%) are common with PSOM, and 2072 (41%) are common with ASOM. There are 1710 formulas (33%) found in the PSOM and/or ASOM spectra that are not present in WSOM.
spectra (Fig. 3a). The formulas present in ASOM and/or PSOM, but not in WSOM, are representative of compounds that are either (1) not water-soluble or (2) outside the analytical window of WSOM using ESI-FTICR-MS. Because of this, we refer to these compounds as “water-insoluble” organic matter (WIOM). It is important to emphasize that the ability of a compound to be detected by ESI-FTICR-MS is highly dependent on its ability to be ionized by negative electrospray ionization, thus any compound that does not contain a polar ionizable functional group (e.g., hydrocarbons) will not be analyzed in any of the solvents and some unknown portion of WIOM will go undetected. One thing to note is that 67% of the formulas are found in WSOM suggesting that WSOM is more complex molecularly than WIOM despite extracting similar amounts of material. This is likely due, in part, to the poor ionization efficiency of aliphatic material and compounds low in oxygen. The $^1$H NMR of the PSOM shows us that pyridine is selective for more aliphatic compounds and compounds that are not extensively substituted with polar functional groups.

The 5106 individual formulas assigned to the three solvents are made up of 2051 CHO (40%), 1472 CHOS (29%), 857 CHON (17%), 599 CHONS (12%), and 127 CHOP(N,S) (2.5%, Fig. 3b). Most (>95%) of the detected compounds are classified as either aliphatic (40%, 2043 formulas) or olefinic (56%, 2837 formulas) based on their low Al_mod values (Fig. 3c). Both anthropogenic and biogenic emission sources release OM that fall under the classification of aliphatic and olefinic such as alkanes, alkenes, alkanoic acids, alkenoic acids, alkanals, alkenals, and terpenes (Rogge et al., 1993a, b, c) which can act as precursors to SOA. The polar compounds are formed through atmospheric processing reactions (i.e., photooxidation or reaction with NOx and SOx) with these
Figure 3. The (a) Venn diagram showing the relative distributions of all molecular formulas (5106 total) present in any of the three solvents, and grey areas represent WIOM. Percentages in areas of overlap are percentages of molecular formulas that appear in both (or all three) of those samples. Percentages in areas of no overlap are molecular formulas that are unique to that individual sample. The (b) histogram of the fractional contributions (%) of molecular formulas from various elemental combinations to the total for all formulas (5106 total), WSOM formulas (3396 total), PSOM formulas (2397 total), or ASOM formulas (3152 total). The c) pie charts showing the fractional contributions (%) of molecular structure classes as determined by AI_{mod} calculations.
biogenically and anthropogenically released precursor molecules (Alfarra et al., 2006; Andreae and Gelencsér, 2006; Jacobson, 2000). Less than 5% of all formulas are classified as aromatic (3.6%, 183 formulas) or condensed aromatic (0.8%, 43 formulas) based on their high AI
text mod. The low abundance of these aromatic species identified in these samples suggests only small contributions from combustion sources, which are known sources of carbonaceous aromatic compounds such as black carbon, oxygenated aromatic compounds, and polycyclic aromatic hydrocarbons. The sampling site from which these aerosols were collected is influenced by local combustion sources (i.e., coal-fired power plant and light vehicular traffic), but not to a large extent. This observation is supported by a previous study of aerosol OM from a similar rural site located 36 km north of our sampling site. They show that aromatic compounds made up a quantitatively small (less than 1% on average) component of the total organic carbon and that only half of that aromatic OM was derived from fossil sources (Wozniak et al., 2012b). The small amount of aromatic material in the WSOM sample detected by FTICR-MS is supported by the lack of intensity (<3% of total spectral intensity) of peaks that represent aromatic protons (chemical shift 6.5 – 8.2 ppm) in the 1H NMR spectra (data not shown). Unfortunately, aromatic protons from the aerosol OM are not distinguishable from the exchanged protons in the pyridine-D5 1H NMR spectra (data not shown); therefore, no conclusion can be made about the amount of aromatic compounds in the PSOM based on 1H NMR.

The WSOM mass spectra contain the greatest number of molecular formulas (3396), which are dominated by 1563 CHO (46%) and 868 CHOS (26%) formulas followed by CHON (671 formulas, 20%), CHONS (214 formulas, 6.3%), and CHOP(N,S) (80 formulas, 2.4%), as displayed in Fig. 3b. This distribution of molecular formulas,
specifically the dominance by CHO formulas, is consistent with other ambient aerosol samples collected in the eastern United States (Wozniak et al., 2008). There are more CHOS than CHON formulas, suggesting that sulfur species (e.g., SO$_4^{2-}$) were important to the atmospheric processes in this region at the time of sampling.

The PSOM contains the fewest number of total formulas (2397); however, the molecular characteristics of PSOM are distinct from that of WSOM or ASOM. PSOM contains mostly CHOS (976 formulas, 41%) and CHO (613 formulas, 26%) formulas, followed by CHONS (489 formulas, 20%), CHON (294 formulas, 12%), and CHOP(N,S) (25 formulas, 1.0%) formulas (Fig. 3b). Nearly half of the PSOM formulas (1030 formulas, 43%) are not found in WSOM (WIOM$_{pyr}$), indicating that they are either truly water-insoluble compounds or do not ionize well in water due to being suppressed by other WSOM components with higher ionization efficiencies. The WIOM$_{pyr}$ is dominated by sulfur-containing species, 442 CHOS (43%) and 311 CHONS (30%) formulas, with smaller contributions from CHO (155 formulas, 15%), CHON (101 formulas, 9.8%), and CHOP(N,S) (21 formulas, 2.0%) compounds (Table 2). A large majority (88%) of the sulfur formulas in the WIOM$_{pyr}$ have an O/S ratio of at least 4, suggesting that many of these formulas represent organosulfates and nitrooxyorganosulfates. Additionally, many of the sulfur compounds are aliphatic (65%) according to their AI$_{mod}$ values. This sulfur predominance suggests that pyridine could either be 1) selective towards organic compounds with sulfur as part of its molecular structure and/or 2) selective for aliphatic compounds, which could be more susceptible than unsaturated compounds to reactions with sulfur species that are co-emitted with the carbonaceous aerosols in the atmosphere.

A study by Schmitt-Kopplin et al. (2010) showed that compounds with higher H/C ratios
can react more efficiently with sulfate aerosols to form organosulfates, providing support for the latter of the two possibilities.

**Figure 4.** Van Krevelen diagrams for molecular formulas assigned to the (a-d) WSOM, (e-h) WIOM_{pyr}, and (i-l) WIOM_{acn} extracts. Any formula present in WSOM has been removed from the WIOM_{pyr} and WIOM_{acn} plots. Each diagram is plotted based on elemental content of each molecular formula (CHO, CHON, CHONS, and CHOS). The labeled regions in (a) WSOM CHO formulas correspond to their aromaticity based on AI_{mod} and these regions are consistent for all of the diagrams. Formulas above the solid line are aliphatic, just below the solid line are olefinic, below the dashed line are aromatic, and below the dotted line are condensed aromatic.
The ASOM fraction contains 3152 formulas, and 1080 of those formulas were not assigned to peaks in the WSOM spectra. Like WSOM, the whole ASOM sample is dominated by CHO (1367 formulas, 43%) and CHOS (1038 formulas, 33%) compounds, followed by CHON (419 formulas, 13%), CHONS (257 formulas, 8.2%) and CHOP(N,S) (71 formulas, 2.3%, Fig. 3b). The formulas present in ASOM, but not in WSOM (i.e., WIOM\text{acyn}), shows a similar atomic distribution to the WSOM formulas (Table 2) with CHO (428 formulas, 40%) and CHOS (387 formulas, 36%) formulas being most abundant, but there are more CHONS (136 formulas, 13%) than CHON (101 formulas, 9.4%) formulas.

There are 1710 WIOM formulas found in either pyridine or acetonitrile (and not water), and 400 of those formulas are common between the two organic solvents. The formulas common between WIOM\text{pyr} and WIOM\text{acn} consist mostly of CHOS (225 formulas, 56%) and CHO (95 formulas, 24%) compounds followed by CHONS (62 formulas, 16%) and a few CHON (16 formulas, 4.0%) and CHOP(N,S) (2 formulas, 0.5%) compounds. The 630 formulas unique to pyridine (i.e., not found in acetonitrile or water) are dominated by sulfur-containing formulas with CHONS (249 formulas, 40%) and CHOS (217 formulas, 34%), and also contains formulas with CHON (85 formulas, 14%), CHO (60 formulas, 10%), and CHOP(N,S) (19, 3.0%). The 680 formulas unique to acetonitrile are dominated by formulas with only CHO (333 formulas, 49%) followed by CHOS (162 formulas, 24%), CHON (85 formulas, 13%), CHONS (74 formulas, 11%), and CHOP(N,S) (26 formulas, 3.8%).

The relative distributions of formulas for each compound class based on molecular structure (as determined by AI\text{mod} values as described above) is shown in Fig. 3c. WSOM and ASOM contain mostly olefinic compounds (60% in each case), and have significant
contributions from aliphatic compounds (36% and 37%, respectively). Contrarily, PSOM is dominated by aliphatic formulas (58%) with a smaller amount of olefinic compounds (39%), and this predominance is consistent with the $^1$H NMR results. In all three extracts, the contributions from aromatic and condensed aromatic compounds are small ($\leq 3.0\%$ and $\leq 0.6\%$, respectively). The relative amount of each molecular structure type based on aromaticity index for the WIOM$_{pyr}$ and WIOM$_{acn}$ are not significantly different than whole PSOM and ASOM, respectively. Unless the WIOM contains a significant portion of non-ionizable (by ESI) aromatic compounds, the WIOM analyzed in this study may not absorb light as efficiently as the WSOM. This is surprising because we expect the insoluble OM (presumably fossil-derived; Wozniak et al., 2012b) to be aromatic in nature. However, all (13 of 13) condensed aromatic structures and most (52 of 67) aromatic formulas identified in the PSOM are not found in WSOM, suggesting that pyridine may be selective for certain aromatic and condensed aromatic compounds. We speculate that the aromatic character in these samples is low due to a lack of a strong combustion source. Unfortunately we cannot verify true aromatic content using these methods due to the signal from pyridine in the aromatic region of the $^1$H NMR spectrum.

Each molecular formula type (e.g., CHO, etc.) was plotted on a van Krevelen diagram based on its presence in WSOM, WIOM$_{pyr}$, or WIOM$_{acn}$ (Fig. 4). Phosphorus-containing formulas were omitted from the figure due to their low number frequency and relatively low spectral intensity. Molecular formulas that appear in WSOM and either PSOM or ASOM were removed from the diagrams for PSOM and ASOM (Fig. 4e-l), so that only the formulas unique to each of the organic solvents (i.e., WIOM$_{pyr}$ and WIOM$_{acn}$) are shown. The lines on each diagram indicate the type of molecular structure (i.e.,
aliphatic, olefinic, aromatic, and condensed aromatic) based on Al\textsubscript{mod} values. Nearly all of the CHO formulas in the WSOM (Fig. 4a) have O/C ratios between 0.2 and 0.8 and H/C ratios between 0.95 and 2.00. Formulas within this region of the diagram are typical of many types of natural OM samples, and have previously been attributed to lignin (e.g., Sleighter and Hatcher, 2007) and carboxylic-rich alicyclic molecules (CRAM; e.g., Stubbins et al., 2010), or SOA (e.g., Wozniak et al., 2008). While lignin itself is not likely to be highly abundant in the atmosphere, the compounds found in this region of the van Krevelen diagram could be molecularly similar to lignin (i.e., a branched polymer-containing aromatic rings and various oxygenated functional groups) or derivatives of lignin. Several of the compounds (~33%) within this region meet the operational definition of CRAM (Hertkorn et al., 2006), and could represent CRAM-like structures (i.e., carboxylated and fused alicyclic rings). A previous study by Wozniak et al. (2008) identified formulas in this region as being consistent with those produced through laboratory aging reactions (e.g., pinene ozonolysis), but FTICR-MS cannot provide direct evidence that the compounds identified in this study are secondary in nature.

The CHON formulas in WSOM (Fig. 4b) are localized to O/C ratios between 0.2 and 0.8 and H/C ratios between 1.00 and 1.75. The formulas in this region above an H/C ratio of 1.50 have previously been attributed to peptides; however, 97% of these formulas have only one nitrogen and cannot truly be peptides because multiple nitrogen atoms would be required. Additionally, all of these CHON formulas have an O/N ratio of at least 3, which suggests that the functionality of the nitrogen may be that of a nitrate group (ONO\textsubscript{2}). We also recognize the possibility of reduced nitrogen functional groups (e.g., amines and azo compounds) present in molecules containing other ionizable functional groups (e.g.,
carboxylic acid), but we are unable to differentiate the two possibilities with this method of analysis. WSOM formulas containing both sulfur and nitrogen (CHONS, Fig. 4c) are predominantly aliphatic with relatively high O/C ratios (>0.5). Most (93%) of these formulas have sufficient oxygen atoms (≥ 7) to contain at least one nitrate and one sulfate functional group, indicating that many of these formulas could be nitroxyorganosulfates which have been identified in previous ambient atmospheric samples (e.g., LeClair et al., 2012; Surratt et al., 2007). CHOS formulas are the second most dominant formula type in the WSOM, and these formulas separate into two distinct regions of the van Krevelen diagram (Fig. 4d). One region contains mostly aliphatic and some olefinic formulas with O/C ratios greater than 0.25 and H/C ratios greater than 1.3. All of the CHOS formulas in this region have O/S of at least 4, suggesting that they are saturated organosulfates or organosulfates with a few double bonds. The other distinct CHOS region contains olefinic and aromatic formulas with a low O/C (<0.4) and H/C ratios less than 1.4. Most (70%) of these formulas have O/S ratios of at least 4, indicating that they could be aromatic organosulfates or organosulfates with multiple unsaturations. The CHOS formulas that do not have sufficient O atoms (O/S <4) to be organosulfates must contain a reduced sulfur functional group (e.g., sulfonates and thiols). Organic compounds with reduced forms of sulfur, specifically thia arenes, have been identified in anthropogenic aerosol emissions sources and are known to be toxic (Eastmond et al., 1984; Rogge et al., 1993d) Sulfonates are ubiquitous in detergents and personal care products (Debelius et al., 2008; Lara-Martín et al., 2006) and have been previously identified in atmospheric OM (Altieri et al., 2009). It is important to recognize that atomic ratios do not confirm the presence of organosulfate or organonitrates; however, these structures have been confirmed in other studies of
atmospheric OM and it is reasonable to suggest their presence in these samples. A study by LeClair et al. (2012) of atmospheric WSOM using FTICR-MS and collision induced dissociation provides direct evidence for neutral losses of HNO$_3$ from 63% of detected CHON compounds and 33% of the detected CHONS compounds, and for neutral losses of SO$_3$ from 85% of detected CHOS compounds and 42% of the detected CHONS compounds. Neutral losses of HNO$_3$ and SO$_3$ were interpreted in that study as indicative of organonitrates and organosulfates, respectively. While differences in sample type and instrumentation limit making a direct quantitative comparison here, their results provide good support for the presence of organonitrates, organosulfates and nitrooxyorganosulfates in atmospheric WSOM including these samples. Reduced forms of nitrogen and sulfur are likely also present as evidenced by the formulas with O/S less than 4 and the neutral loss evidence in the LeClair et al. (2012) study which indicates reduced forms must make up a portion of the CHON and CHOS compounds.

As stated previously, pyridine is able to dissolve or detect 1030 compounds that water does not (table 2). The characteristics for all formulas in WIOM$_{pyr}$ indicate a lower average O/C (0.29) than WSOM (0.46), a higher average H/C (1.54) than WSOM (1.45), and lower average AI$_{mod}$ (0.11) than WSOM (0.15, table 2). The CHO formulas found in the WIOM$_{pyr}$ plot in a region of higher H/C and lower O/C than those identified in the WSOM (Fig. 4e), implying that they are, on average, more aliphatic and less oxidized than the CHO compounds found in WSOM. The CHON compounds in WIOM$_{pyr}$ show variable H/C and O/C ratios (Fig. 4f). Most of these compounds are either aliphatic or olefinic with O/N ratios of at least 3, indicating they may be organonitrates which have been identified previously in atmospheric WSOM (e.g., LeClair et al., 2012). The CHONS formulas make
up a large portion of the WIOM\textsubscript{pyr} formulas (30%) and they plot into two distinct regions on the van Krevelen diagram (Fig. 4g). The first region contains a majority of the formulas, and they are largely aliphatic molecules with O/C ratios greater than 0.5 and H/C ratios greater than 1.25, and the second region contains mostly aromatic formulas with O/C ratios less than 0.4 and H/C ratios less than 1.25. Many (70%) of the CHONS formulas contain enough oxygen atoms to contain at least one sulfate and one nitrate functional group, and are potentially nitrooxyorganosulfates. Most (81%) of the compounds in the high O/C and high H/C region contain sufficient oxygen, but only a few (6%) of the formulas in the low O/C and low H/C region have sufficient oxygen to be nitrooxyorganosulfates. The CHONS formulas that do not have sufficient oxygen to form nitrooxyorganosulfates must contain at least one sulfur or nitrogen atom present in a reduced form. CHOS formulas make up the largest fraction (43%) of WIOM\textsubscript{pyr}, and the bulk (96%) of those formulas are aliphatic or olefinic. Like WSOM, the CHOS formulas in WIOM\textsubscript{pyr} plot in two distinct regions of the van Krevelen diagram (Fig. 4h). The first region contains mostly aliphatic formulas spanning the entire O/C range between 0.03 and 1.2 and have H/C ratios greater than 1.2. The second region contains mostly olefinic and aromatic compounds with O/C ratios less than 0.5 and H/C ratios less than 1.5. The average O/C ratio for CHOS compounds in WIOM\textsubscript{pyr} is nearly the same as that of the WSOM (0.49 ± 0.31 and 0.47 ± 0.23, respectively), but the standard deviation for WIOM\textsubscript{pyr} is greater. This larger deviation indicates that the WIOM\textsubscript{pyr} CHOS compounds are more diverse than those in WSOM. Most (80%) of the CHOS formulas in the WIOM\textsubscript{pyr} have O/S ratios of at least 4, suggesting possible organosulfates. Formulas with O/S ratios less than 4 indicate the presence of a more reduced form of sulfur within the structure. The average AI\textsubscript{mod} of compounds with
more reduced forms of sulfur is much greater than that of compounds with O/S sufficient
to be organosulfates (0.38 and 0.04, respectively). The major difference between WIOM\textsubscript{pyr}
and WSOM is the increased detection of aliphatic organosulfates and
nitroxyorganosulfates in the WIOM\textsubscript{pyr}, suggesting that pyridine is a more suitable solvent
than water for detecting these compounds in aerosol OM using ESI-FTICR-MS.

In spite of having many general molecular formula similarities to WSOM, the
characteristics for all formulas in WIOM\textsubscript{acn} (1080) indicate a lower average O/C (0.39)
than WSOM (0.43), a higher average H/C (1.53) than WSOM (1.45), and an identical
average AI\textsubscript{mod} (0.15). These characteristics suggest that the formulas unique to ASOM are
less oxygenated and/or have longer carbon chains. This is clearly shown by the many
formulas that plot on the left side (low O/C) of the van Krevelen diagram for WIOM\textsubscript{acn}
(Fig. 4i-l). The average number of carbon atoms per formula is slightly larger at 24 carbon
atoms for WIOM\textsubscript{acn} and 22 carbon atoms for WSOM. Both WIOM\textsubscript{acn} and WSOM are
dominated by CHO formulas, but the CHO compounds in the WIOM\textsubscript{acn} are localized to the
upper left corner (low O/C and high H/C) of the diagram (Fig. 4i). Essentially all (99%) of
these formulas are aliphatic or olefinic. There are a small number of CHON formulas (101)
found in WIOM\textsubscript{acn}, and most of these formulas have higher H/C (mean value of 1.66), and
are split between a lower O/C (<0.6) and a high O/C (>0.8). Nearly all (97%) of the CHON
formulas have an O/N ratio greater than 3 indicating the possibility of these compounds to
contain nitrate as part of their structure. The CHONS formulas are also relatively scarce,
and they plot in two separate areas on the van Krevelen diagram (Fig. 4k). Roughly half of
the formulas plot below O/C ratio of 0.4 and the other half above 0.4. All of the formulas
with O/C > 0.4 have sufficient oxygen atoms (at least 7) to form at least one nitrate and
one sulfate group as is found in nitrooxyorganosulfates, but could still contain reduced N and S functional groups. However, only 24% (17 of 70) of the CHONS formulas in the lower O/C region have enough oxygen atoms to form nitrooxyorganosulfates, which indicates the presence of more reduced N- or S-containing functional groups. Like WSOM, CHOS formulas are the second most abundant molecule type in the WIOM$_{acn}$ comprising 387 of the 1080 formulas (36%). These formulas are split into two regions of the diagram (Fig. 4l), where one region is dominated by lower O/C and H/C ratios and contains mostly olefinic and aromatic compounds. The other region is predominantly aliphatic compounds covering the full range of O/C ratios. A majority (76%) of all of the CHOS formulas have sufficient oxygen to form organosulfates (O/S≥4). All of the formulas in the higher H/C and aliphatic region contain sufficient oxygen to form organosulfates, but more than half (55%) of the formulas in the low H/C and low O/C region have O/S ratios less than 4. These formulas in the low O/C and low H/C region have multiple unsaturations and have more reduced forms of sulfur in their structure. The major differences between WIOM$_{acn}$ and WSOM are in the high H/C and low O/C region, suggesting that acetonitrile is a more suitable solvent than water for detecting less polar aerosol OM compounds (i.e., fewer oxygen and heteroatoms and/or larger carbon chains) by ESI-FTICR-MS.

The WIOM compounds have chemical characteristics distinct from those in WSOM. Both organic solvents extracted compounds that were more aliphatic in nature than those found in the WSOM, as indicated by the lower O/C ratios and longer carbon chain lengths (for ASOM) of the CHO formulas. Previous work shows that aliphatic components make up a small fraction of aerosol OC, implying that they are, as expected, largely water-insoluble (Wozniak et al., 2012b). Radiocarbon signatures indicate that the
water-insoluble components are mostly fossil-derived (Wozniak et al., 2012b), but can also come from contemporary plant material (Rogge et al., 1993b). The aliphatic and olefinic hydrocarbon material that is released during fossil fuel combustion can be functionalized through various atmospheric oxidation reactions, thus, increasing its polarity and water-solubility.

Nearly 75% of the formulas unique to PSOM include sulfur as part of the molecular formula, indicating a potential selectivity for organosulfates and nitrooxyorganosulfates. This selectivity may be due, in part, to the increased efficiency of aliphatic species (over unsaturated species) to undergo reactions with SOx, and that pyridine may actually be selective for the aliphatic portion rather than the actual sulfate functional group. Sulfur species, especially SOx, are well known to play important role in atmospheric aging reactions. Organosulfates are formed in the atmosphere through the acid-catalyzed ring-opening reaction of epoxides in the presence of acidic sulfate seed aerosols (Minerath and Elrod, 2009) and these organosulfates can undergo nighttime nitrate radical oxidation and photo-oxidation to form nitrooxyorganosulfates (Surratt et al., 2008). These compounds have been identified in ambient atmospheric OM (e.g., Altieri et al., 2012; Mazzoleni et al., 2012; Mitra et al., 2013; Reemtsma et al., 2006; Schmitt-Kopplin et al., 2010; Wozniak et al., 2008). Sulfate is emitted from numerous anthropogenic and biogenic sources and is ubiquitously in the atmosphere. The aerosol OM at this sampling site was in proximity to a known SOx emission source (coal-fired power plant), providing ample opportunity for atmospheric aging reactions with sulfate to occur and form the observed organosulfate compounds. Organosulfates are very polar in nature which may increase the ability of
aerosol OM to act as cloud condensation nuclei and, therefore, have an indirect radiative effect (Hallquist et al., 2009).

4 Summary and implications

Pyridine and acetonitrile are suitable solvents for analyzing organic aerosols using ESI-FTICR-MS and identify a molecularly-unique portion of aerosol OM when compared to the water-soluble fraction. While the water-soluble fraction is of paramount importance due to the implications those compounds have on environmental processes, such as cloud condensation nuclei formation and mobility in watersheds, analysis of only the WSOM omits a large portion of OM (as much as 90%). The PSOM and ASOM fractions are expected to be more lipophilic and are likely to be more interactive with biological tissues in the environment. Acetonitrile was able to analyze several unique water-insoluble molecular formulas; however, the elemental distributions and formula types (e.g., aliphatic) of these compounds were very similar to those of WSOM. Pyridine elucidated a molecularly unique and, therefore, complementary set of chemical formulas than those in either ASOM or WSOM. PSOM has a stronger preference for extracting or analyzing aliphatic sulfur-containing formulas, which are important aerosol components due to their abundance and hygroscopicity which allows them to act as cloud condensation nuclei and impact climate via the indirect effect. Because WIOM has been found to contain the majority of fossil fuel derived OM, analysis of the WIOM, such as OM found in ASOM and PSOM, provides clues to the molecular composition of the fossil material present in aerosols emitted from anthropogenic sources and therefore, insights into its potential fates and impacts in the environment.
CHAPTER III

MOLECULAR SOURCE APPORTIONMENT OF AMBIENT AEROSOL ORGANIC MATTER USING ADVANCED ANALYTICAL TECHNIQUES AND STATISTICAL ANALYSES

1 Introduction

Organic matter (OM) comprises a significant portion of total aerosol mass, as much as 90% in certain areas (Jimenez et al., 2009; Kanakidou et al., 2005), and is generated by a number of anthropogenic and biogenic emission sources. Organic aerosols (OA) once emitted into the atmosphere as primary OA can undergo a myriad of atmospheric processes forming secondary OA (SOA) that have different chemical structures and associated physical properties. The immense complexity of OA makes it difficult to evaluate and gain the necessary understanding of the net impacts OA has on human health, biogeochemical cycling, and net radiative forcing.

The composition and relative concentrations of OA are expected to vary regionally due to differences in emission inputs and in the secondary aging processes that occur (Jimenez et al., 2009) resulting in the inherent variations in the chemical and physical properties that influence the surrounding environment. For example, combustion emission sources release molecules containing double bonds and rings and those compounds are capable of light absorption, which creates a warming effect. While the atmospheric community has done a good job apportioning sources of aerosols and OA, there still exist gaps in climate modeling schemes indicating insufficient understanding of aerosol inputs as well as the processes that transform and remove them. Understanding the differences
between various OA emission sources at the molecular level is crucial in determining the specific impacts each source has on the surrounding environment.

It is challenging to directly link OA and associated environmental impacts to specific components due to a lack of complete understanding of the chemical composition of aerosols, which results when multiple emission sources with complex OA composition mix in the atmosphere and are subjected to poorly-understood aging reactions. Many studies have addressed similarities and differences among various aerosol sources, as well as seasonal and diurnal variability (Alves et al., 2012; Baduel et al., 2010; Kieber et al., 2012; Samburova et al., 2005; Takegawa et al., 2006; Wozniak et al., 2013). Marine aerosols, urban aerosols (anthropogenic), and biomass burning aerosols as well as some background sites are of particular interest due to their global importance. A study comparing the chemical composition of biogenic and anthropogenic aerosols from air masses over Europe revealed that variations in the odd-to-even ratios of alkanes and alkanoic acids can be helpful in distinguishing aerosol origin and that PAH content is potentially an important indicator of anthropogenic contributions (Alves et al., 2012). Biomass burning aerosols are identified by the presence of tracer compounds, where levoglucosan (a product of the combustion of cellulose) is the most prevalent. Tracer compounds are extremely useful in quickly determining emission source, but do not offer explanation of the processes affecting co-emitted OM. A majority of the light-absorbing brown carbon present in OA is said to be from biomass burning aerosols (Washenfelder et al., 2015), so understanding the chemical composition of these aerosols is imperative for determining their contribution to climate forcing by aerosols. The current chemical
inventory of OA is not comprehensive despite its acknowledged importance, and the inherent chemical diversity among molecules makes studying OA an analytical challenge.

Important molecular and structural details regarding OA have been discovered through the use of powerful analytical techniques such as nuclear magnetic resonance spectroscopy (NMR) and ultrahigh resolution mass spectrometry (UHR-MS). The use of NMR to study OA has recently been thoroughly reviewed (Chalbot and Kavouras, 2014). NMR has been used to determine the relative contributions of major proton groups (e.g., alkyl protons), and also to identify specific compounds such as acetate (Decesari et al., 2001; Moretti et al., 2008; Schmitt-Kopplin et al., 2010; Shakya et al., 2012; Wozniak et al., 2013). NMR is an attractive technique because it provides connectivity information for all components in a complex OA mixture without extensive sample preparation. One of the major drawbacks to NMR is that it does not provide specific molecular details due to the overlapping signals from hydrogens associated with atmospherically relevant functional groups, and therefore, spectral interpretations must be simplified. However, UHR-MS has the ability to fill that molecular void.

UHR-MS has made an important contribution to the enhanced characterization of OA due to its unique ability to analyze complex environmental mixtures with minimal sample manipulation (Sleighter and Hatcher 2007). This type of analysis, particularly Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), allows for the determination of molecular formulas for thousands of high-molecular weight (> 200 Da) compounds present within a single sample providing an invaluable look into the chemical properties of OA. The advantage to this technique is the immense amount of molecular details obtained from a single spectrum due to its ultrahigh resolution and mass accuracy.
This detailed molecular information can theoretically be used to obtain vital fingerprints, in the form of contributions from specific related molecular compound classes, for OA from specific emission sources and/or that have undergone molecular transformations. Numerous studies have used UHR-MS to reveal the molecular details of atmospheric OM (Altieri et al., 2008b; Heaton et al., 2009; Kourtchev et al., 2015; Kourtchev et al., 2014; Laskin et al., 2010; LeClair et al., 2012; Mazzoleni et al., 2010; Mazzoleni et al., 2012; Mead et al., 2013; Mitra et al., 2013; Nguyen et al., 2010; Reinhardt et al., 2007; Schmitt-Kopplin et al., 2010; Willoughby et al., 2014; Wozniak et al., 2008; Wozniak et al., 2013). One of the limitations to UHR-MS techniques is that structural information is not directly provided and generally regarded as non-quantitative, thus it requires the use of additional analyses. Pairing NMR with UHR-MS has been recognized as a powerful combination of analytical techniques that provide maximal molecular and structural information without extensive sample preparation.

These advanced analytical techniques provide an immense amount of data, and observing similarities and differences can be tedious. Advanced statistical analysis has been applied to $^1$H NMR and FTICR-MS data and has had great success in determining key similarities and differences among environmental samples. Principal component analysis (PCA) has been applied to FTICR-MS and $^1$H NMR data sets for dissolved OM, marine aerosol OM, and soil natural OM (Gurganus et al., 2015; Sleighter et al., 2010; Wang et al., 2011; Wozniak et al., 2015; Wozniak et al., 2013; Wozniak et al., 2014). PCA is useful because it reduces a large number of variables (e.g., individual molecular formulas) into a few principal components (PC) allowing for efficient comparison of many
samples. Specific molecular features characteristic of specific sources can be elucidated using PCA, making it a valuable tool for investigating the source apportionment of OA.

The work presented here establishes source-specific molecular characteristics for ambient aerosol samples from key anthropogenic and biogenic emission sources. Multiple ambient aerosol samples were collected from marine, mixed source, biomass burning, and urban emission sources to represent important biogenic and anthropogenic aerosols, and the water-soluble and pyridine-soluble extracts of each were evaluated for molecular characteristics using FTICR-MS and proton NMR (¹H NMR). Compositional differences were elucidated with principal component analysis, and characteristic molecular features for each source type are described in detail, thereby reducing some of the chemical uncertainty that exists among OA.

2 Methods

2.1 Aerosol sample collection

Ambient aerosol total suspended particulates (TSP, n = 14) were collected from four different locations to represent different emission source types. Air was drawn through pre-combusted (4 h, 475 °C) quartz microfiber filters (Whatman QM/A, 20.3 x 25.4 cm, 419 cm² exposed area, 0.6 µm effective pore size) using a TSP high-volume air sampler (model GS2310, Thermo Andersen, Smyrna, GA) at flow rates ranging between 0.7 and 0.9 m³ min⁻¹. Air particles were collected for 8 – 29 hours with total air volumes ranging between 410 and 1170 m³. The filters were transferred to combusted foil pouches immediately after collection and stored at 8 °C until analysis.

Marine TSP samples (n = 4) were collected aboard the R/V Knorr (Woods Hole, Massachusetts) 14 m above sea level in the north Atlantic Ocean. Three of the samples
were collected as part of the 2011 US GEOTRACES program cruise (www.geotraces.org) during the fall (24 – 26 November 2011, 26 – 27 November 2011, and 27 – 28 November 2011). The fourth sample was collected as part of the 2014 second Western Atlantic Climate Study (http://saga.pmel.noaa.gov/index.html) during the summer (2 June 2014). Backward air mass trajectories were used to identify the samples as marine-influenced, (i.e., having minimal influence from 5 day back trajectories that reach continental areas).

Mixed source TSP samples (n = 3) were collected at sea level during the summer (16 – 17 August 2011, 24 – 25 June 2013, and 25 – 26 June 2013) at the Virginia Institute of Marine Science in Gloucester Point, Virginia, USA (37.2482 °N, 76.5005 °W). The area is typical of a rural environment on the East Coast of the United States and is expected to have contributions from several biogenic (i.e., biogenic SOAs) and anthropogenic sources (e.g., fossil fuel combustion, industrial emissions).

Biomass burning TSP samples (n = 2) were collected at sea level during the summer (21 August 2011, 24 – 25 August 2011) in Suffolk, Virginia, USA (36.8934 °N, 76.5020 °W) downwind of heavy smoke pollution from a fire burning at the Great Dismal Swamp (Suffolk, Virginia; 36.6100 °N, 76.4662 °W). The smoldering-peat fire was caused by a lightning strike where peat, brush, and downed trees fueled the fire.

Urban TSP samples (n = 5) were collected ~60 m above sea level on the roof of an academic building during the summer (4 – 5 August 2014, 5 August 2014, 5 – 6 August 2014, 6 August 2014, and 6 – 7 August 2014) at Drexel University in downtown Philadelphia, Pennsylvania, USA (39.9545 °N, 75.1858 °W). The area is urban and the collected TSP are expected to have strong anthropogenic contributions from fossil fuel, industrial, and cooking emissions as each was clearly visible from the sampling site.
A new and pre-combusted QM/A filter was stored alongside the 2011 mixed source and biomass burning aerosols, and these filters were analyzed as storage filter blanks. At the beginning of the sampling period for the urban (4 August 2014), marine (7 November 2011 and 1 June 2014), and 2013 mixed source (24 June 2013) aerosols, a new and pre-combusted QM/A filter was attached to the air sampler for 5 minutes without drawing any air, and was stored under identical conditions. These filters were analyzed as field filter blanks for their respective aerosol samples.

2.2 Aerosol mass and carbon measurements

The QM/A filters were weighed before and after sampling to determine the TSP mass loadings (Table 3), except for the marine samples. The fraction of non-carbonate carbon on each filter was determined using a FlashEA 1112 elemental analyzer (ThermoFinnigan). Triplicate aerosol core plug (2.84 cm$^2$) samples were acidified to remove inorganic carbon by treating the plugs with 1 M HCl followed by drying in an oven (4 h, 80 °C). The acidified plugs were evaluated for total carbon (TC = organic + elemental/black – inorganic carbonates). Quantification was achieved using an aspartic acid standard calibration curve. Acidified field blank filters were analyzed using the same method; however, the signal for carbon was below the detection limit of the instrument in all cases, so no blank subtraction was applied. TC values are expressed as percent of TSP concentrations. Black carbon (BC) amounts were determined using chemothermal oxidation at 375 °C (CTO-375; Gustafsson et al., 1997). Triplicate filter plugs were exposed to HCl vapor for 24 h to remove inorganic carbonates. The filters were heated using a controlled temperature program where the temperature was held at 375 °C for 4 h. The
material remaining (i.e., BC) was analyzed for total carbon using the same method described above for TC analysis, and percentages are expressed relative to the TC value.

2.3 Solvent Extractions

Solvent extracts of the aerosols and respective filter blanks were obtained by combining aerosol filter plugs of known OC masses with ultrapure water (Millipore Synergy Ultrapure Water System) or pyridine (Sigma-Aldrich, ≥ 99.9 %) and thoroughly mixed on an orbital shaker (150 RPM, 4 h, 21 °C). Insoluble particles were removed using a syringe with a 0.45 µm PTFE filter cartridge. The percent of water soluble organic carbon (WSOC) in each filtrate was determined by evaluating the non-purgeable organic carbon using a Shimadzu TOC-VCPH analyzer. The measured WSOC was compared with the TC content (derived from elemental analysis described in Section 2.2 of this chapter) to determine the %WSOC. The %PSOC was determined by dissolving each of the aerosol samples into pyridine-D$_5$ and comparing spectral signals determined by proton nuclear magnetic resonance spectroscopy ($^1$H NMR) to that of a glucose standard. The methods and calculations for this pyridine extraction efficiency determination are described in detail elsewhere (Willoughby et al., 2014).

The water extracts were desalted using an established procedure for Agilent PPL solid-phase extraction cartridges (Dittmar et al., 2008). PPL is expected to retain 60 – 75% of the OM (Dittmar et al., 2008; Stubbins et al., 2012), where low-molecular weight and exceptionally hydrophilic compounds are among the components lost. The desalted sample was eluted in methanol (Acros, 99.9%), and will be referred to as WSOM$_{ppl}$ to differentiate it from WSOM. The pyridine filtrate does not contain salts that interfere with electrospray ionization, and therefore does not require additional manipulation. The solvent extracts
were stored at -8 °C until FTICR-MS analysis, typically within 24 h of preparation. Experimental replicates were prepared and analyzed for at least one of each of the source types to ensure good experimental and instrumental reproducibility.

2.4 FTICR-MS Analysis

The efficiency of FTICR-MS is highly dependent on the ability of organic compounds to ionize, and as a result individual samples must be optimized in order to achieve the maximum ionization possible. All WSOM\textsubscript{PPL} samples were analyzed in both positive and negative electrospray ionization (ESI) mode (WSOM- and WSOM+, respectively), and PSOM were analyzed in negative mode only due to poor signal observed in the positive mode. Immediately prior to analysis, the mixed source and biomass burning WSOM\textsubscript{PPL} samples were each diluted by 2 using LC/MS-grade water with a small amount (<0.1% total volume) of ammonium hydroxide to enhance negative ionization efficiency. The mixed source and biomass burning PSOM were diluted by 2 using methanol with a small amount (<0.1% total volume) of ammonium hydroxide. The marine and urban WSOM were not diluted and analyzed directly in methanol for negative ESI analysis. The marine and urban PSOM were diluted by 2 using methanol. All samples were run directly in methanol for positive ESI analysis. A respective field blank extract was prepared identically and analyzed immediately prior to each of the sample extracts, so that a representative experimental blank spectrum was obtained for each aerosol extract.

Each of the samples was analyzed on a Bruker Daltonics 12 Tesla Apex Qe FTICR-MS with an Apollo II ESI source housed at the College of Sciences Major Instrumentation Cluster at Old Dominion University. The instrument was externally calibrated daily using a polyethylene glycol standard. Electrospray voltages were optimized for each sample, and
ions were accumulated for 0.5 – 2.0 s before transfer into the ICR cell, where 300 transients were co-added. Each spectrum was internally calibrated using the naturally occurring molecules including fatty acids and other homologous series of compounds containing only carbon, hydrogen and oxygen (Sleighter et al., 2008). Peaks consistent with salts (mass defect 0.4 – 0.98 for \( m/z < 400 \), and mass defect 0.6 – 0.97 for \( m/z > 400 \)), blank peaks (those found in the respective filter blank), and \(^{13}\text{C}\) isotopologue peaks were subtracted from the mass list and not considered for formula assignments.

### 2.5 Molecular Formula Assignments

A unique molecular formula was assigned to a majority (82% ± 9%) of the measured peaks having a \( S/N \) ratio of at least 3 using an in-house generated MatLab (The MathWorks Inc., Natick, MA) code according to the criteria \(^{12}\text{C}_{5-80}^{1}\text{H}_{5-200}^{16}\text{O}_{1-30}^{14}\text{N}_{0-5}^{32}\text{S}_{0-2}^{34}\text{P}_{0-2}^{34}\text{Na}_{0-1}^{23}\) for negative ESI and \(^{12}\text{C}_{5-80}^{1}\text{H}_{5-200}^{16}\text{O}_{1-30}^{14}\text{N}_{0-5}^{32}\text{S}_{0-2}^{23}\text{Na}_{0-1}^{23}\) for positive ESI, where the subscripts indicate the range of atoms allowed in a single formula. The assigned formulas were screened to remove any chemically unreasonable formulas for natural OM molecules according to previously published criteria (e.g., Stubbins et al., 2010; Wozniak et al., 2008), and Kendrick mass defect homologous series (\( \text{CH}_2, \text{H}_2, \text{and CO}_2 \)) were used to verify ambiguous assignments. Each of the assigned formulas has a calculated mass within 1 ppm agreement with the measured \( m/z \), where a large majority of the formulas (88% ± 7%) have less than 0.5 ppm error.

### 2.6 \(^1\text{H}\) NMR spectroscopy

Each WSOM extract was diluted immediately before \(^1\text{H}\) NMR analysis using \( \text{D}_2\text{O} \) (100% atom D, Acros Organics) at a ratio of 90:10 WSOM:\( \text{D}_2\text{O} \), where the final dissolved carbon concentrations could be calculated (7.5 – 21.2 mg C L\(^{-1}\)). The deuterated WSOM
solutions were subjected to $^1$H NMR spectroscopy using a Bruker Daltonics 400 MHz NMR with a BBI probe. Each sample was analyzed for 4000 (mixed source, biomass burning, and urban WSOM) or 8000 scans (marine WSOM) using a standard Bruker water-suppression pulse program, where the 90° pulse and the transmitter offset were optimized individually for each sample. The signals obtained from $^1$H NMR spectra were integrated over the entire spectral range to obtain the total signal response, and were also integrated over four specific chemical shift ranges to determine contributions from major proton types (Moretti et al., 2008; Shakya et al., 2012). The signal response was normalized to the total signal in these regions (i.e., total signal = $\text{Area}_{0.6-4.4\text{ppm}} + \text{Area}_{6.0-9.0\text{ppm}}$) to determine the average relative contributions for each region. The regions are defined based on the chemical environment of protons exhibiting signal at those chemical shifts: 1) aliphatic hydrogen (H-C, 0.6 – 1.8 ppm), 2) unsaturated alkyl hydrogen (H-C=C=, 1.8 – 3.2 ppm), 3) oxygenated aliphatic hydrogen (H-C-O, 3.2 – 4.4 ppm), and aromatic hydrogen (Ar-H, 6.0 – 9.0 ppm). Aldehyde and carboxylic acid hydrogen (H-C=O, and HO-C=O) were not detected and would appear downfield of the aromatic protons (i.e., > 9 ppm). Aldehyde and carboxylic acid functional groups are expected to be present in aerosol OM, but these protons readily exchange with the deuterium in the D$_2$O required for analysis resulting in diminished signal in these regions.

### 2.7 Principal component analysis

Principal component analysis was applied separately to the molecular formulas assigned to FTICR mass spectra and peaks present in the $^1$H NMR spectra in order to reveal the components that cause the greatest amount of variance between the source types. The PCA was performed using an in-house MatLab script. The first PC (PC1) explains the most
amount of variance, and the second PC (PC2) is orthogonal to PC1 and explains the second largest portion of the variance. Each successive PC explains less variance until a point of diminishing returns is reached (i.e., < 1% variance explained).

2.7.1 FTICR-MS PCA

All of the molecular formulas from each FTICR mass spectrum for the WSOM-, WSOM+, and PSOM- were compiled into a master formula list and repeating formulas, formulas present in only one sample, and formulas present in all 14 samples were removed to give a total of 14808 formulas. The highest and lowest frequency formulas are not expected to contribute to the variance between samples, and removal of these formulas simplifies the matrix and focuses on the formulas that are responsible for differences between sample types. A 14808 x 14 matrix was created by using an input value of 1 if a formula is present and an input value of 0 for a formula not present within a given sample. The information within the first 3 PCs explains a majority (>60%) of the variance between these aerosol samples, thus only those PCs will be discussed.

2.7.2 $^1$H NMR PCA

All of the peaks in the $^1$H NMR spectrum for each of the aerosol WSOM extracts between 0.0 and 11.0 ppm were binned to a resolution of 1 data point per 0.005 ppm from an initial resolution of 0.0008 ppm between data points. The discrete signal (peak area) at each chemical shift was normalized to the total area in the given spectrum, and the normalized area was used as the data input variables ($n = 2769$) for the PCA. The $^1$H NMR spectra were evaluated using all of the aerosol samples ($n = 14$), and second time omitting the marine aerosols ($n = 10$).
3 Results and Discussion

3.1 Carbon measurements

The aerosol samples from each of the emission sources show OM characteristics that distinguish the sources from one another and relate to their emission source and atmospheric processing. TSP and TC concentrations and BC, WSOC and PSOC percentages (relative to TC) were determined for each of the aerosol samples (Table 3). TSP was not determined for the marine samples, and %BC, and %PSOC could not be determined due to limited sample availability. TSP loadings were highest for the biomass burning samples (73.2 µg m$^{-3}$) followed by the urban (47.1 µg m$^{-3}$) and mixed source (24.1 µg m$^{-3}$) samples. The marine samples show TC loadings (0.5 µg m$^{-3}$) one order of magnitude lower than the mixed source (5.7 µg m$^{-3}$) and urban (6.3 µg m$^{-3}$) samples and two orders of magnitude lower than the biomass burning samples (24.8 µg m$^{-3}$) as one would expect for samples collected over the middle of the ocean away from major terrestrial and anthropogenic sources. In spite of the urban samples having TSP loadings that are approximately twice that of the mixed source samples, they show similar TC concentrations indicating that the urban samples contain high amounts of inorganic materials. The biomass burning samples showed the highest %BC and lowest %WSOC values of the samples which is expected for samples collected in high proximity to biomass combustion processes that produce BC and before the OA can undergo extensive aging processes known to increase water solubility. The marine samples show low but variable %WSOC values (39.6 ± 25.1%). The urban aerosol samples contained a higher %BC (3.4%) and lower %WSOC (40.8%) than the mixed source aerosol (% BC = 1.9, %WSOC = 50.5) samples.
Table 3. Average TSP and TC concentrations and carbon percentages for each aerosol source type.

<table>
<thead>
<tr>
<th>Aerosol Source</th>
<th>n</th>
<th>TSP (µg m⁻³)</th>
<th>TC (µg m⁻³)</th>
<th>%BC</th>
<th>%WSOC</th>
<th>%PSOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Marine</td>
<td>4</td>
<td>-</td>
<td>0.5 ± 0.7</td>
<td>-</td>
<td>39.6 ± 25.1</td>
<td>-</td>
</tr>
<tr>
<td>Mixed source</td>
<td>3</td>
<td>24.1 ± 2.9</td>
<td>5.7 ± 0.7</td>
<td>1.9 ± 2.5</td>
<td>50.5 ± 10.6</td>
<td>44.9 ± 13.0</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>2</td>
<td>73.2 ± 5.3</td>
<td>24.8 ± 4.4</td>
<td>6.5 ± 0.7</td>
<td>33.6 ± 2.6</td>
<td>65.6 ± 20.1</td>
</tr>
<tr>
<td>Urban</td>
<td>5</td>
<td>47.1 ± 11.0</td>
<td>6.3 ± 1.3</td>
<td>3.4 ± 3.2</td>
<td>40.8 ± 5.5</td>
<td>43.9 ± 6.0</td>
</tr>
</tbody>
</table>

*Some parameters for the marine aerosols could not be evaluated due to limited sample availability.

The %PSOC amounts were calculated from ¹H NMR data (see Table S1 in Appendix C) after Willoughby et al. (2014) and are useful for understanding the amount of material analyzed in PSOM extracts for FTICR MS analyses of insoluble OM. Because the pyridine extractions were conducted in parallel to the water extractions, the sum of these two percentages (%WSOC + %PSOC) may be more or less than 100%. The biomass burning samples can be expected to contain significant amounts of water-insoluble primary OA, and this is reflected in the high %PSOC and low %WSOC values. The calculation for PSOC percentage by the ¹H NMR technique omits aromatic peaks due to interference by the exchanged pyridine protons. Because the biomass burning samples are expected to have high aromatic contributions, as indicated by the larger BC percentage and increased signal in aromatic region of the ¹H NMR spectrum for the WSOM (discussed in Section 3.4), this PSOC value may be considered a low estimation. The urban and mixed source aerosols have considerably lower %PSOC (urban = 43.9%; mixed = 44.9%) reflecting their higher water solubility and suggesting that these two sample types have more influence from secondary and aging reactions that produce OA insoluble in pyridine.

The average properties calculated from formula assignments in the WSOM-, WSOM+, and PSOM- FTICR mass spectra show further differences that establish the four
sample types described here as distinct and characteristic of the emission sources. Formulas identified in the PSOM- spectra are included in this analysis, and the major difference between WSOM- and PSOM- is that PSOM contains more of CHOS and aliphatic formulas (Willoughby et al., 2014).

### 3.2 Mass spectra and molecular characteristics

Each of the ESI-FTICR mass spectra for the ambient aerosol extracts average thousands of peaks across a broad range of 200 – 800 \( m/z \) (Fig. 5). Molecular formulas were assigned to a majority (82.2 ± 8.9%) of the peaks with \( S/N \) of at least 3. The biomass burning aerosols averaged the highest number of formulas (3146 ± 470) assigned in each spectrum, followed by urban aerosol extracts (2869 ± 1072), mixed aerosol extracts (1852 ± 552), and marine aerosol extracts (1024 ± 496). The average number of formulas is consistent with the TSP and TC concentrations in that a higher concentration yielded more detected peaks and assigned formulas.

Information about the types and the relative aromaticity of the compounds in a sample can be gleaned from the elemental constituents in the assigned molecular formulas. All of the formulas assigned to the peaks found in each FTICR spectrum for WSOM-, WSOM+, and PSOM- were combined to obtain a master formula list for each aerosol sample (eliminating any duplicate formulas found in multiple extracts or ionizations), and average elemental properties for each aerosol sample from a given source were calculated from this master list of formulas (Table 4). The molecular characteristics for each of the aerosols is described in detail.
Figure 5. Representative full ESI(-) FTICR mass spectra for WSOM\textsubscript{PPL} extracts of (a) marine, (b) mixed source, (c) biomass burning, and (d) urban aerosols between 200 – 800 m/z. Some intense peaks are shown off scale.

3.2.1 Marine aerosols

The marine aerosols were collected over the North Atlantic Ocean, and were previously shown via air mass trajectory analyses and PCA to be representative of marine aerosols (i.e., not influenced by continental air masses; Wozniak et al., 2014). These aerosols have low carbon content (TC = 0.5 µg m\textsuperscript{3}) relative to the aerosols collected over
Table 4. Total formulas and average elemental properties for aerosol WSOM$_{PPL}$ and PSOM from each emission source determined using FTICR mass spectra. The distribution of molecular formulas based on atomic content and AI$_{mod}$ structure type are listed as number of formulas with the percentage of total formulas in parentheses directly below.

<table>
<thead>
<tr>
<th></th>
<th>Marine aerosols</th>
<th>Mixed source aerosols</th>
<th>Biomass burning aerosols</th>
<th>Urban aerosols</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n = 4$</td>
<td>$n = 3$</td>
<td>$n = 2$</td>
<td>$n = 5$</td>
</tr>
<tr>
<td>Average formulas</td>
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<td>6579 ± 173</td>
<td>6527 ± 173</td>
</tr>
<tr>
<td>Total formulas</td>
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<td>6134</td>
<td>7891</td>
<td>10701</td>
</tr>
<tr>
<td>Average O/C</td>
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<td>0.44 ± 0.23</td>
<td>0.32 ± 0.19</td>
<td>0.45 ± 0.23</td>
</tr>
<tr>
<td>Average H/C</td>
<td>1.56 ± 0.39</td>
<td>1.46 ± 0.35</td>
<td>1.35 ± 0.39</td>
<td>1.44 ± 0.37</td>
</tr>
<tr>
<td>Average AI$_{mod}$</td>
<td>0.18 ± 0.26</td>
<td>0.18 ± 0.23</td>
<td>0.29 ± 0.27</td>
<td>0.18 ± 0.24</td>
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</table>

<table>
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<tr>
<th>Atomic Content</th>
<th>Marine aerosols</th>
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<tr>
<td>CHO</td>
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<td>2182</td>
<td>2617</td>
<td>3318</td>
</tr>
<tr>
<td>(41.1%)</td>
<td></td>
<td>(35.6%)</td>
<td>(33.2%)</td>
<td>(31.0%)</td>
</tr>
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<td>CHON</td>
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<td>2699</td>
<td>3472</td>
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<tr>
<td>(16.2%)</td>
<td></td>
<td>(25.7%)</td>
<td>(34.2%)</td>
<td>(32.4%)</td>
</tr>
<tr>
<td>CHOS</td>
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<td>1333</td>
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<td>1910</td>
</tr>
<tr>
<td>(20.9%)</td>
<td></td>
<td>(21.7%)</td>
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<td>(17.8%)</td>
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<td>CHONS</td>
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<td>961</td>
<td>1560</td>
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<tr>
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<td>(15.4%)</td>
<td>(12.2%)</td>
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<td>CHOP(N,S)</td>
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<td>101</td>
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<td>(8.4%)</td>
<td></td>
<td>(1.6%)</td>
<td>(0.7%)</td>
<td>(4.1%)</td>
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<table>
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<tr>
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<th>Biomass burning aerosols</th>
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<td>2442</td>
<td>1864</td>
<td>4024</td>
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<td>(39.8%)</td>
<td>(23.6%)</td>
<td>(37.6%)</td>
</tr>
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<tr>
<td>(51.9%)</td>
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<td>(50.3%)</td>
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<td>(52.5%)</td>
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<td>583</td>
</tr>
<tr>
<td>(5.4%)</td>
<td></td>
<td>(5.8%)</td>
<td>(16.7%)</td>
<td>(5.4%)</td>
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<tr>
<td>Condensed aromatic</td>
<td>234</td>
<td>253</td>
<td>523</td>
<td>473</td>
</tr>
<tr>
<td>(5.1%)</td>
<td></td>
<td>(4.1%)</td>
<td>(6.6%)</td>
<td>(4.4%)</td>
</tr>
</tbody>
</table>

land masses, but contain a sufficient amount of OM analyzed by FTICR-MS. A total of 4570 formulas were identified in all of the marine aerosol samples, averaging 2569 (± 467) formulas per aerosol sample (i.e., WSOM-, WSOM+, and PSOM- combined). The marine
aerosols share the lowest average O/C ratio (0.32 ± 0.19; Table 4) with the biomass burning aerosols, indicating that the OM contained within these samples is less oxidized than the mixed source and urban aerosols in this study. The marine aerosols contain more saturated carbon chains than any of the other aerosols, as indicated by having the highest average H/C ratio (1.56 ± 0.39). The average AI\textsubscript{mod} (0.18 ± 0.26) is identical to the mixed source and urban aerosols, and is representative of olefinic/alcyclic compounds. The distribution of molecules within each AI\textsubscript{mod} structural classification is also comparable to the mixed source and urban aerosols, where most of the formulas are olefinic/alcyclic (51.9%) and aliphatic (37.6%), with few aromatic (5.4%) and condensed aromatic (5.1%) formulas (Table 4).

The OM in the marine aerosols contains the largest fraction of CHO formulas (41.1%, 1880 formulas), and have the smallest fraction of CHON formulas (16.2%, 741 formulas) among the aerosols investigated in this study (Table 4). Molecular formulas containing only CHO can represent an assortment of oxidized functional groups including carboxylic acids, ketones, aldehydes, esters, ethers, and alcohols. Nitrogen-containing OM has been identified in other marine aerosols, and has been attributed to primary biological production and includes peptides (Wozniak et al., 2014), though secondary nitrate compounds are possible. CHON formulas can contain nitrate, amine, amide, or heterocyclic nitrogen functionalities. A large fraction (~60 %) of the CHON formulas contain enough oxygen atoms to contain a nitrate functional group (O/N ≥ 3), but there is no way to distinguish a compound that contains a nitrate functional group and one that contains an amino group and an oxygenated functional group such as a carboxyl group based on molecular formula alone, as they both can ionize sufficiently and be detected.
The relative distribution of CHOS and CHONS formulas (20.9% and 13.4%, respectively) is comparable to the other sources, accounting for approximately one-third of the formulas identified in the marine aerosols. Nearly all of the CHOS formulas have an O/S ratio of at least 4, indicating they have sufficient oxygen to contain a sulfate functional group. The presence of a sulfate cannot be confirmed with this type of analysis, but they are ubiquitous in atmospheric OM and have been identified in samples collected over marine and terrestrial environments (Altieri et al., 2009; Claeys et al., 2010; Hawkins et al., 2010; Pratt et al., 2013; Reemtsma et al., 2006; Romero and Oehme, 2005; Surratt et al., 2008; Wozniak et al., 2008; Wozniak et al., 2014). They can form through reactions of organic precursors with inorganic sulfur compounds under a variety of atmospheric conditions (Surratt et al., 2006; Surratt et al., 2008; Surratt et al., 2007). Inorganic sulfur in the marine environment is expected to be largely derived from the biologically (phytoplankton) emitted dimethyl sulfide as it is a major constituent in the marine atmosphere (Andreae and Raemdonck, 1983). The marine aerosols are the only source containing a significant amount (8.4%, 382 formulas) of CHOP(N,S) formulas, which include CHOP, CHOPN, and CHOPS. Some of these formulas are consistent with phospholipids which would indicate a biological origin.

More than half (58.7%) of the formulas in the marine aerosols plot in the upper-left quadrant (O/C ≤ 0.6, H/C ≥ 1.5) of the van Krevelen diagram (Fig. 6), a region consistent with biologically-derived molecules (lipids, proteins, etc.). Less than 40% of the formulas in any of the other aerosol sources are found in this region of the van Krevelen, suggesting that biologically-derived molecules are an important distinguishing characteristic of marine aerosols from those collected in a terrestrial environment. Bubble bursting
mechanisms at the sea surface are expected to contribute substantially to marine aerosol OM, as well as marine biological emissions (Gantt and Meskhidze, 2013).

3.2.2 Mixed source aerosols

The mixed source aerosols were collected in a rural area and are expected to be influenced by a variety of biogenic and anthropogenic emission sources including those similar to the marine, biomass burning, and urban aerosols evaluated in this study. The TSP and TC concentrations (24.1 and 5.7 µg m\(^{-3}\), respectively) are the lowest of the aerosols collected over terrestrial environments; however 23.7 % of the TSP is TC, which is in between the biomass burning and urban aerosols. An average of 4104 (± 467) formulas were assigned to each sample, and a total of 6134 unique formulas identified in all of the mixed source aerosols (Table 4). The average O/C ratio (0.44), H/C ratio (1.46), and AI\(_{mod}\) (0.18 ± 0.23) are all very similar or identical to those calculated for the urban samples making them almost indistinguishable based on these properties alone (Table 4). The O/C ratio value is higher than either the marine or biomass burning aerosols, suggesting that the mixed source aerosols have a source that introduces inherently more oxidized OM, or that these molecules have been subject to atmospheric oxidation reactions more extensively. The latter implies that these molecules have been in the atmosphere for a longer period of time and are likely being collected farther from their emission source, or that environmental conditions promote increased reactions rates. On average, the OM in the mixed source aerosols is olefinic/alicyclic, comprising 50.3% (3086 formulas) with a large portion of aliphatic compounds (39.8%, 2442 formulas; Table 4). A small fraction (9.9%, 606 formulas) are either aromatic or condensed aromatic compounds. BC and functionalized derivatives of BC would fall under the AI\(_{mod}\) class of condensed aromatic species. The
Figure 6. Van Krevelen diagrams for molecular formulas identified in the FTICR mass spectra for the marine, mixed source, biomass burning, and urban aerosols. Each row represents a different source, and each column represents only those formulas with a specific elemental makeup (CHO, CHON, or CHOS). Each “×” represents one or more molecular formulas.
presence of some condensed aromatic compounds is supported by the BC measurements, and suggests the presence of BC compounds with polar functional groups. BC is traditionally regarded as a product of combustion, as in fossil fuel combustion or the combustion of biomass. It has been recently shown that BC-like compounds are also produced from non-pyrogenic sources (Chen et al., 2014; Waggoner et al., 2015), but it has not been evaluated whether this process is atmospherically relevant. Regardless of origin, these aromatic and condensed aromatic species are capable of absorbing UV radiation resulting in a positive radiative forcing (i.e., climate warming; Andreae and Gelencsér, 2006).

Like the marine aerosols, the mixed source aerosols are dominated by CHO (35.6%, 2182 formulas; Table 4). However, CHON formulas (25.7%, 1574 formulas) make up a sizeable portion of the sample, and these aerosols also have the largest fraction of CHONS formulas (15.4%, 944 formulas). This abundance of CHON and CHONS formulas suggests that reactions with nitrogen, likely in the form of inorganic nitrates and ammonia, are important processes influencing these aerosols as will be discussed in greater detail in Chapter IV. The CHON formulas plot in two distinct regions of the van Krevelen diagram (Fig. 6). A majority of the CHON formulas plot with O/C ratios between 0.05 and 0.80 and have H/C ratios greater than 1.0. This region contains formulas that are primarily aliphatic and olefinic/ Alicyclic, and many of these formulas have the potential to be organonitrates (i.e., N/O ≥3). The other cluster of CHON formulas have substantially lower O/C (0.05 – 0.40) and H/C (<1.0) ratios, indicating that they may contain reduced nitrogen functional groups such as amines or have heterocyclic rings. These types of compounds could represent black nitrogen (heterocyclic aromatic nitrogen produced during biomass
combustion), or derivatives of BC that have undergone reactions with inorganic nitrogen (Wagner et al., 2015).

CHOS formulas represent 21.7% (1333 formulas) of all of the formulas, also plotting into two distinct regions of the van Krevelen diagram (Fig. 6). One region contains many of the formulas with O/C ratios between 0.10 and 1.20 and H/C ratios greater than 1.0. Most of these formulas are aliphatic and contain sufficient oxygen to represent organosulfates (O/S ≥ 4). Aliphatic molecules react with inorganic sulfate preferentially as compared to their unsaturated counterparts (Schmitt-Kopplin et al., 2010). The second CHOS region contains formulas with much lower O/C and H/C ratios (O/C < 0.4, H/C < 1.2) and generally less saturated. Most of these formulas do not contain sufficient oxygen to be organosulfates, and therefore must represent more reduced forms of organic sulfur (e.g., thiols and sulfonates). This second cluster of compounds appears in all of the aerosols collected over terrestrial environments, and is generally absent in the marine aerosols. Sulfonates are a common anthropogenic pollutant and are ubiquitous in personal care products, and have been previously identified in aerosol OM (Altieri et al., 2009), and their abundance in North American continental relative to marine aerosols lends support to the idea that this group of compounds may be anthropogenically-derived.

3.2.3 Biomass burning aerosols

The TSP concentration for these aerosols is the highest, and a large portion (33.9%) of the aerosol mass is carbonaceous (TC = 24.8 μg m⁻³; Table 5). This high OM content is reflected by the detection of an average of 6579 (± 173) formulas being assigned to each biomass burning sample, and a total of 7891 formulas total (Table 4). The average O/C and H/C ratios are the lowest (0.32 ± 0.19 and 1.35 ± 0.39, respectively) of any of the aerosol
sources indicating a large number of unsaturated molecules and molecules that have not undergone extensive oxidation reactions. The lower H/C ratio suggesting unsaturated molecules is reflected in the higher average $A_{\text{imod}} (0.29 \pm 0.27)$, indicative of olefinic/alicyclic compounds. The biomass burning aerosols have a substantially different distribution of molecules based on $A_{\text{imod}}$ structure classification, and have substantially more aromatic (16.7%, 1318 formulas) and condensed aromatic (6.6%, 523 formulas), and fewer aliphatic (23.6%, 1864 formulas) formulas than any of the other emission sources in this study. Aromatic and condensed aromatic compounds have higher potential for being light-absorbing molecules than more saturated molecules (Andreae and Gelencsér 2006), and may contribute to a class of light-absorbing OM known as brown carbon. The brown color of the sample filters suggests that these samples do contain significant amounts of brown carbon which, like BC, has no unequivocal chemical definition (Andreae and Gelencsér 2006). Brown carbon is formed alongside BC in combustion processes (Andreae and Gelencsér 2006), and has also been formed through model reactions of aqueous SOA with NH$_3$ (Bateman et al., 2010; Lee et al., 2014), but the global importance of brown carbon is still a topic of debate.

The biomass burning aerosols contain nearly equal amounts of CHO and CHON compounds (2617 and 2699 formulas, respectively), together making up two-thirds of all the formulas (Table 4), which is similar to the distributions found in the urban aerosols. The CHON formulas all have relatively low O/C ratios (range 0.05 – 0.50) and span the H/C range (0.30 – 2.20; Fig. 6). There are 976 CHON formulas that are classified as aromatic or condensed aromatic, which is three times more than any of the other aerosols, suggesting that aromatic and condensed aromatic CHON formulas are important in
distinguishing biomass burning aerosols from other combustion sources such as those that influence the urban aerosols. The elevated amounts of organic nitrogen in biomass burning aerosols has been observed previously (Dou et al., 2015; Laskin et al., 2009; Lin et al., 2012; Sannigrahi et al., 2006). The average O/N ratio for these compounds is 2.3, and fewer than half of the CHON compounds (47%) could contain a nitrate functional group (O/N ≥ 3) indicating reduced nitrogen species (imidazoles, amines, etc.) are dominant. In addition to levoglucosan, imidazole has been suggested as a possible tracer for aqueous SOA (Ervens et al., 2011). Compounds containing CHOS make up a significant portion of the biomass burning OA comprising 19.8% (1560 formulas) of all the molecular formulas, and these CHOS formulas span the O/C range (0.10 – 1.20) and have H/C ratios of at least 1.00 (Fig. 6). Most of the CHOS formulas have an O/S ratio of at least 4, indicating that most of the formulas could be organosulfates which are expected to be formed through esterification between existing OM and SOx. Like the mixed source and urban aerosols, there is a cluster of low O/C and low H/C CHOS formulas, but the O/C ratios in this cluster are much lower (O/C < 0.1) implying that these formulas likely do not represent the anthropogenic sulfonates suggested in the mixed source and urban aerosols.

3.2.4 Urban aerosols

The urban aerosols were collected in Philadelphia, PA, USA, an urban region heavily influenced by industrial processes, fossil fuel combustion, and other anthropogenic emissions. The TSP concentrations are high relative to the other samples in this study (47.1 µg m⁻³), but the fraction of carbonaceous material is the lowest measured of the aerosol sources in this study (13.4%, TC = 6.3 µg m⁻³) indicating a substantial amount of inorganic aerosols (Table 3). Despite the low TC percentage, the urban aerosols average 6527 (± 173)
formulas per sample and a total of 10701 formulas in all samples (Table 4). The average O/C ratio (0.45 ± 0.23) is the highest of all the samples, supporting previous work that OM is highly oxidized near urban regions (Zhang et al., 2005). The average H/C ratio (1.44 ± 0.37), AI_{mod} (0.18 ± 0.24), and distributions of compounds into each structural AI_{mod} class are comparable to the marine and mixed source aerosols (Table 4).

One of the major features that distinguishes the urban aerosols from the marine and mixed source aerosols is that the urban aerosols contain a substantial amount of CHON formulas. Like the biomass burning aerosols, the urban aerosol contain nearly equal amounts of CHO and CHON formulas (31.0 – 32.4%; Table 4). There are 3318 CHO formulas, which have O/C ratios ranging between 0.05 and 1.00 and H/C ratios above 0.80 (Fig 2). The 3472 CHON formulas span similar O/C and H/C ranges, with a group of low O/C and low H/C formulas (Fig. 6). The urban samples differ from the biomass burning samples in that their CHO and CHON formulas on average have higher O/C and H/C ratios and the urban aerosol formulas contain more heteroatoms (O + N + S + P; urban formulas = 0.38 heteroatoms per carbon, biomass formulas = 0.38 heteroatoms per carbon) per carbon. The average O/N ratio for the CHON formulas in the urban samples is 4.46 (nearly double that of the biomass burning CHON formulas), and 78% of the formulas contain sufficient nitrogen to contain at least one nitrate functional group. The remaining 22% of CHON formulas have low O/C and H/C ratios are largely classified aromatic and condensed aromatic based on their AI_{mod} values, which could be indicative that they belong to a class of compounds called black nitrogen.

It is expected that urban areas are also influenced by biomass burning aerosols, and some studies group urban and biomass burning aerosols into a single category (Hu et al.,
2015). In the case of these aerosols, less than 20% of the formulas overlap. Most of the formulas that are in both the biomass burning aerosols and the urban aerosols include CHO and CHOS formulas. Very few of the CHON formulas (369 formulas) are present in both urban and biomass burning aerosols, which represents 6% of all the CHON formulas identified in both of the aerosol sources (5802 CHON formulas). This further supports that the nitrogen-containing formulas could be important in distinguishing OA from different emission sources.

The chemical characteristics provided by the formulas identified in the FTICR mass spectra provide important details regarding the molecular composition of each of these types of aerosols, and provides important clues about their primary emission sources and potential environmental impacts. However, it is tedious to evaluate the differences between the samples due to the massive number of molecular formulas identified, and PCA can reveal key features that are not readily apparent.

### 3.3 FTICR-MS PCA

The scores for the PCA results reveal that the first three principal components (PC1, PC2, and PC3) accounts for a majority (66.0%) of the differences between the aerosol samples (Fig. 7). PC1 explains 32.5%, PC2 explains 22.4%, and PC3 explains 11.1% of the differences between the samples. The signs (+/-) for PCs 1-3 are different for each of the sources. All of the marine samples have a negative PC1 score, a positive PC2 score, and a positive PC3 score. The mixed source samples have a positive PC1, a positive PC2, and negative PC3. The biomass burning samples have a negative PC1, a negative PC2, and a positive PC3. The urban samples have a positive PC1, a negative PC2, and a positive PC3. These sign differences were used to identify the loadings, where a loading represents
a single molecular formula, characteristic for each source. For example, if a molecular formula has negative PC1 loadings, and positive PC2 and PC3 loadings, it is classified as a formula characteristic of marine sources. This resulted in the identification of 1078 formulas characteristic for marine aerosols, 693 formulas characteristic for mixed source aerosols, 4174 formulas characteristic of biomass burning aerosols, and 3484 formulas characteristic of urban aerosols. The remaining 5379 formulas contain characteristics that are represented by multiple sources indicating that they are not diagnostic of a particular source and may be ubiquitous in aerosol OM or inconsistently present in a given source.

The biomass burning aerosols contain the most number of distinguishing formulas, according to the PCA. They are characterized by having the lowest average O/C and H/C values, and the highest AI_{mod} values (Table 5), which is consistent with the bulk properties discussed in section 3.2.3 (Table 4). The low H/C and high AI_{mod} are supported by the biomass burning aerosols having the largest fraction of aromatic and condensed aromatic formulas (32.4%). Additionally, more than 80% of the formulas are CHON (45.4%) and CHO (34.7%), suggesting that other formulas (S- and P-containing formulas) are present but not a defining characteristic for biomass burning aerosols. It is evident in the van Krevelen diagram that CHON and CHO formulas make up a large portion of those aromatic and condensed aromatic compounds, as indicated by their presence in the low O/C and low H/C regions (Fig. 8c).

The urban aerosols are also characterized by a large number of CHON (38.0%) and CHO (33.4%) formulas, but they appear to have significantly higher O/C ratios than those found in the biomass burning aerosols (Fig. 8d). The average O/C (0.55 ± 0.21) is double and the average AI_{mod} (0.18 ± 0.22) is half that of the biomass burning aerosols, suggesting
that the key differences between these aerosol sources is the presence of more highly oxidized and more aliphatic compounds. Fossil fuel combustion and biological emissions are major sources for aliphatic compounds in the atmosphere (Alves et al., 2012), and the presence of heavy traffic and heavy industrial activity in short and long range proximity of the urban sampling site suggests that fossil fuel combustion processes are largely responsible for these compounds.

Much like the bulk characteristics, the PCA-identified formulas for the marine and mixed source aerosols are dominated by CHO formulas (31.6 and 45.0%, respectively). The marine aerosols have the largest fraction of CHOS formulas (27.4%), which are consistent with organosulfate compounds formed via photochemical aging, and P-containing formulas consistent with biologically-derived phospholipids. Most of the marine aerosols formulas identified by PCA are localized to the upper-left region of the

Figure 7. PCA score plots for PC2 versus PC1 (left) and PC3 versus PC1 (right). PCA was performed using molecular formulas identified in FTICR mass spectra for aerosol OM extracts from marine, mixed source, biomass burning, and urban areas.
Table 5. Total formulas and average elemental properties for molecular formulas identified by PCA. Distributions of formulas based on atomic content and AI\textsubscript{mod} structure type are listed as percentage of total formulas.

<table>
<thead>
<tr>
<th></th>
<th>Marine aerosols</th>
<th>Mixed source aerosols</th>
<th>Biomass burning aerosols</th>
<th>Urban aerosols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total formulas</td>
<td>1078</td>
<td>693</td>
<td>4174</td>
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<tr>
<td>Average O/C</td>
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<td>0.33 ± 0.18</td>
<td>0.26 ± 0.13</td>
<td>0.55 ± 0.21</td>
</tr>
<tr>
<td>Average H/C</td>
<td>1.55 ± 0.41</td>
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<td>1.24 ± 0.37</td>
<td>1.36 ± 0.34</td>
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<tr>
<td>Average AI\textsubscript{mod}</td>
<td>0.20 ± 0.25</td>
<td>0.20 ± 0.21</td>
<td>0.37 ± 0.23</td>
<td>0.18 ± 0.22</td>
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</tbody>
</table>

Atomic Content (%)

<table>
<thead>
<tr>
<th></th>
<th>Marine aerosols</th>
<th>Mixed source aerosols</th>
<th>Biomass burning aerosols</th>
<th>Urban aerosols</th>
</tr>
</thead>
<tbody>
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<td>CHON</td>
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<td>CHOS</td>
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</tr>
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<td>CHONS</td>
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<td>CHOP(N,S)</td>
<td>8.6</td>
<td>5.6</td>
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<td>2.8</td>
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Structure Type (%)

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<th></th>
<th>Marine aerosols</th>
<th>Mixed source aerosols</th>
<th>Biomass burning aerosols</th>
<th>Urban aerosols</th>
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<tbody>
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<td>Aliphatic</td>
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<td>12.0</td>
<td>34.1</td>
</tr>
<tr>
<td>Olefinic/yclic</td>
<td>56.6</td>
<td>67.8</td>
<td>55.6</td>
<td>60.6</td>
</tr>
<tr>
<td>Aromatic</td>
<td>5.5</td>
<td>4.9</td>
<td>26.8</td>
<td>3.1</td>
</tr>
<tr>
<td>Condensed aromatic</td>
<td>6.6</td>
<td>3.3</td>
<td>5.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

van Krevelen diagram, which is the region containing many biologically-relevant compounds (lipids and proteins), suggesting that biological activity is an important driver for the formation and transformation of marine aerosols. The mixed source aerosols contain the fewest formulas identified by PCA, indicating it those samples have few compounds specific to a unique source and shares many molecular features with the other aerosols.

It is evident that heteroatoms as well as formulas containing only CHO are important to each of the aerosol sources. The formation and transformation of these molecules are influenced by many factors including OM source, meteorological conditions, and the chemical and physical properties of co-emitted species, and several atmospherically-relevant transformations that are investigated in Chapter IV.
Figure 8. Van Krevelen diagrams for molecular formulas identified by PCA for (a) marine, (b) mixed source, (c) biomass burning, and (d) urban aerosols. Each data point is colored according to the atomic content of the molecular formula.

While ESI-FTICR-MS provides an incredible amount of molecular information regarding complex OM mixtures, the limitations are well-established. The ability of a compound to be analyzed is highly dependent on its ability to ionize, and non-polar and non-ionizable compounds (e.g., hydrocarbons and carbohydrates) are largely omitted from this analysis. Additionally, this analysis is necessarily qualitative because a combination of charge competition, concentration, and ionization efficiency drive the peak intensities.
However, $^1$H NMR does not have the same bias for the detection of OM, and provides a complementary set of information regarding the chemical makeup of these complex samples.

3.4 $^1$H NMR analysis

The WSOM for each of the aerosols display an array of proton types spanning the spectral region between 0 and 11 ppm (Fig. 9). The observed chemical shifts are related to the chemical environment of each proton, and provides clues to the structural connectivity of the atoms within each sample. The region between 0 and 4.4 ppm contains at least 90% of the signal in each of the spectra. Most of the spectra contain broad peaks indicating similar proton types attached to varying carbon chain lengths or located in varying proximity to polar functional groups. These broad peaks exemplify the complexity of aerosol WSOM, and make it difficult to identify individual compounds. However, the region in which a proton signal is detected can indicate the general class of compounds to which that proton belongs. For example, the most intense peak in each spectrum is located at 1.2 ppm and is indicative of protons that are part of a CH$_2$ group, which represent those that are part of an alkyl chain. This peak is broadest in the urban aerosols, suggesting the alkyl chains are longer, and there is a larger variety of CH$_2$ protons in these aerosols. Conversely, the narrower CH$_2$ peak in the marine, mixed source, and biomass burning aerosols suggests shorter chain lengths and less diversity regarding chemical environments among CH$_2$ groups. Smaller chain lengths could indicate decomposition of larger molecules by photochemical degradation, or suggest that the molecules have not undergone substantial oligomerization reactions, such as those that add small volatile species like isoprene.
Dividing the spectrum into key proton regions and evaluating the relative contributions of the total spectral intensity can reveal important differences among the different sources (Table 6). The region (6 – 9 ppm) where signal from aromatic protons are found is the most variable among the sources. A broad signal is observed in the aromatic region of the biomass burning aerosols spectra (Fig. 9 inset) and it makes up 9.2% of the total intensity, a percentage more than 4 times greater than the other sources (Table 6). Protons in this region are attached to aromatic or condensed aromatic rings, and the broadness of the peak indicates a high degree of structural diversity among the aromatic protons in these aerosols. There is little signal in the aromatic region in the urban and mixed source aerosols and essentially no signal in the marine aerosols, indicating there are either very few aromatic compounds in these aerosols or that the only water-insoluble aromatic species are present. The observation of a much larger intensity in the aromatic region of the biomass burning aerosols supports the detection of more aromatic and condensed aromatic formulas in the FTICR mass spectra as well as the higher concentration of BC, and suggests that the biomass burning aerosols contain a larger quantity of chromophoric OM than the other aerosol sources investigated here.

As previously mentioned, the majority of the signal in each NMR spectrum falls in the region between 0.6 and 4.4 ppm, and the relative signal in each of the major proton regions does not vary greatly between the sources. At least 50% of the signal falls in the H-C region (0.6 – 1.8 ppm) in all cases, indicating that a majority of the protons are part of alkyl groups. The larger H-C fractions observed in the urban and mixed source aerosols suggests that OM contains larger carbon backbones (linear or branched). Carbon can be added to existing OM via oligomerization reactions, and the larger carbon chains
Figure 9. $^1$H NMR spectra for WSOM of mixed source, biomass burning, and urban aerosols, where each colored line represents a different sample spectrum. The region between 6 – 9 ppm represents aromatic protons, and is expanded in the inset of each spectrum.
Table 6. Average relative contributions of total spectral intensity for integrations of major proton regions in $^1$H NMR spectra for each of the aerosol sources. Standard deviations of the relative signal in each region among aerosols from the same source are provided.

<table>
<thead>
<tr>
<th>Aerosol Source</th>
<th>H-C (0.6 – 1.8 ppm)</th>
<th>H-C-C= (1.8 – 3.2 ppm)</th>
<th>H-C-O-R (3.2 – 4.4 ppm)</th>
<th>Ar-H (6.0 – 9.0 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine</td>
<td>50.3 ± 5.5</td>
<td>34.2 ± 3.9</td>
<td>14.5 ± 3.6</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>Mixed source</td>
<td>57.0 ± 1.3</td>
<td>32.9 ± 0.4</td>
<td>8.4 ± 0.8</td>
<td>1.7 ± 0.3</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>50.9 ± 3.4</td>
<td>31.1 ± 0.6</td>
<td>9.4 ± 0.9</td>
<td>9.2 ± 1.9</td>
</tr>
<tr>
<td>Urban</td>
<td>53.2 ± 1.5</td>
<td>35.0 ± 2.0</td>
<td>9.4 ± 1.1</td>
<td>2.4 ± 0.6</td>
</tr>
</tbody>
</table>

The presence of these aerosols suggests that these aerosols have undergone oligomerization reactions more extensively than the marine and biomass burning aerosols. Protons that are more downfield in this region (1.4 – 1.8 ppm) may be part of H-C group that is β to a carbon attached to heteroatoms (H-C-C-C-X, where X = N, S, or O). The presence of a large number of heteroatomic compounds identified in the mass spectra (CHON, CHOS, and CHONS) indicates some portion of the signal in this region represents these species as can be expected for OA and was noted previously (Section 3.2).

Approximately one-third of the signal intensity falls in the unsaturated alkyl region (H-C-C=), which includes carbonyl, carboxyl, alkenes, and also hydrogen attached to carbons adjacent to a nitrogen or sulfur (i.e., amines, thiols, etc.). The marine and urban aerosols have the highest relative percentage of proton signal in this region, but are also the most variable. On average, approximately 9% of the proton signals are found in the oxygenated aliphatic region (3.2 – 4.4 ppm) for the aerosols collected over terrestrial environments and a slightly higher percentage is observed in the marine aerosols (14.5%). The greater signal intensity in this region of the marine aerosols is surprising given the low O/C ratios of the molecules identified in the FTICR mass spectra, but this could be due to
the presence of small oxygenated species that are outside of the mass spectral window (i.e., <200 \text{ m} / \text{z}) as suggested by the presence of a sharp, intense peak in this region. This region includes protons attached to carbons that are singly bound to an oxygen atom such as ethers, esters, and alcohols. The complexity of aerosol OM limits the ability to identify individual components within the mixture, but provides valuable information regarding the connectivity of the compounds present. These features can be observed more clearly with the help of PCA.

3.4 $^1$H NMR PCA

PCA was performed on the whole $^1$H NMR spectra for each of the aerosol WSOM extracts, similar to previous studies (Decesari et al., 2011; Wozniak et al., 2015; Wozniak et al., 2013). The initial PCA results indicate that the marine aerosols are significantly different than the mixed source, biomass burning, and urban aerosols and inclusion of the marine aerosols does not adequately explain the variance between the three terrestrial sources (Fig. 10a). The differences highlighted include the fact that the marine aerosols contain few sharp peaks (e.g., methane sulfonic acid at 2.7 ppm), and the other aerosols contain multiple broad signals throughout each spectrum. The PCA was evaluated a second time using only the mixed source, biomass burning, and urban aerosols, and key differences among those sources are discussed further. The key features of marine aerosol WSOM that distinguish them from continentally-influenced air masses have been discussed at length in previous studies (Wozniak et al., 2015; Wozniak et al., 2013). Briefly, the marine aerosols differ from those influenced by the North American continent in that the marine aerosols have more saturated aliphatic chains and are less structurally diverse.
The first two principal components (PC1 and PC2) explain more than 80% of the variance between the mixed source, biomass burning, and urban aerosol WSOM. The urban aerosols have lower PC1 scores than the mixed source and biomass burning aerosols, the biomass burning aerosols have lower PC2 scores than the urban and mixed source aerosols, and the mixed source aerosols do not have unique PC values (Fig. 10b). Thus, PC1 shows the spectral characteristics that differentiate the urban aerosols from the biomass burning and mixed source aerosols, and PC2 shows the spectral characteristics that differentiate the biomass burning aerosols from the other aerosols.

The most intense peak in the variable loadings plot for PC1 (Fig. 11a) is positive and represents a CH$_2$ group (1.2 ppm), suggesting that alkyl chain length may be important.
in distinguishing aerosol emission sources. The CH$_2$ peak in the mixed source and biomass burning aerosols is more narrow than in the urban aerosols, so the positive peak in the PC1 loadings may be indicative of shorter alkyl chains (i.e., less variability). A splitting of the CH$_3$ peak (0.9 ppm) is observed, and the negative peak is more downfield than the positive peak. This splitting suggests that the urban aerosols (represented by negative PC1 variable loadings) contain terminal methyl groups in closer proximity to polar functional groups, which is supported by the presence of broad peaks in the region where polar functional groups appear (1.8 – 3.2 ppm). Another intense positive peak is found around 2.1 ppm, which can represent hydrogen bound to a carbon α to a carbonyl group (Fig. 11a.). There is an intense peak in this area in each of the whole sample spectra, but the width of the peaks vary (Fig. 9) indicating varying structural diversity of similar functional groups. This peak is sharper in the mixed source and biomass burning aerosols, and broad in the urban aerosols. In fact, the edges of the peak at 2.1 can be found as negative peaks in PC1 indicating that the broadness of that peak is characteristic of the urban aerosols. While protons bound to carbon adjacent to a carbonyl group are widespread among the aerosols as indicated by a strong signal around 2.1 ppm being apparent in each $^1$H NMR spectrum, the urban aerosols contain protons that are in more diverse chemical environments.

The variable loadings plot for PC2 (Fig. 11b) shows the spectral characteristics important to the biomass burning aerosols. A broad negative peak in the aromatic region (6 – 9 ppm) is apparent, and is equivalent to the aromatic signal observed in the individual spectra of the biomass burning aerosols. Peaks consistent with levoglucosan (3.36, 3.52, 3.75, and 3.93 ppm; Decesari et al., 2001) are identified in the negative PC2 loadings, indicating that they are important in distinguishing the biomass burning aerosols from the
other source. Levoglucosan is a common product of the combustion of cellulose material and is widely used as a tracer compound for biomass burning aerosols (Simoneit et al., 1999). Levoglucosan does produce additional $^1$H NMR peaks, but they are obscured by the water-suppression pulse program due to their proximity to the peak generated by water (~4.7 ppm). A slight negative peak at 2.3 ppm is consistent with hydrogen attached to nitrogen. The peak is broad indicating that there are many compounds with the same functional group attached to varying carbon structures. Without standards, it cannot be confirmed that this peak represents amino groups, but the large number of CHON formulas identified in the FTICR mass spectra supports the presence of a diverse suite of N-containing OM in the biomass burning aerosols.

Overall, there is good consistency between the $^1$H NMR and FTICR-MS techniques. Both techniques identify aromatic compounds and nitrogen-containing compounds that are not extensively oxidized as important for distinguishing the OM from biomass burning aerosols from the other sources. The lower degree of oxidation in the OM found in the biomass burning and also the marine aerosols suggests that these aerosols are collected close to their source and/or have not been exposed to conditions that promote extensive oxidative or oligomeric transformations. The urban aerosols are characteristically more polar as indicated by $^1$H NMR peaks that are shifted more slightly downfield than in the other aerosols and also the higher O/C ratios of the formulas, with more structurally diverse carbon chains. This structural diversity may be represented by longer and/or more branched carbon chains indicative of more oligomeric or other chain elongation reactions. While some of these features were readily apparent, the PCA was able to highlight and confirm some of these variations.
Figure 11. Variable loadings plots for (a) PC1 and (b) PC2 resulting from PCA using full $^1$H NMR spectra of mixed source, biomass burning, and urban aerosol WSOM. Some peaks are labeled with the functional group region and some peaks labeled with a single letter to indicate a specific compound, where A = acetic acid or acetate and L = levoglucosan.

The combination of $^1$H NMR and FTICR-MS provides an incredible amount of molecular-level information regarding the chemical composition of aerosol OM. While $^1$H NMR overcomes some of the bias introduced by ESI-FTICR-MS, it comes with its own
limitations. The $^1$H NMR analysis used here requires a liquid sample, so the water-insoluble OM is not analyzed by this method. Solid-state NMR techniques that analyze a whole solid sample do exist but require very large samples that can only be obtained over weeks of sampling. Additionally, the water-suppression removes all signal in the region of 4.7 ppm and may reduce the signal in the region within ±0.5 ppm including protons directly attached to carbon-carbon double bonds (H-C=C) which are typically found around 5 ppm.

4 Summary and Implications

The OM contained within aerosols from different sources have distinct molecular characteristics that provide clues to the primary inputs as well as the atmospheric processes responsible for transforming it. Marine aerosols contain molecules consistent with biological inputs including lipids and phospholipids as well as a large fraction of organosulfate compounds. The primary input of OA is likely biological in origin, and reactions with inorganic sulfate, likely derived from dimethyl sulfide, are an important aging process. The carbon backbones of these molecules are not as diverse as those found in the terrestrial aerosols, and the OM is overall less oxidized. The OM in biomass burning aerosols is characteristically aromatic and nitrogen incorporation reactions play a major role in the formation or transformation of these aerosols. These highly aromatic, nitrogen compounds are likely an important component of atmospheric brown carbon, which makes a significant contribution to light-absorbing carbon in the atmosphere. The urban aerosols also have a large amount of nitrogen-containing compounds, but are not as aromatic. These compounds, in part, may represent biomass burning OA that has undergone ring-opening reactions or extensive oxidation reactions. Biomass burning aerosols are expected to have a widespread impact, and not just in close proximity to the combustion source. The urban
aerosols are also characteristically more complex, which is reflected in the elevated heteroatom content per unit carbon.

Here we provide an approach to elucidating the molecular differences between specific aerosol emission sources. Analysis by FTICR-MS and $^1$H NMR provide a complementary set of information regarding OA chemical composition, and PCA provides a useful tool for deconstructing the important components that define each of the aerosol sources. While this study presents several aerosols from some key sources, application of this method to a larger number of samples from more emission sources would provide a more comprehensive inventory for OA that would benefit the aerosol community. Additionally, pairing this analysis with a more time-resolved method, such as aerosol mass spectrometry would provide an excellent accounting of the inorganic ions and volatile OM that influence the chemical transformation.
CHAPTER IV

MOLECULAR CHARACTERIZATION OF AMBIENT AEROSOL ORGANIC MATTER USING KENDRICK MASS DEFECT ANALYSIS: A NEW APPROACH FOR ELUCIDATING MOLECULAR TRANSFORMATIONS IN THE ATMOSPHERE

1 Introduction

Organic aerosols (OA) are a complex mixture of organic compounds resulting from direct emission into the atmosphere or formation through reactions of volatile precursors. OA is quantitatively significant with regards to total aerosols mass, having inputs from numerous anthropogenic and biogenic sources (Jimenez et al., 2009; Kanakidou et al., 2005). There is general agreement that the impacts of OA on human health, biogeochemical cycling, and in particular, climate are significant, yet largely uncertain (Andreae and Gelencsér, 2006; Bond et al., 2013; Jacobson, 2000; Jimenez et al., 2009; McNeill, 2015; Ramanathan et al., 2001).

Much of the uncertainty associated with OA effects on climate can be attributed to insufficient molecular characterization. The molecular characteristics of OA are important determinants for the resultant climate-relevant atmospheric impacts on hygroscopicity, cloud formation, and light absorption (Andreae and Gelencsér, 2006; Hallquist et al., 2009; IPCC, 2013). Yet, the relationships between aerosol sources, aerosol molecular characteristics, and these impacts still confound the atmospheric community. Immense progress has been made through laboratory smog chamber and ambient aerosol studies leading to the discovery of a multitude of chemical reactions that are responsible for forming and transforming OA in the atmosphere, which partially explain the presence of
many types of organic compounds (Ervens et al., 2011; Hallquist et al., 2009; McNeill, 2015). For example, highly reactive natural and anthropogenic volatile organic compounds (e.g., isoprene, \(\alpha\)-pinene, \(\beta\)-pinene, limonene, toluene, etc.) are known to form a diverse suite of secondary OA (SOA; Ervens et al., 2011 and references within). These SOA and primary OA compounds can undergo a series of reactions that alter the structure, including photochemical and/or dark reactions with other organic compounds or inorganic compounds (e.g., hydroxyl radical, ammonia, nitrogen oxides, and sulfur oxides; Ervens et al., 2011; Hallquist et al., 2009; McNeill 2015). These aging reactions have been recognized to progressively oxidize OA compounds throughout their atmospheric lifetime resulting in higher average O/C ratios and oxidation states of carbon (Heald et al., 2010; Jimenez et al., 2009; Kroll et al., 2011). In spite of these advances, emissions-based OA modeling studies still underestimate ambient measurements of OA, suggesting that the atmospheric chemistry community still doesn’t have a firm grasp on the chemical composition of OA components and the processes that form and transform them (Jimenez et al., 2009; McNeill 2015). An understanding of the molecular level processes that form OA are vital for closing this gap, and analytical improvements are necessary to evaluate OA chemical composition and the fate and impacts of these species in the atmosphere.

Fortunately, great progress has been made in the last few decades regarding the chemical characterization of aerosol OM. Ultra-high resolution mass spectrometry (UHR-MS), in particular, has made an important contribution to this enhanced characterization due to its unique ability to analyze complex environmental mixtures at extremely high resolution and mass accuracies with minimal sample manipulation (Sleighter and Hatcher 2007). UHR-MS studies have confirmed the presence of a highly complex, diverse suite of
organic compounds contained within ambient aerosols, fog water, and rainwater (e.g., Altieri et al., 2012; Mazzoleni et al., 2010; Schmitt-Kopplin et al., 2010; Willoughby et al., 2014; Wozniak et al., 2008). The formation of some of these compounds have been supported by laboratory-generated aerosol studies where model precursor compounds (e.g., glyoxal, isoprene, and phenols) are subject to various atmospheric aging reactions (Ervens et al., 2011 and references within). Other UHR-MS studies have identified the defining characteristics of various emission sources to marine aerosol water-soluble OM (Wozniak et al., 2014), identified biogenic SOA in ambient aerosols and rainwater (Altieri et al., 2009; Kourtchev et al., 2014), and directly characterized polar functional groups in fog water using fragmentation analysis (LeClair et al., 2012).

While UHR-MS has been useful for helping to understand ambient OA composition and SOA and aging reaction pathways, there is still quite a lot to be learned. With the development of UHR-MS techniques comes the challenge of innovating new ways to analyze and visualize these large datasets in ways that provide new information about atmospheric processes. Here, we present two methods for evaluating the extent of OA aging processes evident in FTICR-MS data generated from extracts of ambient OA known to have distinct emission sources (marine, biomass burning, urban, and mixed sources). The first of these methods uses Kendrick mass defect (KMD) analysis to evaluate the extent of OA processing due to oligomerization reactions. The second method examines mass differences between CHO and CHON or CHOS formulas to investigate the extent of reactions due to the incorporation of inorganic ionic species. These data analysis techniques offer ways to extract important information on the relative importance of various
atmospheric transformations in OA thereby enhancing the amount of qualitative information atmospheric chemists can obtain from extensive FTICR-MS datasets.

2 Methods

2.1 Aerosol sample collection and carbon measurements

Ambient aerosol total suspended particulates (TSP, n = 14) were collected from four different locations in the eastern United States and over North Atlantic Ocean to represent different emission source types. A description of the sampling methods, sampling locations, and collection dates are described in detail in the method section of Chapter III. Briefly, TSP samples from a mixed source (n = 3) in Gloucester Point, VA, USA, a biomass burning event (n = 2) in Suffolk, VA, USA during a smoldering peat fire, and an urban area (n = 5) in downtown Philadelphia, PA, USA were collected in the summer between 2011 and 2014. Marine TSP samples (n = 4) were collected as part of the 2011 US GEOTRACES program cruise (www.geotraces.org) and 2014 Western Atlantic Climate Study II cruise (http://saga.pmel.noaa.gov/index.html) aboard the RV Knorr (Woods Hole, MA). A storage or field blank filter was collected for each sampling period and were analyzed as blanks for their respective samples.

Experimental details and results for the determination of TSP and TC concentrations as well as %BC (Chapter III, Table 3). Briefly, the QM/A filters were weighed before and after sampling to determine the TSP mass loadings. Total carbon (TC = organic + elemental/black – inorganic carbonates) was determined for each sample using a FlashEA 1112 elemental analyzer (ThermoFinnigan). Black carbon (BC) amounts were determined using chemothermal oxidation at 375 °C (CTO-375) and elemental analysis
with the FlashEA 1112, and the %BC is expressed relative to TC. TSP and %BC values were not obtained for the marine aerosols due to limited sample amounts.

2.2 Solvent Extractions

Aerosol filter plugs of known OC masses were combined with either ultrapure water (Millipore Synergy Ultrapure Water System) or pyridine (Sigma-Aldrich, ≥ 99.9 %), and thoroughly mixed on an orbital shaker (150 RPM, 4 h, 21 °C). Insoluble particles were separated from each filtrate using a 0.45 µm PTFE filter cartridge and syringe. The amount of water-soluble organic carbon (WSOC) in each water filtrate was determined by measuring non-purgeable organic carbon using a Shimadzu TOC-VCPH analyzer, and %WSOC relative to TC was calculated for each sample. The amount of pyridine-soluble organic carbon (PSOC) was determined by proton nuclear magnetic resonance (1H NMR) analysis, and %PSOC relative to TC was determined for each sample.

The water extracts were desalted using an established procedure for Agilent PPL solid-phase extraction cartridges (Dittmar et al., 2008), and the desalted sample was eluted in methanol (Acros, 99.9 %). The pyridine filtrate does not contain salts that interfere with electrospray ionization, and therefore does not require additional manipulation. The solvent extracts were stored at -8 °C until FTICR-MS analysis, typically within 24 h of preparation. Experimental replicates were prepared and analyzed for at least one of each of the source types to ensure good experimental and instrumental reproducibility.

2.3 FTICR-MS Analysis

All WSOM samples were analyzed in both positive and negative electrospray ionization (ESI) mode (WSOM- and WSOM+, respectively), and PSOM were analyzed in negative mode only due to poor signal observed in the positive mode. Each of the samples
was prepared individually to achieve the maximum ionization possible, and specific details regarding sample preparation and instrument optimization are described in Chapter III (Section 2.4). A respective field blank extract was prepared identically and analyzed immediately prior to each of the aerosol sample extracts, so that a representative experimental blank spectrum was obtained for each aerosol extract.

Each of the samples was analyzed on a Bruker Daltonics 12 Tesla Apex Qe FTICR-MS with an Apollo II ESI source housed at the College of Sciences Major Instrumentation Cluster at Old Dominion University. The instrument was externally calibrated daily using a polyethylene glycol standard. Electrospray voltages were optimized for each sample, and ions were accumulated for 0.5 – 2.0 s before transfer into the ICR cell, where 300 transients were co-added. Each spectrum was internally calibrated using the naturally occurring molecules including fatty acids and other homologous series of compounds containing only carbon, hydrogen and oxygen (Sleighter et al., 2008). Peaks consistent with salts, blank peaks, and $^{13}$C isotopologue peaks were not considered for formula assignments.

### 2.4 Molecular Formula Assignments

A unique molecular formula was assigned to a majority (82% ± 9%) of the measured peaks having a $S/N$ ratio of at least 3 using an in-house generated MatLab (The MathWorks Inc., Natick, MA) code according to the criteria $^{12}$C$_{5-80}$$^{1}$H$_{5-200}$$^{16}$O$_{1-30}$$^{14}$N$_{0-5}$$^{32}$S$_{0-2}$$^{34}$P$_{0-2}$ for negative ESI and $^{12}$C$_{5-80}$$^{1}$H$_{5-200}$$^{16}$O$_{1-30}$$^{14}$N$_{0-5}$$^{32}$S$_{0-2}$$^{23}$Na$_{0-1}$ for positive ESI. The assigned formulas were screened to remove any chemically unreasonable formulas for natural OM molecules according to previously published criteria (e.g., Stubbins et al., 2010; Wozniak et al., 2008), and KMD series (CH$_2$, H$_2$, and CO$_2$) were used to verify ambiguous assignments. Each of the assigned formulas has a calculated mass within 1 ppm
agreement with the measured $m/z$, where a large majority of the formulas (88% ± 7%) have 
less than 0.5 ppm error.

2.5 **Data Analyses**

The modified aromaticity index ($\text{AI}_{\text{mod}}$) is a metric developed by Koch and Dittmar (2006) that provides a classification of the relative aromaticity of a molecular formula. $\text{AI}_{\text{mod}}$ is calculated for any molecular formula comprised of C, H, O, N, S, and/or P using Eq. 1 (Chapter II, section 3.2). $\text{AI}_{\text{mod}}$ structurally classifies a compound as aliphatic ($\text{AI}_{\text{mod}} = 0$), olefinic/ Alicyclic ($0 < \text{AI}_{\text{mod}} < 0.5$), aromatic ($\text{AI}_{\text{mod}} \geq 0.5$), or condensed aromatic ($\text{AI}_{\text{mod}} \geq 0.67$, Koch and Dittmar, 2006).

KMD analysis using a variety of functional groups highlights compounds that are in a homologous series, meaning compounds with the same KMD value have molecular formulas that differ only by that functional group. The KMD for any functional group is calculated using Eq. 2 and Eq. 3.

\[
\text{Kendrick Mass (KM)} = \text{Exact } m/z \text{ value } \times (\text{nominal unit mass/exact unit mass}) \tag{2}
\]

\[
\text{KMD} = \text{KM} – \text{nominal KM} \tag{3}
\]

The exact $m/z$ refers to the calculated $m/z$ value of the assigned molecular formula, the exact unit mass is the mass of the functional group, the nominal unit mass is the integer value of the exact unit mass, and the nominal KM is the integer value of the KM. Several functional group units were investigated in this study including $\text{C}_2\text{H}_2\text{O}_2$ (exact unit mass = 58.005479 Da), $\text{C}_3\text{H}_4\text{O}_2$ (72.021129 Da), $\text{C}_4\text{H}_6\text{O}$ (70.041865 Da), $\text{CH}_2$ (14.015650 Da), $\text{H}_2$ (2.015650 Da), $\text{CO}_2$ (43.989829 Da), and $\text{O}_2$ (31.989829 Da). A KMD series refers to three or more molecular formulas having the same exact KMD value, indicating their molecular formulas differ only by the specified functional group unit. KMD series are identified if
the formulas present are all found in any three of the extract/ionization modes (WSOM-, WSOM+, or PSOM-) of the same aerosol sample.

3 Results and Discussion

3.1 Molecular properties

Molecular formulas assigned to mass spectral peaks detected in each of the aerosols reveal a diverse suite of organic compounds and molecular properties that are distinct for each emission source. The marine aerosols have the fewest assigned formulas, likely, in part, due to having the lowest carbon amounts (Chapter III, Table 3). They are characterized by a large fraction of CHO formulas (41%) and the largest fraction of CHOP(N,S) formulas (8%) of any of the aerosol sources in this study. Many of the formulas, including CHO and CHOP(N,S), have high H/C ratios and are consistent with biologically-derived compounds such as lipids and phospholipids. The marine aerosols share the lowest average O/C ratio (0.32) with the biomass burning aerosols. Greater O/C ratios can be reflection of more extensive atmospheric processing, as a number of transformational processes add oxygen (e.g., ozonolysis, carboxlation, etc.), and O/C is a good proxy but not all aging reactions yield a higher O/C (Ervens et al., 2011; Heald et al., 2010; Kroll et al., 2011). The lower O/C ratios suggest that the marine and biomass burning aerosols are less atmospherically aged than the mixed source and urban aerosols, and numerous atmospheric transformations of OA involving organic and inorganic species will explored in subsequent sections.

The urban aerosols are the most influenced by inorganic material indicated by the lowest percent of total carbon (TC/TSP = 13%), and the biomass burning aerosols are comprised of the most organic and black carbon (TC/TSP = 34%). Urban aerosols are
dominated by CHON (3472 formulas, 32% of total urban formulas) and CHO formulas (3318 formulas, 31%; Chapter III, Table 4). The biomass burning aerosols shares a very similar distribution of molecular formulas based on atomic content to the urban aerosols, but differ in relative aromaticity. The average AI_{mod} is considerably higher for biomass burning aerosols (0.29) than urban (0.19), and the fraction of aromatic and condensed aromatic compounds (1841 formulas, 23%) is more than double that of the urban aerosols (1056 formulas, 10%).

Each of the aerosols contain a number of N- and S-containing molecular formulas, indicating that incorporation of these heteroatoms into OM is widespread. In Chapter III, we speculate the presence of organonitrates and organosulfates based on calculated O/N and O/S ratios, which are ubiquitous components of OA (Laskin et al., 2012). Marine and biomass burning aerosols consistently have the lowest O/N and O/S ratios, and the mixed source and urban aerosols have considerably higher O/N and O/S ratios. Despite the biomass burning aerosols having the largest fraction of CHON formulas, the average O/N ratio (4.1) is much lower than the mixed source and urban aerosols (7.1 and 9.0, respectively) indicating the processes that incorporate N into OM vary among the emission sources. These variations may result from a number of factors including initial OM input, concentrations of inorganic N- and S- species, concentrations of other inorganic species (e.g., OH radical), and meteorological conditions (Hallquist et al., 2009 and references within). Organic compounds formed through varying atmospheric transformation processes can have substantially different chemical and physical properties that influence their ability to act as cloud condensation nuclei or absorb light. Thus, it is important to
understand the chemical transformations that alter OM in order to assess the potential impacts they have on the surrounding environment.

The marine, mixed source, biomass burning, and urban aerosols represent a broad set of aerosol emission sources having varying anthropogenic and biogenic inputs, varying influence from inorganic species, and a diverse range of atomic and aromatic properties. A more detailed description of the character and defining features can be found in Chapter III. Assigning compound classes to the identified molecular formulas using visualization diagrams (e.g., van Krevelen diagrams) and other chemical metrics provides important information regarding the composition of aerosol OM and has been extensively explored; however, it only allows for speculation regarding the fate and origin of the organic compounds present in ambient OA. Analysis of KMD series and reactions with inorganic species provides evidence for processes important to the production and consumption of atmospheric OM from different emission sources.

3.2 Atmospheric transformations

3.2.1 Oligomerization

Each of the aerosol samples from the various sources contain multiple homologous KMD series of CH₂, O₂, H₂, and CO₂ elemental constituents (Table 7 and Fig. 12) indicative of some of the important reactions responsible for the formation or decomposition of OM. The specified reactions in Table 7 refer to those which increase molecular weight, and it is important to note that the reverse reaction is also possible (e.g., carboxylation or decarboxylation). The CH₂, O₂, H₂, and CO₂ KMD formula extension approaches have proven useful for assigning molecular formulas to FTICR-MS peaks because they represent chain elongation (CH₂), oxygenation (O₂), hydrogenation (H₂), and
carboxylation (CO\textsubscript{2}) reactions that are common to the formation of biogenic and anthropogenic natural organic matter (e.g., Hughey et al., 2001; Kujawinski and Behn, 2006; Reinhardt et al., 2007; Roach et al., 2011; Waggoner et al., 2015). Chain elongation, oxygenation, and hydrogenation reactions are not expected to be unique to atmospheric processing of OA, and KMD series based on these elemental constituents are more likely to result from processes that are ubiquitous to the formation of organic molecules or due to the high complexity of natural OM which by happenstance contains molecules that result in these series. Thus, it is not surprising that patterns observed for KMD series are common among the aerosol samples from different sources (Fig. 12). These three KMD series (CH\textsubscript{2}, H\textsubscript{2}, O\textsubscript{2}) show the highest percentages of formulas that are in a KMD series (Table 7) and show similar chain lengths for each KMD series among all sample sources (Fig. 12).

In contrast, the length of CO\textsubscript{2} KMD series do vary with emission source (Fig. 12c). Heald et al. (2011) suggested that the changes in the relative elemental abundance of OA due to atmospheric aging can be approximated by the progressive addition of CO\textsubscript{2}. As a result, one would expect to observe differences in the relative abundance and chain length of CO\textsubscript{2} KMD series that relate to the amount of atmospheric aging those aerosols have experienced. The CO\textsubscript{2} KMD series are present at much lower relative abundance than the CH\textsubscript{2}, H\textsubscript{2}, and O\textsubscript{2} series (Table 7). Importantly, the longest KMD series are observed for the mixed source and urban aerosols (Fig. 12) which are likely to have undergone more extensive atmospheric processing than the marine and biomass burning aerosol samples. The mixed source and urban aerosols likely incorporate aerosols from many local and distant primary and secondary sources and have been subjected to high concentrations of atmospheric oxidants (e.g., NO\textsubscript{x}, SO\textsubscript{x}, O\textsubscript{3}) relative to what is observed over marine
environments. The biomass burning aerosol samples were collected approximately 25 miles north of a natural fire, and the predominant OA compounds are not expected to have undergone significant processing relative to their initial emission form. The longer CO$_2$ KMD series for the mixed source and urban aerosols thus parallel the expected extents of atmospheric aging, and this KMD series may be a good tracer for tracking the prevalence of carboxylation and decarboxylation reactions.

**Figure 12.** Fractional contributions for KMD oligomer series of varying lengths for each aerosol source for (a) CH$_2$, (b) H$_2$, (c) CO$_2$, and (d) O$_2$. 
Table 7. Average percentage and standard deviations of total molecular formulas that are part of a specific KMD series in each aerosol source.

<table>
<thead>
<tr>
<th>KMD Series</th>
<th>*Reaction</th>
<th>Marine</th>
<th>Mixed</th>
<th>Biomass Burning</th>
<th>Urban</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂</td>
<td>chain elongation</td>
<td>78 ± 6</td>
<td>91 ± 1</td>
<td>95 ± &lt;1</td>
<td>92 ± 2</td>
</tr>
<tr>
<td>H₂</td>
<td>hydrogenation</td>
<td>64 ± 9</td>
<td>83 ± 2</td>
<td>91 ± &lt;1</td>
<td>86 ± 1</td>
</tr>
<tr>
<td>CO₂</td>
<td>carboxylation</td>
<td>39 ± 11</td>
<td>67 ± 4</td>
<td>66 ± 2</td>
<td>75 ± 3</td>
</tr>
<tr>
<td>O₂</td>
<td>oxidation</td>
<td>61 ± 8</td>
<td>82 ± 2</td>
<td>85 ± 1</td>
<td>85 ± 1</td>
</tr>
<tr>
<td>C₂H₂O₂</td>
<td>oligomerization</td>
<td>38 ± 11</td>
<td>69 ± 3</td>
<td>64 ± 3</td>
<td>76 ± 3</td>
</tr>
<tr>
<td>C₃H₄O₂</td>
<td>oligomerization</td>
<td>36 ± 11</td>
<td>66 ± 4</td>
<td>59 ± 2</td>
<td>73 ± 3</td>
</tr>
<tr>
<td>C₄H₆O</td>
<td>oligomerization</td>
<td>38 ± 12</td>
<td>66 ± 5</td>
<td>65 ± 2</td>
<td>67 ± 2</td>
</tr>
</tbody>
</table>

*Only reactions that increase molecular weight are listed. The opposite reaction is a possibility.

The apparent correlation of CO₂ KMD series length with expected extent of aging for aerosol source type suggests that other atmospherically-relevant KMD series related to atmospheric aging should show similar patterns as the one observed for CO₂. Isoprene is the second most abundant hydrocarbon in the atmosphere (Guenther et al., 2006) and isoprene and its oxidation products (i.e., glyoxal, methylglyoxal, methacrolein/methyl vinyl ketone; MACR/MVK) influence SOA production globally including remote marine environments (Henze and Seinfeld 2006). For this reason, we examined KMD series that represent glyoxal (C₂H₂O₂), methylglyoxal (C₃H₄O₂), and MACR/MVK (C₄H₆O), all of which are known to be quantitatively important derivatives of isoprene (Jenkin et al., 2015; Squire et al., 2015).

Each of the aerosol sources contain multiple homologous KMD series differing by these glyoxal, methylglyoxal, and MACR/MVK fragments (Table 7; Figure 2). The marine aerosols contain the smallest fraction of molecular formulas that contribute to a KMD series in all cases (Table 7), which is likely partially related to the identification of the
fewest number of formulas overall. The percent of formulas involved in oligomerization reactions (36 – 38%), as indicated by their presence in a KMD series, is substantially less than the aerosols collected over terrestrial environments (Table 7). A majority (59 – 76%) of the formulas in the mixed source, biomass burning, and urban aerosols contribute to an oligomerization KMD series (Table 7), suggesting that reaction with isoprene-related products could be an important aging process to the compounds found in these aerosols. Isoprene concentrations are lower over marine environments relative to continental environments (Arnold et al., 2009) including the eastern United States where the abundance of deciduous vegetation is a major source (Hu et al., 2015; Seinfeld and Pandis, 2012), and supports the observation of a significantly smaller fraction of formulas present in isoprene-related oligomer series in the marine environment.

As observed for the CO₂ KMD series, the relative percentage of formulas present in isoprene-related oligomer series is similar between the mixed source, biomass burning, and urban aerosols, but there is a difference in the chain length (i.e., the number of formulas in a series). A C₂H₂O₂ series of three indicates that two molecules of C₂H₂O₂ have been added to an existing OM molecule, but a series of five would indicate that four molecules of C₂H₂O₂ have been added. At least 80% of the oligomer KMD series in the biomass burning or marine aerosols are short chains (3 – 4 formulas), and at least 33% of the oligomer KMD series in the urban and mixed source aerosols are long chains (≥ 5 formulas; Fig. 13a-c). This difference between chain length is most pronounced for C₂H₂O₂ and C₃H₄O₂ series (Fig. 13a and 13b), but is also evident for C₄H₆O series (Fig. 13c). A larger number of short chains suggests that aging reactions involving these compounds have not occurred as extensively as in the aerosols that have more long chain series. The proximity
of the biomass burning sampling site to the natural fire again explains the lesser apparent atmospheric aging for the biomass burning samples relative to the mixed source and urban aerosol samples. Interestingly, the longest chains of apparent isoprene KMD series are observed for the urban aerosol samples (Fig. 13) despite the fact that isoprene is largely derived from biological sources (Guenther et al., 2006). The longer KMD series in urban aerosols suggests that the higher concentrations of inorganic oxidants found in urban environments stimulate the observed oligomerization reactions with isoprene derivatives that are likely derived from outside the urban environment.

It is important to note that the mass differences that correspond to these elemental fragments do not give structural confirmation for transformations that correspond to these specific compounds as they could represent isomers with the same molecular formulas, and experiments are needed to confirm that these series result specifically from isoprene-related aging. Addition of units such as glyoxal or methylglyoxal have been observed in oligomeric studies of model compounds in the formation of SOA (Altieri et al., 2008a; Tan et al., 2010; Tan et al., 2009). However, the longer series apparent in the urban and mixed source aerosol samples which are expected to be more ‘aged’ provide strong evidence that we are indeed observing oligomers of these isoprene derivatives.

The extent of OA aging is often associated with an increase in O/C ratio, which also offers a convenient extension to properties such as hygroscopicity that directly correlate with O/C ratio (Jimenez et al., 2009; Lambe et al., 2011). The impacts that these oligomerization reactions have on the average elemental ratios of the OA pool are somewhat dependent on the nature of both the predominant oligomers being added and the initial POA and SOA compounds. For example, if C₂H₂O₂, C₃H₄O₂, and C₄H₆O were each
Figure 13. Fractional contributions for KMD oligomer series of varying lengths for each aerosol source for (a) C₂H₂O₂ (glyoxal and isomers), (b) C₃H₄O₂ (methylglyoxal and isomers), and (c) C₄H₆O (MVK/MACR and isomers). KMD plots for select formulas in one of the biomass burning aerosols for (d) C₂H₂O₂ series, (e) C₃H₄O₂ series, and (f) C₄H₆O series. Arrows indicate that the points along that line represent molecular formulas differing by the specified functional group (e.g., SO₃).
separately added to the starting molecule C$_{15}$H$_{16}$O$_3$ (O/C = 0.20, H/C = 1.07, AI$_{\text{mod}}$ = 0.42), the compounds C$_{17}$H$_{18}$O$_5$ (O/C = 0.29, H/C = 1.06), C$_{18}$H$_{20}$O$_5$ (O/C = 0.28, H/C = 1.11), and C$_{19}$H$_{22}$O$_4$ (O/C = 0.28, H/C = 1.11) would be produced, respectively. Each product has a higher O/C ratio than the starting compounds, and the H/C can increase or decrease. If the starting compounds is more aliphatic, such as C$_8$H$_{14}$O$_5$ (O/C = 0.63, H/C = 1.75, AI$_{\text{mod}}$ = 0), the products of reactions with each C$_2$H$_2$O$_2$, C$_3$H$_4$O$_2$, and C$_4$H$_6$O are C$_{10}$H$_{16}$O$_7$ (O/C = 0.70, H/C = 1.60), C$_{11}$H$_{18}$O$_7$ (O/C = 0.64, H/C = 1.64), and C$_{12}$H$_{20}$O$_6$ (O/C = 0.50, H/C = 1.67), respectively. A decrease in O/C ratio is observed after the addition of a C$_4$H$_6$O group, and a decrease in H/C ratio is observed in all cases. The varying impact that oligomerization reactions have on atomic ratios indicates O/C ratio alone cannot always predict the extent of aging that has occurred. However, the higher average O/C ratios observed in the mixed source and urban aerosols is consistent with the presence of longer chain KMD oligomer series, and together suggest that these aerosols have undergone more extensive aging reactions than the marine and biomass burning aerosols.

Homologous series in a KMD plot can be viewed on a horizontal line (e.g., molecules that have the same KMD value), where each point on that line represent molecules differing only by that specified KMD unit. However, molecular patterns other than those on the horizontal KMD line are also apparent demonstrating that the reactions occurring in the atmosphere are plentiful and not simply linear. For example, Fig. 13d – 13f show KMD plots for the isoprene-related oligomer series and reactions with CH$_2$, O, H$_2$, and inorganic N and S species are identified. These plots were made using select formulas found in one of the biomass burning aerosols to clearly show the molecular patterns that can be identified using KMD series. Similar patterns can be found in each of
the aerosols throughout the entire KMD plots, and in plots for the other aerosols. These plots show that any one compound can be related to other molecules by multiple types of reactions, as one might expect. For example, the formula C\textsubscript{11}H\textsubscript{18}O\textsubscript{4}, represented by the point at the beginning of each of the three arrows in Fig. 13d, may be related to the other points along each of the arrow lines. The horizontal arrow shows that C\textsubscript{2}H\textsubscript{2}O\textsubscript{2} is added to the molecule three times, the positively sloped arrow shows several molecules that are sequentially larger and differ only by CH\textsubscript{2} units, and the negatively sloped green arrow shows molecules that differ only by an SO\textsubscript{3} group (Fig. 13d). All of the points in this figure represent molecules and each of those has similar relationships with other molecules as the ones just described, simultaneously showing the ubiquity of these processes and the true complexity of aerosol OM. The relationships represented by the non-horizontal arrows in Fig. 13d – 13f could be summarized using KMD analysis for those functional groups. However, due to the smaller number frequency of nitrogen and sulfur atoms in OA, KMD analysis does not adequately evaluate the addition of heteroatomic functional groups like SO\textsubscript{3}, NO\textsubscript{2}, and NH\textsubscript{3} and these relationships are explored in the following section. KMD analysis shows important relationships between individual compounds found in aerosol OM, and the KMD technique, when coupled with extensive FTICR MS datasets, has promise for elucidating important atmospheric aging oligomerization reactions involving reactive gas-phase species such as derivatives of isoprene and other quantitatively important atmospheric compounds (e.g., \(\alpha\)-pinene, limonene, and toluene).

3.2.2 Reactions with inorganic nitrogen and sulfur species

Many of the CHON and CHOS formulas contain only one nitrogen or sulfur in the formula, rendering KMD analysis an inefficient method for observing the occurrence of
reactions between organic compounds and NOx, NH3, or SOx which are known to be important atmospheric aging reactions (Ervens et al., 2011; Hallquist et al., 2009). These transformations were instead evaluated by searching for precursor CHO formulas that have a corresponding product exactly 44.985078 Da (+NO2 - H), 60.979993 Da (+NO3 - H), 17.026549 Da (+NH3), 79.956815 Da (+SO3), or 95.951729 Da (+SO4) mass units higher, reactions that are supported by model compound and ambient aerosol studies (e.g., Fry et al., 2011; Nguyen et al., 2012; Noziere et al., 2009; Schmitt-Kopplin et al., 2010; Surratt et al., 2006). For example, the formulas C11H18O4 (exact mass = 214.120508 Da) and C11H18SO7 (exact mass = 294.077323 Da) are shown in Fig. 13d as the two points along the green arrow, and differ exactly by the mass of an SO3 group (79.956815 Da). For simplicity, CHON formulas that represent possible products of reactions between OM and NO2 or NO3 are referred to collectively as NOx products, and CHOS formulas that represent possible products of reactions between OM and SO3 or SO4 are referred to collectively as SOx products. Each aerosol sample was evaluated individually to ensure precursors and products are found together in the same sample, and formulas found in any three of the spectra (i.e., WSOM-, WSOM+, or PSOM-) for a given sample were considered as possible reaction precursors and products. Each of the aerosol sources contain numerous formulas that represent possible precursors (CHO formulas) and NOx, NH3, and SOx products (CHON and CHOS formulas; Table 8). Only CHO formulas were considered as precursors for simplicity, though other types of formulas (i.e., CHON or CHOS) can serve as precursors to these reactions.

Most (> 65%) of the CHO formulas in each the mixed source, biomass burning, and urban aerosols are identified as possible precursors for reactions with NOx, NH3, or
SOx (Table 8), and a much smaller percentage (28%) of the CHO formulas in the marine aerosols may be precursors. This substantial difference suggests that the aerosol OM emitted in the marine environment does not contain many compounds that serve as precursors to reactions with these species, atmospheric conditions in this marine environment do not promote reactions with these inorganic species, and/or these inorganic species are not present in substantial atmospheric concentrations to promote incorporation into OM. Reactions of aerosol OM with NOx, NH₃, and SOx are known ubiquitous processes in the atmosphere (Laskin et al., 2012; Seinfeld and Pandis, 2012) and the presence of CHON and CHOS compounds that represent possible products of these reactions in each of the aerosol emission sources supports this (Table 8).

Each of the aerosol emission sources contains CHON and CHOS formulas that may represent an existing CHO compound that has incorporated NO₂, NO₃, NH₃, SO₃, or SO₄ into its molecular formula, indicating the ubiquity of reactions with these inorganic species

Table 8. Number and percentage of formulas that represent potential CHO precursors and their products after reaction with NOx, NH₃, or SOx for each aerosol emission source.

<table>
<thead>
<tr>
<th>Aerosol Source</th>
<th>CHO precursor formulas # formulas (% CHO)</th>
<th>NOx products formulas # formulas (% CHON)</th>
<th>NH₃ products formulas # formulas (% CHON)</th>
<th>SOx products formulas # formulas (% CHOS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine</td>
<td>337 ± 201 (28 %)</td>
<td>70 ± 42 (20 %)</td>
<td>113 ± 63 (33 %)</td>
<td>227 ± 221 (43 %)</td>
</tr>
<tr>
<td>Mixed source</td>
<td>1081 ± 169 (65 %)</td>
<td>622 ± 105 (62 %)</td>
<td>722 ± 123 (72 %)</td>
<td>496 ± 123 (57 %)</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>1679 ± 35 (73 %)</td>
<td>966 ± 110 (44 %)</td>
<td>1127 ± 150 (51 %)</td>
<td>895 ± 143 (70 %)</td>
</tr>
<tr>
<td>Urban</td>
<td>1899 ± 103 (76 %)</td>
<td>1284 ± 123 (67 %)</td>
<td>1263 ± 129 (66 %)</td>
<td>866 ± 54 (74 %)</td>
</tr>
</tbody>
</table>
throughout multiple atmospheric environments. The marine aerosols contain the fewest total and relative proportion of NOx products (70 formulas, 20% of total CHON formulas), NH$_3$ products (113 formulas, 33% of CHON formulas), and SOx products (227 formulas, 43% of CHOS formulas; Table 8). The biomass burning aerosols have the next lowest relative fraction of NOx and NH$_3$ products (44% and 51%, respectively), though they contain more total formulas than the mixed source aerosols (Table 8) suggesting that much of the N in biomass burning OA is primary in nature. There are more NH$_3$ products than NOx products in all cases except for the urban aerosols, which have nearly equal amounts of possible NH$_3$ products (1263 formulas, 66%) as NOx products (1284 formulas, 67%; Table 8). Ammonia is abundant in urban and remote aerosols, whereas nitrate is more prevalent in urban environments (Jimenez et al., 2009; Zhang et al., 2011). The aerosols collected over a terrestrial environment contain more total possible SOx products, and also a larger percentage of the CHOS formulas are represented. The biomass burning aerosols contain the largest total number of SOx products (895 formulas), and the urban aerosols have the largest percentage of CHOS formulas represented as potential SOx products (74%). The data shows an inherent variation in the propensity for aerosol OM to react with inorganic nitrogen and sulfur species among aerosol environments. These variations could be influenced by multiple factors including atmospheric concentrations of these inorganic and organic species, the presence of other species such as hydroxyl radical, other environmental parameters including sunlight exposure and relative humidity, and the inherent chemical properties of the OM (Hallquist et al., 2009).

The aromaticity of the precursor CHO compounds varies among the emission sources, suggesting inherent differences in OA reactivity. More than half of all the aliphatic
and olefinic/alicyclic CHO compounds in each source were determined to be precursor compounds in the mixed source, biomass burning, and urban aerosols (Fig. 14), suggesting these compounds have widespread reactivity and olefinic/alicyclic compound are more reactive than aliphatic ones in these environments. Olefinic compounds by definition contain double bonds, which can serve as reaction sites and supports the widespread reactivity observed here. Many of the aliphatic CHO precursors have corresponding CHOS formulas, indicating a propensity to react with SOx compounds. This affinity of aliphatic OM reacting to form organosulfate compounds has been previously proposed by Schmitt-Kopplin et al. (2010). The aromatic and condensed aromatic CHO compounds in the biomass burning aerosols are highly reactive, as indicated by large percentage of aromatic CHO compounds (93%) and condensed aromatic CHO compounds (86%) that are precursors to reactions with NOx, NH₃, and/or SOx (Fig. 3). Most of aromatic CHO compounds are precursors to CHON formulas and less than 5% are precursors to CHOS formulas, indicating a high propensity for aromatic compounds to react with NOx or NH₃ over SOx. Additionally, a significant portion of the aromatic CHO compounds in the mixed source and urban aerosols are possible precursors, and are also largely precursors to CHON compounds. The highly reactive nature of the aromatic compounds is consistent with previous studies of aerosol OM (Zhao et al., 2015), and in studies of dissolved OM (Stubbins et al., 2010).

The mechanisms for the formation of organosulfates and organonitrates from SOA have been evaluated in great detail (Iinuma et al., 2007; Minerath and Elrod, 2009; Schmitt-Kopplin et al., 2010; Surratt et al., 2008), and alternate oxidation pathways and reactions that incorporate N and S into a molecular structure exist and are likely to have resulted in
Figure 14. Average percentage of CHO formulas identified as precursors to a NOx, NH$_3$, and/or SOx product based on relative aromaticity. Percentages are relative to the total number of CHO formulas with that AI$_{mod}$ classification for each source (e.g., the aliphatic marine precursor CHO percentage is relative to the total number of aliphatic CHO formulas in the marine aerosols).

Some of the CHON and CHOS compounds observed in this study. Nonetheless, the ultrahigh resolution mass spectral data presented here provide strong evidence for simple addition (or decomposition) reactions that have been described in previous work wherein a precursor CHO formula can react with an inorganic species such as SO$_3$ and create a product that has a molecular weight that is higher than the precursor by the exact mass of SO$_3$ (e.g., Surratt et al., 2008) lending support to the method presented in this study.

One of the limitations to the top-down approaches used in this study regarding atmospheric aging reactions is that the relationship between the molecules and the direction of the reactions (i.e., whether species are being added or removed) cannot be confirmed. In
some instances the direction of the reaction can be gleaned by evaluating the relative intensity of each of the formulas in a KMD series, and the relative intensity patterns (i.e., increasing or decreasing intensity with molecular weight) varied irregularly among all of the samples. We believe this to be due to the fact that OM can be formed by numerous types of reactions, and can subsequently undergo numerous other reactions, and that a linear correlation will not be observed unless the process we are investigating is the dominant one. Additionally, this approach does not consider alternate reactions, such as fragmentation, that are known to occur in the atmosphere (Hallquist et al., 2009). We rely on the observations of these oligomerization reactions and reactions with inorganic species in mechanistic studies to speculate that similar reactions will occur in the atmosphere and that OM is being captured at multiple stages throughout these ubiquitous processes (Altieri et al., 2008b; Altieri et al., 2009; Ervens et al., 2011; Hallquist et al., 2009; Noziere et al., 2009; Nozière et al., 2010; Nozière et al., 2006; Reinhardt et al., 2007). However, the relationships observed for each of these sources is consistent with what is expected based on a multitude of literature regarding aerosol reactivity, and thus we are confident that these observations are representative of atmospheric OM transformations.

4 Summary and Implications

Here, we describe differences between aerosols from four different emission sources that verify the utility of the technique for demonstrating both the ubiquity of these processes as well as how they vary depending on emission source in an expected fashion. The mixed source and urban aerosols contain the longest KMD series, highest O/C ratios, and generally the largest fraction of CHON and CHOS compounds that are products of inorganic reactions with OM, supporting that these aerosols have undergone more
atmospheric processing reactions. The biomass burning and marine aerosols have the shortest oligomer KMD series and lowest O/C ratios, indicating they are less atmospherically aged than the other aerosols. However, the biomass burning aerosols appear to have more precursor and product compounds associated with atmospheric inorganic reactions than the marine aerosols, indicating these reactions are more prevalent over terrestrial environments. Given the success of the KMD technique using isoprene derivatives, it is highly probable that it can be extended for use with several other atmospherically-important gas-phase species to address questions regarding the relative degree of aging for ambient and laboratory-derived OA.

FTICR can provide a wealth of molecular information about the OM present in aerosols, but the challenge for the atmospheric and mass spectral communities is to develop atmospherically-relevant ways to utilize these immense FTICR datasets to understand atmospheric processes. This work introduces two methods for using FTICR-MS data for the evaluation of OA transformations in the atmosphere that offer promise as techniques for better understanding OA processing of high molecular weight species in future ambient and laboratory experiments. The approach complements SOA and aging laboratory studies by examining precursor molecules, products, and oligomer series to identify compounds that are likely abundant throughout the global atmosphere.

Most commonly, atmospheric aging studies use a bottom-up approach to evaluate model SOAs, and studies of this kind will be valuable for corroborating the method presented here, but are limited in that they evaluate highly controlled conditions that do not effectively capture the complexity of ambient OM. The reality in nature is that thousands of compounds are available for reaction with inorganic species and gas-phase organics and
that these compounds react in numerous ways to produce a highly complex mixture that we still don’t fully understand. The atmospheric modeling community has done an excellent job of distilling overall changes, but studies examining the molecular details in these complex mixtures are still valuable for understanding how OA is processed in the atmosphere.

While there have been numerous studies that effectively identified OM generated by model reactions in ambient aerosols, there is still much information to be gained by pairing time resolved ambient measurements to ultrahigh resolution mass spectrometric characterization. There would be great value in pairing highly time-resolved AMS measurements with UHR mass spectrometric data to evaluate the high and low molecular weight OM present in ambient aerosol to give a more representative picture of the aging processes that influence different regions.
CHAPTER V

FLUORESCENCE AND MOLECULAR PROPERTIES OF CHROMOPHORIC WATER-SOLUBLE ORGANIC MATTER IN ORGANIC AEROSOLS

1 Introduction

Characterization of the molecular components in organic aerosols (OA) remains an important goal in the atmospheric community in an attempt to understand the role of carbonaceous compounds in global biogeochemical cycling and also to evaluate their influence on climate forcing, human health, and ecological health. Atmospheric aerosols are ubiquitous and contain components that scatter or absorb light. Recent work estimates aerosols to have a net negative radiative forcing (-1.9 to -0.1 W m$^{-2}$ yr$^{-2}$), a net cooling effect on the Earth’s radiative balance (IPCC, 2013; Myhre, 2009) but aerosols represent the largest uncertainty in global radiative forcing estimates (IPCC 2013).

In spite of the net cooling effect on the Earth’s radiative budget, there are components of aerosols that absorb light and contribute to a positive radiative forcing which offsets some of the cooling. The light absorbing components of aerosols include black carbon (BC) and a subset of OA termed brown carbon (Andreae and Gelencsér, 2006; Bond et al., 2013; Krivacsy et al., 2000). Inconsistencies in the way BC and brown carbon are measured and quantified has led to much confusion in the literature regarding classification. Nonetheless, there is general agreement that BC is strongly light absorbing, refractory, and water-insoluble (Bond et al., 2013). Brown carbon is weakly light absorbing, can be water soluble, and is released concurrently with BC or can be formed through oligomerization reactions in the atmosphere (Andreae and Gelencsér, 2006; Bond
et al., 2013; Lee et al., 2014). The specific origins and molecular properties of brown carbon are unclear.

The ability of a compound to absorb light, scatter light, or to fluoresce is directly related to its chemical structure. Organic compounds containing areas of unsaturation (double bonds, rings, and fused rings) experience \( n \rightarrow \pi^* \) and \( \pi \rightarrow \pi^* \) electronic transitions that cause the compound to absorb ultraviolet (UV) or visible light (Andreae and Gelencsér, 2006; Robertson and O’Reilly, 1987), and some of these chromophores reemit light as the excited electron returns to the original ground state and are fluorophores (Mopper et al., 1996). The fused ring structures present in BC are responsible for its strong light-absorbing and fluorescent properties (Bond et al., 2013). Aliphatic structures do not undergo these electronic transitions and thus do not absorb light at wavelengths present in sunlight. Thus, it is evident that chemical structure determines the net impact OA has on radiative forcing.

Many studies have confirmed the presence of a diverse suite of organic compounds contained within ambient aerosols, fog water, and rainwater (e.g., Altieri et al., 2012; Mazzoleni et al., 2010; Schmitt-Kopplin et al., 2010; Willoughby et al., 2014; Wozniak et al., 2008). Several polar functional groups are represented in aerosols and include hydroxyl, carboxyl, carbonyl, ether, amino, nitrate and sulfate groups, as well as structures ranging from aliphatic chains to fused aromatic ring structures (e.g., Decesari et al., 2007; Jimenez et al., 2009; LeClair et al., 2012; Mayol-Bracero et al., 2002; Surratt et al., 2007; Wozniak et al., 2008). OA contain a chemically complex, often quantitatively important component that has been termed humic-like substances (HULIS) due to its proposed similarity to terrestrial humic and fulvic acids, and this HULIS is regarded as a major
contributor to the chromophoric nature of aerosol OM (Graber and Rudich 2006). Atmospheric HULIS differs structurally from terrestrial humic material in that HULIS is generally lower molecular weight, less aromatic, and more thermally labile (Duarte and Duarte, 2008; Graber and Rudich, 2006). These differences may be due in part to the fact that typical HULIS isolations follow a protocol that is quite different from a traditional humic extraction and in part to the fact that they have distinctly different sources and chemical properties. In spite of the different isolation protocols, so-called atmospheric HULIS does share certain similarities with terrestrial humic material with regard to functional groups (i.e., polycarboxyphenolic components) as reflected in numerous studies (Graber and Rudich 2006 and references within). Furthermore, there is evidence of important similarities in the absorbance properties of atmospheric and aquatic humic material that allow for meaningful comparisons of their molecular and chromophoric properties (Kieber et al., 2006; Kiss et al., 2003; Mladenov et al., 2012), but must be done so with caution (Duarte et al., 2007).

Only a small percentage (1%) of organic compounds present in natural OM samples are expected to fluoresce (Leehneer and Croué, 2003); however, fluorescence spectra can provide information regarding the origin, composition, and processing of natural OM samples. Additionally, fluorescent OM is regarded as source of photochemically-generated peroxides in aquatic environments (Faust and Zepp, 1993; Herut et al., 1998; Moore et al., 1993; Scully et al., 1996), but the importance in atmospheric environments is a subject of debate (Nakajima et al., 2008). Fluorescence characterization using excitation emission matrix spectrometry (EEMs) has emerged as a popular analytical technique for measuring fluorescence properties of dissolved organic matter (DOM) because it is rapid, inexpensive,
and requires minimal sample preparation. It has been suggested that chromophoric DOM from aquatic sources may have similar optical properties to chromophoric OM in the atmosphere (Duarte et al., 2007; Kieber et al., 2006; Kiss et al., 2003), and that EEMs may be a highly valuable and underutilized technique for evaluating OA. The information regarding fluorescence properties of aerosol OM is, however, surprisingly scarce.

Several EEMs studies of atmospherically-relevant OM including rainwater, snow, aerosol WSOM, and fog water have been conducted (Duarte et al., 2005; Kieber et al., 2006; Kieber et al., 2007; Matos et al., 2015; Mladenov et al., 2011a; Mladenov et al., 2012; Nakajima et al., 2008). EEM spectra for DOM often display two strong fluorescent peaks found at excitation/emission maxima (Ex/Em = 260/380–460 nm and Ex/Em = 350/420–480 nm) which have been termed “humic peaks” because these features are largely attributed to the aromatic moieties found in lignin, tannins, and polyphenols associated with humic material (Del Vecchio and Blough, 2004). Similar fluorescent peaks are observed in atmospheric OM EEM spectra, but peaks are generally observed at shorter excitation and emission wavelengths than those observed in DOM spectra. This shift to shorter wavelengths suggests that humic-like substances in aerosol OM contains a lower content of aromatic structures, a higher aliphatic content, and/or compounds with a lower molecular weight (Duarte et al., 2005; Krivacsy et al., 2001; Krivacsy et al., 2000). A recent study by Stubbins et al. (2014) pairs the molecular resolution capabilities of FTICR-MS with EEMs analysis for numerous DOM samples, and proposes specific molecular properties associated with EEMs fluorescence peaks based on statistical correlations between the optical and molecular signatures for DOM. The identification of molecular families associated with specific fluorescence is an important advancement for the DOM
community, but it is unknown whether these classifications are universal to all types of natural OM. Nonetheless, the study provides an analytical foundation for evaluating the link between molecular and optical characteristics and determining the origin and fate of organic compounds found in all environments, including OA.

This present study aims to combine the powerful analytical techniques of Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) and EEMs to evaluate the molecular and optical characteristics of ambient aerosol WSOM samples influenced by three different sources in the eastern United States. The melding of these two techniques is a powerful approach that will shed light on the molecular level basis for aerosol optical properties in these samples. The comparison of aerosols from multiple sources provides important information regarding molecular and optical properties that are widespread among different aerosol emission sources as well as those that are defining features and allow for a better source apportioning for aerosol optical properties.

2 Methods

2.1 Aerosol sample collection and measurements

Ambient aerosol total suspended particulates (TSP, n = 10) were collected from three different locations in the eastern United States to represent different emission source types. A description of the sampling methods, sampling locations, and collection dates are described in detail in Chapter III. Briefly, TSP samples from a mixed source (n = 3), a biomass burning event (n = 2), and an urban area (n = 5) were collected in the summer time between 2011 and 2014. A storage or field blank filter was collected for each sampling period and were analyzed as blanks for their respective samples.
Experimental details and results for the determination of TSP and TC concentrations as well as %BC (Chapter III, Table 3). Briefly, the moisture-free QM/A filters were weighed before and after sampling to determine the TSP mass loadings. Total carbon (TC = organic + elemental/black – inorganic carbonates) was determined for each sample using a FlashEA 1112 elemental analyzer (ThermoFinnigan). Black carbon (BC) amounts were determined using chemothermal oxidation at 375 °C (CTO-375) and elemental analysis with the FlashEA 1112, and the %BC is expressed relative to TC.

2.3 Solvent extractions

Solvent extracts of the aerosols and respective filter blanks were obtained by combining aerosol filter plugs of known OC masses with ultrapure water (Millipore Synergy Ultrapure Water System) and thoroughly mixed on an orbital shaker (150 RPM, 4 h, 21 °C). Insoluble particles were removed using a syringe with a 0.45 μm PTFE filter cartridge, and the filtrate will be referred to as WSOM. The percent of water soluble organic carbon (WSOC) in each filtrate was determined by evaluating the non-purgeable organic carbon using a Shimadzu TOC-VCPH analyzer. The measured WSOC was compared with the TC content (derived from elemental analysis described in Section 2.2) to determine the %WSOC. The WSOM extracts were stored at 4 °C until EEMs analysis, typically within 4 h of preparation. WSOM extracts for FTICR-MS analysis were immediately acidified to pH 2 with 1.0 M HCl and desalted using an established procedure for Agilent PPL solid-phase extraction cartridges (Dittmar et al., 2008). The desalted sample was eluted into methanol (Acros, 99.9 %), and these elutes will be referred to as WSOM_{PPL}. The PPL extracts were stored at -8 °C until FTICR-MS analysis, typically within 24 h of preparation.
2.4 FTICR mass spectrometry

All WSOM\textsubscript{PPL} samples and their respective field blanks were analyzed in both positive and negative electrospray ionization (ESI) mode (WSOM- and WSOM+, respectively. Each of the samples was analyzed on a Bruker Daltonics 12 Tesla Apex Qe FTICR-MS with an Apollo II ESI source housed at the College of Sciences Major Instrumentation Cluster at Old Dominion University. Details of this analysis can be found elsewhere (Chapter III, Section 2.4).

Unique molecular formulas were assigned to measured peaks having a S/N ratio of at least 3 using an in-house generated MatLab (The MathWorks Inc., Natick, MA) code according to the criteria $^{12}$C$_{5-80}$H$_{5-200}$O$_{1-30}$N$_{0-5}$S$_{0-2}$P$_{0-2}$ for negative ESI and $^{12}$C$_{5-80}$H$_{5-200}$O$_{1-30}$N$_{0-5}$S$_{0-2}$P$_{0-2}$Na$_{0-1}$ for positive ESI, where the subscripts indicate the range of atoms allowed in a single formula. The formulas were screened to remove any chemically unreasonable formulas for natural OM molecules according to previously published criteria (e.g., Stubbins et al., 2010; Wozniak et al., 2008), and homologous series (CH$_2$, H$_2$, and CO$_2$) were used to verify ambiguous assignments. Each formula was structurally classified using a modified aromaticity index (AI$_{mod}$; Chapter II, Eq. 1) developed by Koch and Dittmar (2006).

2.5 EEMs analysis

An EEM spectra was collected for WSOM extracts for each of the aerosols at known dissolved carbon concentrations (1.0 – 11.0 mg C L$^{-1}$) in a 1 cm quartz cuvette using a Horiba Scientific Aqualog spectrofluorometer scanning over an excitation range of 240 – 600 nm at 3 nm intervals, and an emission range of 214 – 622 with 3.28 nm intervals, with an integration time of 4 sec. The acquired spectra were corrected for inner filter effects
and Rayleigh masking using the Aqualog software. The fluorescence intensity was converted to Raman units (RU) using the integrated area of a water Raman peak according to the method developed by Lawaetz and Stedmon (2009), and further normalized to the known dissolved carbon concentration.

3 Results and Discussion

3.1 Molecular characteristics of chromophoric OM

Each of the aerosols contains colored material, suggesting they each contain chromophoric OM. The biomass burning aerosols are brown, indicating the presence of brown carbon (Andreae and Gelencsér, 2006). The urban aerosols are gray, suggesting they contain BC or colored inorganic species. The mixed source aerosols are lighter in color and have both gray and brown coloration. The lighter color of the mixed source aerosol filters is consistent with having the lowest TSP loading (24.1 µg m⁻³). The TSP loadings of the urban and biomass burning aerosols are nearly double and triple that (47.1 µg m⁻³ and 73.2 µg m⁻³, respectively) of the mixed source aerosols (Chapter III, Table 3).

The biomass burning aerosols have the largest TC concentrations (24.8 µg m⁻³) of the emission sources, where 6.5% is BC and 33.6% WSOC. The low %WSOC indicates that much of the non-BC organics (including brown carbon) that are co-emitted are also insoluble. The urban aerosols contain approximately four times less TC (6.3 µg m⁻³) and have the lowest fraction of TC (13.4%) of the sources, indicating most of the aerosol mass consists of inorganic material. BC accounts for 3.4% (ranges 2.3 – 5.9 %) of the TC material, and a considerable amount of the TC is WSOC (40.8%), representing polar organic material. The amount of TC in the mixed source aerosols (5.7 µg m⁻³) is comparable to the urban aerosols but represents a larger fraction of the TSP (24.8%). These
aerosols have the lowest fraction of BC (1.9% of TC) and the highest fraction of WSOC (44.9%), and the inverse relationship between BC and WSOC in the mixed source and biomass burning aerosols is intuitive since BC is largely water-insoluble (Bond et al., 2013).

Each of the aerosol WSOM$_{PPL}$ produced positive and negative ESI-FTICR mass spectra consisting of thousands of peaks representing OM across a broad mass range (200 – 800 m/z). The biomass burning aerosols averaged the highest number of formulas (3392 ± 352) assigned in each WSOM- or WSOM+ spectrum, followed by urban aerosols (3156 ± 1179), and the mixed source aerosols (2105 ± 460). The formulas identified in the WSOM- and WSOM+ mass spectra of the same source were combined and the total formulas in each source were evaluated for their molecular properties. A detailed description of the molecular composition for each of the sources is beyond the scope of this study, but can be found elsewhere (Chapter III, Section 3.2). Chromophoric OM are the primary interest of this study, therefore only compounds with potential chromophoric properties will be discussed.

Compounds classified as aromatic and condensed aromatic based on their calculated AI$_{mod}$ values (i.e., AI$_{mod}$ > 0.5) have conjugated electronic structures that likely impart observable chromophoric properties, and will be referred to as “chromophoric formulas” for simplicity. The biomass burning aerosols contain the most chromophoric formulas (1787), followed by the urban (720 formulas), and the mixed source aerosols (570 formulas; Table 9). More than half (1360 formulas, 58%) of the total chromophoric formulas (2346 formulas) identified in any of the sources are unique to the biomass burning aerosols, and few formulas (10%) are common among all three sources (Fig. 15). Around
half of the formulas found in each the urban (379 formulas, 53%) and mixed source (272 formulas, 48%) aerosols are also identified in the biomass burning aerosols. An important caveat to state is that the presence of the same formulas in different samples does not necessarily indicate the same compound, as they could represent structural isomers with different carbon backbones and/or functional groups. Biomass burning aerosols are thought to be widespread in atmospheric OM and are largely responsible for the light-absorbing properties of OA (Washenfelder et al., 2015).

Figure 15. Venn diagram for the distribution of chromophoric molecular formulas identified in FTICR mass spectra for aerosol WSOM\textsubscript{PPL}. Regions where circles overlap indicate the percentage of common formulas. Circle sizes are proportional to the number of chromophoric formulas.
More than 60% of the potentially chromophoric formulas contain nitrogen (CHON or CHONS) regardless of source indicating that nitrogen-incorporation to aromatic structures is widespread among the aerosol sources. Reactions of OM with inorganic nitrogen (i.e., NOx and NH$_3$) are ubiquitous and can form CHON compounds (Noziere et al., 2009; Seinfeld and Pandis, 2012), and combustion of biomass does generate heterocyclic nitrogen compounds (e.g., imidazole compounds; Dou et al., 2015; Laskin et al., 2009; Lin et al., 2012). One key difference in the chromophoric nitrogen compounds among the sources is that the biomass burning contains mostly CHON formulas (1069 formulas, 60%) and relatively few CHONS (100 formulas, 6%), and the mixed source and urban aerosols each contain nearly 50% CHON (276 and 351 formulas, respectively) and much higher CHONS fractions (124 and 120 formulas, 22 and 17%, respectively; Table 9). However, the total number of CHONS does not vary significantly among the sources (100 – 124 formulas) indicating these formulas are likely ubiquitous among the aerosol sources.

Chromophoric formulas having only CHO in their formula vary considerably among the sources. The biomass burning aerosols contain the largest fraction (29%), followed by urban and mixed source aerosols (23 and 13%, respectively). The urban CHO formulas have more oxygen atoms per unit carbon (O/C = 0.31 ± 0.17) and the biomass burning CHO compounds are more aromatic indicated by the highest AI$_{mod}$ (0.59 ± 0.07, Table 9). There are roughly the same number of potential chromophoric CHOS (71 – 94 formulas) formulas in each source type, but the O/C ratio of these compounds differs substantially among sources. The urban and mixed source CHOS formulas have significantly higher O/C ratios (0.20 and 0.19, respectively) than the biomass burning
Table 9. Molecular formula distributions for chromophoric formulas identified in FTICR mass spectra for aerosol WSOM<sub>PPL</sub>.

<table>
<thead>
<tr>
<th>Aerosol source</th>
<th>Elemental composition</th>
<th># of formulas</th>
<th>% of formulas</th>
<th>O/C</th>
<th>H/C</th>
<th>AI&lt;sub&gt;mod&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed Source</td>
<td>CHO</td>
<td>75</td>
<td>13</td>
<td>0.28 ± 0.14</td>
<td>0.87 ± 0.13</td>
<td>0.56 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>CHON</td>
<td>276</td>
<td>48</td>
<td>0.19 ± 0.17</td>
<td>0.66 ± 0.25</td>
<td>0.79 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>CHOS</td>
<td>94</td>
<td>16</td>
<td>0.19 ± 0.09</td>
<td>0.84 ± 0.11</td>
<td>0.57 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>CHONS</td>
<td>124</td>
<td>22</td>
<td>0.23 ± 0.18</td>
<td>0.82 ± 0.22</td>
<td>0.84 ± 0.43</td>
</tr>
<tr>
<td></td>
<td>CHOP(N,S)</td>
<td>1</td>
<td>0.2</td>
<td>0.75</td>
<td>1.08</td>
<td>0.80</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>570</td>
<td>100</td>
<td>0.21 ± 0.16</td>
<td>0.75 ± 0.23</td>
<td>0.73 ± 0.26</td>
</tr>
<tr>
<td>Biomass Burning</td>
<td>CHO</td>
<td>515</td>
<td>29</td>
<td>0.26 ± 0.11</td>
<td>0.81 ± 0.13</td>
<td>0.59 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>CHON</td>
<td>1069</td>
<td>60</td>
<td>0.22 ± 0.12</td>
<td>0.84 ± 0.20</td>
<td>0.65 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>CHOS</td>
<td>97</td>
<td>5</td>
<td>0.09 ± 0.10</td>
<td>0.77 ± 0.14</td>
<td>0.63 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>CHONS</td>
<td>100</td>
<td>6</td>
<td>0.27 ± 0.16</td>
<td>0.79 ± 0.26</td>
<td>1.05 ± 1.01</td>
</tr>
<tr>
<td></td>
<td>CHOP(N,S)</td>
<td>6</td>
<td>0.3</td>
<td>0.36 ± 0.03</td>
<td>0.60 ± 0.25</td>
<td>0.79 ± 0.18</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1787</td>
<td>100</td>
<td>0.23 ± 0.13</td>
<td>0.83 ± 0.18</td>
<td>0.65 ± 0.28</td>
</tr>
<tr>
<td>Urban</td>
<td>CHO</td>
<td>166</td>
<td>23</td>
<td>0.31 ± 0.17</td>
<td>0.83 ± 0.15</td>
<td>0.57 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>CHON</td>
<td>351</td>
<td>49</td>
<td>0.20 ± 0.17</td>
<td>0.67 ± 0.22</td>
<td>0.75 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>CHOS</td>
<td>71</td>
<td>10</td>
<td>0.20 ± 0.13</td>
<td>0.77 ± 0.16</td>
<td>0.60 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>CHONS</td>
<td>120</td>
<td>17</td>
<td>0.30 ± 0.22</td>
<td>0.84 ± 0.25</td>
<td>0.97 ± 0.60</td>
</tr>
<tr>
<td></td>
<td>CHOP(N,S)</td>
<td>12</td>
<td>2</td>
<td>0.87 ± 0.34</td>
<td>0.72 ± 0.25</td>
<td>0.87 ± 0.40</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>720</td>
<td>100</td>
<td>0.25 ± 0.19</td>
<td>0.75 ± 0.22</td>
<td>0.73 ± 0.28</td>
</tr>
</tbody>
</table>

CHOS formulas (0.09), suggesting that urban and mixed source CHOS compounds are a result of aging, and that biomass burning CHOS formulas could contain heterocyclic sulfur.

There are very few chromophoric CHOP(N,S) formulas (≤ 12 formulas) in any of the aerosols, indicating the processes that incorporate phosphorous plays an insignificant role in the formation or transformation of these chromophoric OA.

The chromophoric CHO and CHON compounds fall into homologous series based on their double bond equivalent (DBE). DBE is a measure of the double bond density, and differs from AI<sub>mod</sub> in that DBE does not consider double bonds between carbon and oxygen. DBE is calculated using Eq. 4:
$$\text{DBE} = 1 + \frac{(2C - H + N + P)}{2},$$

(4)

for any molecular formula comprised of C, H, N, O, S, and P. An H/C ratio versus carbon plot for the chromophoric CHO and CHON compounds in each of the aerosols highlights DBE homologous series (Fig. 16). Formulas appearing in the same DBE homologous series have identical DBE values, indicating a similar carbon backbone. Similar to a KMD CH$_2$ series, points along a DBE homologous series differ in the number of CH$_2$ groups. A DBE homologous series differs from a CH$_2$ KMD homologous series in that the number of heteroatoms in a DBE series is not necessarily fixed. Because the carbon backbone is most likely to influence the chromophoric nature of a molecule, the DBE homologous series provides a better representation of the molecular variation of chromophoric OM among the aerosol sources. The general molecular formulas corresponding to each series are listed in Table 10. The biomass burning plots display the most number of series and the most complete series (fewer missing formulas along each homologous series). The plots for the urban and mixed source aerosols show similar DBE homologous series to the biomass burning aerosols, indicating that the carbon backbone for these molecules may be the same. The urban and mixed source aerosols have CHO series with lower DBE ($< 14$) and CHON series with higher DBE ($\geq 14$), and the biomass burning aerosols contain series across the DBE range ($6 - 20$).

There are a number of “gaps” in the homologous DBE series found in the urban and mixed source aerosols, whereas the biomass burning aerosols generally have compounds present continuously across each homologous series. These gaps along with evidence that the urban and mixed source aerosols have been subject to more extensive aging reactions indicated in Chapter IV suggests that the missing compounds in a given
series may have been present at some point, but were removed by transformation processes upon atmospheric transit. Photolysis is a known removal process for organic nitrogen compounds (Lee et al., 2014; Zhao et al., 2015), and photolysis reactions could partially explain the gaps in the CHON homologous series observed in the mixed source and urban aerosols. The missing compounds in these series suggest that certain members of these DBE homologous series are more persistent in the atmosphere than others, either due to their production or resistance to photochemical degradation. This would indicate that high DBE CHO and low DBE CHON compounds are degraded or transformed more rapidly than the low DBE CHO and high DBE CHON compounds.

Table 10. General molecular formulas corresponding to the homologous DBE series displayed in Fig. 16.

<table>
<thead>
<tr>
<th>DBE</th>
<th>*CHO formula</th>
<th>*CHON formulas</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>C_xH_{2x-12}O_y</td>
<td>C_xH_{2x-10+z}O_yN_z</td>
</tr>
<tr>
<td>7</td>
<td>C_xH_{2x-14}O_y</td>
<td>C_xH_{2x-12+z}O_yN_z</td>
</tr>
<tr>
<td>8</td>
<td>C_xH_{2x-16}O_y</td>
<td>C_xH_{2x-14+z}O_yN_z</td>
</tr>
<tr>
<td>9</td>
<td>C_xH_{2x-18}O_y</td>
<td>C_xH_{2x-16+z}O_yN_z</td>
</tr>
<tr>
<td>10</td>
<td>C_xH_{2x-20}O_y</td>
<td>C_xH_{2x-18+z}O_yN_z</td>
</tr>
<tr>
<td>11</td>
<td>C_xH_{2x-22}O_y</td>
<td>C_xH_{2x-20+z}O_yN_z</td>
</tr>
<tr>
<td>12</td>
<td>C_xH_{2x-24}O_y</td>
<td>C_xH_{2x-22+z}O_yN_z</td>
</tr>
<tr>
<td>13</td>
<td>C_xH_{2x-26}O_y</td>
<td>C_xH_{2x-24+z}O_yN_z</td>
</tr>
<tr>
<td>14</td>
<td>C_xH_{2x-28}O_y</td>
<td>C_xH_{2x-26+z}O_yN_z</td>
</tr>
<tr>
<td>15</td>
<td>C_xH_{2x-30}O_y</td>
<td>C_xH_{2x-28+z}O_yN_z</td>
</tr>
<tr>
<td>16</td>
<td>C_xH_{2x-32}O_y</td>
<td>C_xH_{2x-30+z}O_yN_z</td>
</tr>
<tr>
<td>17</td>
<td>C_xH_{2x-34}O_y</td>
<td>C_xH_{2x-32+z}O_yN_z</td>
</tr>
<tr>
<td>18</td>
<td>C_xH_{2x-36}O_y</td>
<td>C_xH_{2x-34+z}O_yN_z</td>
</tr>
<tr>
<td>19</td>
<td>C_xH_{2x-38}O_y</td>
<td>C_xH_{2x-36+z}O_yN_z</td>
</tr>
<tr>
<td>20</td>
<td>C_xH_{2x-40}O_y</td>
<td>C_xH_{2x-38+z}O_yN_z</td>
</tr>
</tbody>
</table>

*6 ≤ x ≤ 47; 1 ≤ y ≤ 26; 1 ≤ z ≤ 5
Figure 16. H/C ratio versus carbon plot for chromophoric CHO and CHON formulas identified in FTICR mass spectra for aerosol WSOM_{PPL}. Data points are colored based on DBE values, and the formulas for each homologous DBE series are listed in Table 10. Sample DBE series (trendlines) are labeled with their corresponding DBE value are provided in the biomass burning CHO plot, and the general molecular formula for the DBE = 10 series is shown where $x = 6$ to 47 and the number of O is displayed as an average.
Several of the general formulas listed in Table 10 are consistent with O- or N-substituted polycyclic aromatic hydrocarbons (PAHs), or quinones, which have been identified in fossil fuel and biomass combustion-derived aerosols (Rogge et al., 1993c, 1998). PAHs can react rapidly with atmospheric oxidants (ozone, hydroxyl radical, and NOx) to form O- and N-substituted products, which can also react further (Ringuet et al., 2012). For example, the substituted PAH 1-nitropyrene (C_{16}H_{9}O_{2}N) found in diesel emissions (e.g., Ringuet et al., 2012) is consistent with the general formula C_{x}H_{2x-24+z}O_{y}N_{z} (Table 10) and has a DBE of 13. The molecular formula for this specific compound was not identified in any of the samples, likely due to water-insolubility. However, the consistency of identified formulas with O- and N-substituted PAHs and the ubiquity of such species suggests that these compounds may influence some portion of the OM found in these aerosols.

Numerous highly aromatic molecular formulas were identified in the FTICR mass spectra for each of the aerosol WSOM_{PPL} in this study, indicating they are ubiquitous throughout the atmosphere and are likely responsible, in part, for the light-absorbing nature of OA. One of the well-known limitations of FTICR-MS is that measurements are only semi-quantitative due to the dependence of peak intensity on ionization efficiency of the molecule, and that only polar, ionizable compounds can be detected. However, the larger number of aromatic and condensed aromatic compounds identified in the mass spectra are supported by the detection of aromatic protons in the ^1H NMR spectra of the WSOM for each aerosol (Chapter III, Fig. 9 insets). On average, 9.2% of the protons detected are directly bound to an aromatic ring in the biomass burning WSOM, and 2.4% of the protons in the urban WSOM, and 1.7% in the mixed source WSOM (Chapter III, Table 6). The
aromatic signal is broad indicating high structural diversity among the aromatic compounds, consistent with the variety of compounds identified using FTICR-MS. While chromophoric properties can be inferred by the aromatic properties found in the molecular formulas identified by FTICR-MS and the aromatic proton signal in the $^1\text{H}$ NMR spectra, measurement of fluorescence properties by EEMs confirms the chromophoric nature of OA in these aerosols.

### 3.2 EEMs analysis

The carbon-normalized fluorescence intensity measured in each EEM spectrum were averaged to obtain representative EEMs plot for WSOM from each aerosol source (Fig. 17). Even with carbon-normalization, the biomass burning aerosol samples display significantly higher EEMs intensity (> 1 order of magnitude) than the other aerosols (Fig. 17) indicating biomass burning aerosols contain more fluorophores and/or stronger fluorophores than urban and mixed aerosols. This higher fluorescence intensity is consistent with the greater relative aromatic signal in the $^1\text{H}$ NMR spectra and the higher number of aromatic and condensed aromatic formulas identified in the FTICR mass spectra. Despite a lower signal intensity, the urban and mixed source aerosols do contain fluorescent compounds. The maximum signal for the urban aerosols is double that of the mixed source aerosols and may reflect the higher combustion influence expected in the Philadelphia, PA urban environment versus the rural mixed source environment in Gloucester Point, VA (Fig. 17). The fluorescent properties of organic compounds are strongly correlated to UV absorbance (Kieber et al., 2006; Nakajima et al., 2008), and the strong fluorescence signal suggests that the biomass burning aerosols are more likely to absorb UV light than the other aerosols. UV visible spectra were collected at the same time
as the EEM spectra, but the resolution and limited spectral range did not allow for the corrections necessary for a thorough analysis. However, uncorrected UV visible spectra support this relationship between absorbance and fluorescence where the biomass burning aerosols display the greatest absorbance, followed by the urban aerosols, and the mixed source aerosols display the least absorbance (Appendix C, Fig. S3). In addition to variations in fluorescence intensities, there are apparent differences in the EEMs peak locations suggesting variations in OM composition, origin, and processing among the aerosol sources.

Fluorescent peaks consistent with those previously identified in DOM and other aerosol OM studies are present in these EEM spectra (Fig. 17), which are classified using a one letter identifier system (A, B, C, M, N, and T) developed by Coble (1996). Conventional EEMs peak nomenclature was initially developed to describe marine DOM and not aerosol OM, but these classifications offer a convenient framework for relating fluorescence peaks to compound class. Similarities in peak locations found in the aerosol WSOM samples to those found in DOM suggest that structurally similar fluorophores are likely present (Kieber et al., 2006; Kiss et al., 2003; Mladenov et al., 2011a), and traditional peak identifications as well as alternative characterizations will be discussed. Each of the resulting EEMs spectra for the aerosol WSOM contain a peak maxima around 250/405 (Ex/Em wavelengths, nm) which corresponds to peak A according to conventional EEMs nomenclature (Coble, 1996; Coble et al., 1998). This region is the only common feature among all three sources, and has been suggested to represent terrestrially-derived (i.e., vascular plants) humic material that is high-molecular weight, UV active, has conjugated aromatic structural features (Coble et al., 1998) or dissolved black carbon (Stubbins et al.,
Figure 17. Averaged EEMs contour plots for WSOM extracted from (a) mixed source, (b) biomass burning, and (c) urban aerosols. Peaks A, B, C, M, N, and T locations are labeled according to major peaks identified by Coble et al. (1998) and are provided as points of reference.

This peak is present in numerous EEMs studies of ambient atmospheric OM (Kieber et al., 2006; Kieber et al., 2007; Mladenov et al., 2011a; Mladenov et al., 2010; Mladenov et al., 2012; Nakajima et al., 2008). Interestingly, poorly-resolved fluorescence is observed in the region of peak A in limonene SOA aged via ozonolysis in the absence of ammonia (Bones et al., 2010), and the peak is absent when ammonia is present (Lee et al., 2014).
Peak A is absent in naphthalene SOA aged via ozonolysis in the presence of ammonia and in studies investigating biologically relevant aerosol standards (Pöhlker et al., 2012). The apparent presence or absence of peak A in some SOA and not others is evidence that emission source and chemical processes play an important role in the formation of chromophoric OA. The exact emission and excitation wavelengths defining peak A varies slightly among the different aerosol types. Peak A in the biomass burning aerosol spans the largest area (Ex/Em = 240–270/340–460 nm; Table 11), suggesting that the peak A fluorescent material in biomass burning aerosols may be more structurally diverse than the urban and mixed source aerosols. This peak in the urban aerosols is shifted to slightly higher emission wavelengths (Ex/Em = 240–270/390–460 nm; Table 11), which could indicate that the fluorophores contributing to this peak are of higher molecular weight (Leehneer and Croué, 2003).

The mixed source aerosols contain only one other significant peak (Ex/Em maxima = 305/405 nm) located close to traditional peak M, which is attributed to in-situ marine DOM (Coble, 1996; Coble et al., 1998). The urban aerosols also have a peak (Ex/Em maxima = 325/410 nm) close to this region, but it is shifted to slightly higher wavelengths compared to the peak in the mixed source spectra lies in between traditional peaks M and C. Fluorescent compounds with maxima close to peak M have been identified in other atmospheric OM studies including those from European and Saharan aerosols (Mladenov et al., 2011a), as well as those found in wet deposition in the United States (Kieber et al., 2006; Mladenov et al., 2012). Peak M was originally associated with in-situ marine DOM and is thought to be less aromatic and lower molecular weight than the compounds in peak A or C (Fellman et al., 2010), and suggests that chromophoric aerosol OM could be similar
to marine chromophoric DOM in terms of molecular weight and relative aromaticity. The biomass burning aerosols do not have a well-defined peak near M and C, but the fluorescence intensity in this region is still higher than that of either the mixed source or urban aerosols, indicating there are still structurally similar compounds present in comparable amounts.

The biomass burning aerosols display a significant amount of fluorescence peaking central to traditional peak N, extending slightly into peaks T and M (Fig. 17). The peak (Ex/Em range = 270–290/325–390 nm) is not as well resolved as other peaks indicating that many conjugated fluorescence molecules are present (Fellman et al., 2010), which is consistent with the apparent structural diversity of compounds identified by FTICR-MS and the broad aromatic signal in \(^1\)H NMR spectra. Peak N is not attributed to a humic-like compounds, rather it has been associated with newly-formed chromophoric dissolved OM (Coble et al., 1998; Fellman et al., 2010). Compounds fluorescing in this region have been identified as being enriched in nitrogen, having low aromaticity, and low molecular weight compared to compounds producing fluorescence peaks in other regions (Stubbins et al., 2014). While previous findings related to peak N are all based on DOM samples, they all imply that the compounds responsible found in this Ex/Em region represent newly-formed OM. Compounds that fluoresce in the region of peak T are typically associated with proteins and amino acids (specifically tryptophan), and have also been more generally described as aromatic amines (Nakajima et al., 2008; Stubbins et al., 2014) which expands the classification of peak T to compounds of non-biological origin.

The urban aerosols contain two unique peak maxima at Ex/Em 275/325 nm and 240/305 nm (Table 11). The higher excitation peak (Ex/Em = 275/325 nm) is consistent
Table 11. Descriptions of peaks identified in EEMs for aerosol WSOM. Approximate peak maxima and peak ranges are provided as well as traditional and alternate peak characterizations.

<table>
<thead>
<tr>
<th>Peak maxima (Ex/Em, nm)</th>
<th>Range (Ex/Em, nm)</th>
<th>Traditional Classification</th>
<th>Alternate Classifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>250/405</td>
<td>240-260/ &gt;350</td>
<td>A</td>
<td>Aged limonene SOA&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>240-270/ &gt;340</td>
<td>(terrestrial humic)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>240-270/ &gt;390</td>
<td>M</td>
<td>(marine humic)</td>
</tr>
<tr>
<td>305/405</td>
<td>300-310/ 400-410</td>
<td>N and T</td>
<td>Aromatic amines&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>270-290/ 325-390</td>
<td>(Unknown and tryptophan-like)</td>
<td>Naphthalene/phenanthrene&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>275/375</td>
<td>-</td>
<td>T and B</td>
<td>Brown carbon proxy&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>310-340/ 390-430</td>
<td>(marine humic and terrestrial humic)</td>
<td>Napthalene&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>325/410</td>
<td>-</td>
<td>Between M and C</td>
<td>Diesel&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>260-280/ 310-330</td>
<td>(tryptophan-like and tyrosine-like)</td>
<td></td>
</tr>
<tr>
<td>275/325</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>240/305</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Coble et al., 1998  
<sup>b</sup>Bones et al., 2010  
<sup>c</sup>Nakajima et al., 2008  
<sup>d</sup>Pöhlker et al., 2012  
<sup>e</sup>Lee et al., 2014  
<sup>f</sup>Courvoisier et al., 2006  
<sup>g</sup>Du et al., 1998
with the traditional peaks T and B, which are attributed to proteins containing aromatic amino acids (tryptophan and tyrosine; Coble, 1996; Mopper and Schultz, 1993); however, PAHs can have similar spectral features as biological fluorophores (Courvoisier et al., 2006). The EEM spectra for the urban aerosols contains some similar structural features as the EEM spectra for diesel exhaust WSOM (Mladenov et al., 2011a) which is a logical source for urban-influenced aerosols, suggesting that these low Ex/Em peaks are derived from fossil fuel combustion rather than having a biological origin. While the presence of biologically-derived molecules is possible, the multiple sources of PAHs in the sampling area (e.g., vehicular traffic), the spectral similarities to those of diesel exhaust, and the identification of compounds in molecular families similar to PAHs in the mass spectra suggest that naphthalene and related compounds are likely responsible for these spectral characteristics. While the conventional fluorescence peak classifications are highly useful, they must be applied with caution as chromophoric OM from different systems may fall under different molecular classes and exhibit similar fluorescence patterns.

It is a challenge to directly correlate specific compounds in aerosol OM to the EEMs peaks that are generated due to the inherent complexity and diversity of the structures. A study using laboratory-generated SOA created from naphthalene does contain fluorescent OM exhibiting a peak (Ex/Em = 305/425 nm) in the EEM spectrum consistent with those identified in ambient aerosol WSOM, which is located at a slightly higher emission wavelength than traditional peak M (Lee et al., 2014). The same study also generated SOA using limonene as a precursor, and the peak maximum occurs at higher Ex/Em wavelengths than those found in ambient aerosols, but the peak maximum shifts to lower Ex/Em (350/425 nm) after photolysis similar to traditional peak C. This SOA study
suggests that the peaks identified close to traditional peaks C and M may be representative of aged SOA. Further studies including analysis of laboratory-generated SOA alongside ambient OA would provide much-needed verification regarding these peak identifications.

One of the major drawbacks to EEMs analysis is the potential for interference due to the presence of inorganic species, such as iron or nitrates, which can diminish fluorescence signal. Inorganic nitrate is ubiquitous globally and in the region where the samples in this study were collected (Jimenez et al., 2009), and have significant regional, seasonal, and diurnal fluctuations. Nitrate concentrations for the urban samples range between 0.16 and 0.20 µg m\(^{-3}\), an order of magnitude lower than WSOC concentrations, according to simultaneous aerosol mass spectrometry measurements (personal communication with P. DeCarlo). Measurements for the mixed source and biomass burning aerosols are not available, but we can speculate that they are lower in these regions compared to the urban aerosols due to the high contribution of NOx expected from anthropogenic emissions. Nitrate concentrations are observably lower on average for remote locations compared to geographically similar urban locations (Jimenez et al., 2009).

Iron is produced during industrial processes and the combustion of biomass (Luo et al., 2008), and is likely to be present in the TSP of these aerosols. Total iron concentrations present in marine aerosols collected off the coast of Massachusetts, USA measure between 0.31 and 1.44 nmol m\(^{-3}\), and less than 3% is water-soluble (Wozniak et al., 2015). Kieber et al. (1999, 2003) conducted studies of nitrate and iron in rainwater collected in southeastern North Carolina, USA, and report that even at the highest measured concentrations no significant contribution to total absorbance of chromophoric DOM was found. Based on these previous studies, we are confident that iron and nitrate do not
interfere significantly with the EEMs analysis used in this study, but fluorescence intensities must be interpreted with this in mind. Additionally, solution pH is known to influence the observed signal, and pH (slightly acidic) of the solutions in this study was not altered and are all similar to one another, and bias due to pH is not a major concern.

3.3 Molecular signatures for fluorescence peaks

It is challenging to draw direct connections between fluorescence signatures and the individual molecular components that are responsible due to the immense complexity of natural OM and a lack atmospherically-relevant OM standards. One study to date directly correlates specific molecular formulas identified by FTICR-MS to the EEMs fluorescence signals for riverine DOM (Stubbins et al., 2014). AI$_{mol}$, molecular weight, and nitrogen content were identified as key distinguishing properties responsible for the different EEMs peaks. Comparison of the chromophoric formulas common among the aerosol sources can be used to draw connections to common fluorescence signals in EEM spectra (e.g., peak A), and chromophoric formulas unique to an aerosol source can provide molecular characteristics for unique fluorescence peaks (e.g., peak N in the biomass burning aerosols). A summary the EEMs peak identifications and associated molecular properties is provided, as well as a comparison to the DOM study that uses the same techniques.

An intense peak A is observed in each of the aerosol WSOM EEM spectra, suggesting that chromophoric molecular formulas commonly identified in the mass spectra for each of the aerosols play a role in this fluorescence peak. Fluorescence intensity is observed in the regions between peak M and C in all three of the aerosol sources, but the peak maxima location and intensity vary. This variation suggests that there may be
formulas present in two or more of the sources may be responsible for the fluorescence observed between peaks M and C. Formulas common to all three aerosol sources (224 formulas) contain mostly CHON (116 formulas, 52%), have similar amounts of CHONS and CHO (56 and 47 formulas, 25 and 21%, respectively), and very few CHOS (5 formulas, 2%). These common formulas average a high $A_{I_{mod}}$ (0.78) with a moderate molecular weight (357 Da; Table 12). Formulas common in any two of the aerosols (283 formulas) are also dominated by CHON (143 formulas, 51%) with more CHO (82 formulas, 29%), fewer CHONS (37 formulas, 13%) and more CHOS formulas (20 formulas, 7%). These formulas are less aromatic and have lower molecular weight (average $A_{I_{mod}} = 0.69$, MW = 341 Da) compared to all of formulas common to all three aerosols (Table 12). Due to the significant overlap in these fluorescence regions among the aerosols, it is possible that all of the compounds found in two or more of these aerosols contribute to peak A and the region between peaks M and C.

Molecular formulas in DOM correlated directly with peak A have been classified as high molecular weight (536 Da), nitrogen-deficient, and have high $A_{I_{mod}}$, and formulas corresponding to the region between peaks M and C are lower molecular weight (316 Da), nitrogen-rich, and have lower $A_{I_{mod}}$ (Stubbins et al., 2014). Some consistencies in these properties are observed for the same fluorescence peaks in the aerosol WSOM.

Chromophoric formulas found in all three aerosols generally have higher molecular weights and $A_{I_{mod}}$ values than formulas found in only two of the aerosol WSOM, but there is little variation in nitrogen content among the aerosols (Table 12). This could indicate that molecular weight and aromaticity play a more important role in the location of the fluorescence peaks than nitrogen-content. Comparison of molecular weight between these
Table 12. Key characteristics of chromophoric molecular formulas suggested as important for classic fluorescence peaks in EEM spectra of aerosol WSOM.

<table>
<thead>
<tr>
<th>Fluorescence peak</th>
<th>No. of formulas</th>
<th>Average AI$_{mod}$</th>
<th>Average MW (Da)</th>
<th>%CHON</th>
<th>*Formula presence</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>224</td>
<td>0.78</td>
<td>357</td>
<td>52</td>
<td>MS, BB, and U</td>
</tr>
<tr>
<td>M-C</td>
<td>283</td>
<td>0.69</td>
<td>341</td>
<td>51</td>
<td>MS and BB, MS and U, or BB and U</td>
</tr>
<tr>
<td>N</td>
<td>1360</td>
<td>0.63</td>
<td>368</td>
<td>63</td>
<td>BB only</td>
</tr>
<tr>
<td>T-B</td>
<td>261</td>
<td>0.73</td>
<td>406</td>
<td>44</td>
<td>U only</td>
</tr>
</tbody>
</table>

*MS = mixed source aerosols, BB = biomass burning aerosols, U = urban aerosols

two studies should be viewed cautiously, as there are biases in molecular weight due to the use of different instruments as well as inherent differences due to source. However, the similar relationships regarding molecular weight and aromaticity lend support that these properties are important drivers in peak fluorescence location.

The fluorescence that spans conventional peaks N and T is a unique feature to the biomass burning aerosols, suggesting that chromophoric molecular formulas unique to the biomass burning aerosols are largely responsible for this peak. Most (63%) of the chromophoric molecular formulas unique to the biomass burning aerosols correspond to aromatic CHON formulas (851 CHON formulas of 1360 total formulas unique to biomass burning aerosols), representing 64% of all the chromophoric CHON formulas detected regardless of source (851 of 1321 total chromophoric CHON formulas). The molecular weight and aromaticity of these 851 unique CHON formulas are on average lower (molecular weight = 359 Da, AI$_{mod}$ = 0.63) than all of the other chromophoric formulas (molecular weight = 370 Da, AI$_{mod}$ = 0.72). The molecular characteristics of the formulas
unique to the biomass burning aerosols are consistent with the previous observation that DOM compounds fluorescing in this region (peak N) are nitrogen-rich, lower molecular weight, and less aromatic than other fluorophores (Stubbins et al., 2014).

Numerous molecular formulas are unique to the urban aerosols (261 formulas) and offer potential logical sources for the corresponding unique features in the EEM spectra (peaks B and T). These formulas are dominated by CHON (116 formulas, 44%) and CHO (51 formulas, 20%) followed by CHOS (50 formulas, 19%) and CHONS formulas (32 formulas, 12%). These unique urban formulas have higher average AI$_{\text{mod}}$ (0.73), O/C (0.30), and molecular weight (406 Da) than all of the other chromophoric formulas (AI$_{\text{mod}}$ = 0.66, O/C = 0.23, and molecular weight = 364 Da). The enrichment of N-containing compounds supports that aromatic amines are responsible for fluorescence in the region of conventional peaks B and T, and could be from biological or anthropogenic origins. The molecular characteristics of this region are inconsistent with those observed in the Stubbins et al. (2014) study of DOM which found a surprising lack of N-containing formulas correlating with this fluorescence region and much lower characteristical molecular weights (244 Da). The importance of these peaks to N-deficient aquatic DOM compounds and urban-influenced aerosol WSOM enriched in N compounds demonstrates the difficulties of extracting molecular information from EEM spectra and suggests the need for further studies relating molecular level information to EEMs for natural OM of all types.

The molecular formula and fluorescence relationships in this study represent an important advancement in determining the specific links between molecular character and optical properties found in aerosol OM. Our approach is limited in that relationships must
be inferred based on presence or absence in certain samples, and, conservatively, only aromatic and condensed aromatic compounds are considered. However, it lays the foundation for many future studies of chromophoric aerosol OM that involve a more comprehensive set of aerosols as well as the incorporation of model SOA compounds, ultimately working towards the goal of the complete source apportionment of light-absorbing OA.

4 Summary and Implications

The detection of fluorescing compounds with similar excitation and emission wavelengths to those found in other aerosols and natural OM sources indicates that organic fluorophores are widespread, and that there are many structural similarities among the sources and physical environments. The measured fluorescence intensity is indicative of the amount of fluorescent material, and provides a unique way to evaluate OM and associated chromophoric properties. The higher fluorescence signal found in the biomass burning aerosol WSOM indicates it exhibits more fluorescence and therefore greater absorbance per unit of carbon implying they contribute to a more positive radiative forcing than the urban or mixed source aerosols. Unique fluorescence features found in the urban and biomass burning aerosols spectra indicate important differences in the chemical species responsible for fluorescence in these aerosols. The biomass burning aerosols contain a fluorescence feature characteristic of freshly-produced nitrogen species, which is absent in the urban and mixed source aerosol consistent with the suggestion that they are more atmospherically aged than the biomass burning aerosols. The urban aerosols contain a unique fluorescence feature believed to be caused by PAH compounds that have been identified in diesel exhaust, possibly indicating an anthropogenic origin.
This is the first study offering molecular formula information regarding chromophoric organic compounds responsible for fluorescence in aerosols OM and contributes to the understanding of fluorescence in natural OM samples. Analysis of aerosol OM by EEMs and FTICR-MS provides an important way to reduce the uncertainties associated with OA source allocation and the relative impact chromophoric OM contributes radiative forcing.
CHAPTER VI

CONCLUSIONS AND FUTURE WORK

1 Summary and Conclusions

The primary goal of this study was to relate light-absorbing properties of organic aerosols (OA) to their molecular components. Through the use of multiple advanced analytical instrumentation, source-dependent patterns of chemical structure and associated chromophoric properties were elucidated for key aerosol emission sources. The results obtained are particularly valuable as they provide necessary molecular details of OA linking to their origin and fate, as well as potential impacts on radiative forcing.

Obtaining an enhanced chemical understanding of the components that make up OA was made possible by combining several advanced analytical instruments that offer complementary information. Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) provided molecular formula details for thousands of individual compounds contained within each of the aerosols. While FTICR-MS is limited in the dependence on ionization ability, proton nuclear magnetic resonance spectroscopy (\(^1\)H NMR) relies on the presence of protons, and provides connectivity and relative amounts of protons present in each mixture. Excitation emission matrix spectroscopy (EEMs) provide unique fluorescence signatures for each of the aerosol samples, highlighting important variations in light-absorbing characteristics between emission sources. Many of the discoveries and conclusions discussed are attributed to this unique combination of advanced analytical instrumentation.

Characterization of complex OA mixtures inevitably leaves some portion of the mixture unanalyzed due to various analytical limitations. To obtain a more comprehensive
characterization, a method for analyzing water-insoluble organic matter (WIOM) was developed using extraction of OM by organic solvents in parallel with water-soluble organic matter (WSOM). Analysis of the WIOM with FTICR-MS provided molecular information previously omitted by analysis of WSOM alone including the detection of more sulfur-containing compounds and more aliphatic compounds. WIOM had been previously demonstrated to be enriched in anthropogenically-derived material, whereas the WSOM contained primarily biogenically-derived material. Human activity has played a major role in transforming the chemical composition of the atmosphere and analysis of anthropogenic species is essential in advancing our understanding of the role OM plays in the atmosphere and the negative influences they may impart.

Molecular source apportionment was one of two major goals in this study. FTICR-MS and $^1$H NMR show significantly different spectral features among the aerosol sources demonstrating the molecular diversity. Principal component analysis deconstructs the important molecular features defining of each aerosol emission source. Kendrick mass defect analysis for atmospherically-relevant oligomers reveal that isoprene-derivatives play an important role in transforming OA. Additionally, precursors and products of reactions between OM and NOx, NH$_3$, and SOx reveal these inorganic species play a vital role incorporating nitrogen and sulfur into OA. EEMs analysis reveal unique fluorescence signatures for each of the aerosol source that could be related to molecular properties of the chromophoric compounds.

The distinguishing feature of marine aerosols is the presence of primary biologically-derived compounds. A large fraction of the molecular formulas are consistent with lipids, phospholipids, and organosulfates. The carbon backbones of these aerosols are
less diverse and the OM is generally less oxidized suggesting a primary input when compared to the other sources. The marine aerosols contain relatively few isoprene-related oligomer KMD series, and the series are short. The KMD oligomer series patterns are consistent with the CO$_2$ KMD series, which has been suggested as a proxy for atmospheric aging reactions. Unlike the aerosols collected over terrestrial environments, relatively few of the molecular formulas are precursors or products of reaction with inorganic NOx or NH$_3$, suggesting that atmospheric conditions in the marine environment do not promote the same reactions, or to the same extent, as those in more anthropogenically-influenced regions. Reaction with SOx appears to be the most significant process, likely driven by high dimethyl sulfide concentrations common to marine environments. Unfortunately, sample limitations prevented EEMs analysis of the marine aerosols, and direct analysis of the light-absorbing nature of these aerosols was not obtained. The primary biological nature of these aerosols suggest proteins and protein-like compounds would be the dominant fluorophores.

The biomass burning aerosols share the primary nature of marine aerosols, but are otherwise unsimilar. The amount of aromatic compounds is a clear distinguishing features of these aerosols, specifically aromatic nitrogen compounds. The enrichment of these aromatic nitrogen compounds in this presumably primary OA mixture and relative absence indicates that they are rapidly transformed upon atmospheric transit, or are removed by physical processes. A large fraction of the biomass burning OM serves as precursors or represent products of reactions with NOx, NH$_3$, and SOx, suggesting these reactions are responsible for the initial transformation of this OM. Many of the formulas are part of short KMD oligomer and CO$_2$ series, further supporting the idea that these aerosols are relatively
fresh and extensive aging has not yet occurred. These aerosols displayed unique fluorescence features consistent with freshly-emitted OM and nitrogen-containing species. Not only are the aromatic nitrogen species an important distinguishing molecular feature, they are responsible for unique optical properties, and their absence in other aerosols suggests that they may be labile. Other intense fluorescence features representative of humic material are also found in the urban and mixed source aerosols indicate fluorophores that are more resistant to degradation reactions, or that are formed ubiquitously.

The urban aerosols are characteristically the most oxidized, most structurally diverse, and most extensively aged. The amount of nitrogen-containing compounds is comparable to the biomass burning aerosols, but they are substantially less aromatic. These aerosols are overall more aliphatic, and are more substituted with polar functional groups. The urban aerosols have, by far, the longest oligomeric and CO$_2$ KMD series. Additionally, these aerosols have the highest relative number compounds involved in reactions between OM and inorganic species. These observations indicate the urban aerosols have undergone the most extensive aging and this secondary nature suggests these aerosols have been transported long-range. It was somewhat surprising to find a large number of isoprene-related oligomer given the biogenic organic, and the expected anthropogenic influence in such a region. These findings indicate the importance of both biogenic and anthropogenic influences on OA in highly-developed areas. Some fluorescence features are common between the urban and biomass burning aerosols, indicating their widespread importance to the optical activity of OA. A unique fluorescence feature in the urban aerosols is consistent with highly-condensed aromatic compounds found in diesel emissions,
indicating anthropogenic emissions play an important role in the light-absorbing properties of OA.

The mixed source aerosols contains molecular features similar to each of the other three emission source, and with few distinguishing characteristics indicating that these aerosols are influenced by multiple emission sources. There are few aromatic compounds, and a large number of compounds consistent with organosulfates and organonitrates suggesting a secondary nature. Many of the formulas appear in isoprene-derived oligomer KMD series, and the series are generally longer than the marine and biomass burning aerosols, and shorter than the urban aerosols. This could indicate a moderate amount of processing, or that removal processes are more influential. Most of the compounds participate in reactions with inorganic species, much like the urban and biomass burning aerosols. These aerosols display the lowest fluorescence intensity, consistent with the lowest measured aromatic content. The fluorescent peaks observed share similarities with those found in the biomass burning and urban aerosols, and are indicative of humic material. This humic material appears to be widespread among numerous aerosols, and not just the ones in this study, indicating their persistence and importance to the light-absorbing properties of aerosol OM.

Collectively these analyses allow for the verification of the proposed hypotheses: 1) aerosols containing substantial amounts of highly-aromatic organic compounds will correspond to stronger light-absorbing properties, and 2) there are source-dependent patterns of chemical structure that can provide a specific molecular signature for each key emission source. The biomass burning aerosols contained substantially more aromatic and condensed aromatic compounds, serving as potential chromophores. Substantially
increased fluorescence intensity was observed for these aerosols, and drastically lower fluorescence intensity was observed the aerosols from other sources that have substantially less aromatic moieties. Fluorescence intensity is a proxy for light-absorbing ability, and the biomass burning OA absorbs more light on a per carbon basis indicating they make the largest contribution to positive radiative forcing (i.e., warming). The unique fluorescent features identified by EEMs indicates emission source and secondary atmospheric processing each play a critical role influencing fluorescence properties.

Key molecular characteristics were identified for each of the principal emission sources, and the mixed source aerosols shared many of the key characteristics indicating contributions from numerous sources. Aromaticity, nitrogen content, and extent of aging reactions were among the most important distinguishing features for these aerosols.

The atmosphere is a highly dynamic system, and the molecular features identified in these aerosols represent only a snapshot of the true chemical complexity. Atmospheric aging reactions rapidly form and transform OA, and it is important to understand the molecular composition as well as the processes that chemically alter these aerosols to assess their net impacts. While this study provides important qualitative advancements in OA characterization, it also indicates the need for further studies.

2 Future work

The research presented here offers many logical extensions for future studies. The most intriguing study involves pairing the methods presented in this study with aerosol mass spectrometry (AMS). AMS offers high time resolution and provides measurements for low-molecular weight OM (e.g., isoprene) as well as inorganic species and black carbon. The methods presented in this study provide incredible mass resolution and offer
molecular information regarding the high-molecular weight OM, believed to be largely responsible for the light-absorbing nature of OA. Pairing of these techniques would offer new insights into the changes occurring to OA, allowing for a more direct link between the atmospheric transformations that are responsible for ambient OA. This approach would provide a more accurate representation of OA than do current model SOA studies.

Another intriguing study would involve the direct manipulation of these aerosol samples to investigate how the molecular and fluorescence properties change upon exposure to an atmospherically relevant process, such as photoirradiation. I speculate that the aromatic nitrogen compounds found in the biomass burning aerosols are labile, and photooxidation is a process known to decompose aromatic species. Additionally, there are many compounds present in each of the sources with shared fluorescence features, which I expect represent more refractory OM. It is believed that biomass burning aerosols play a significant role in all terrestrial environments, and monitoring the specific molecular changes would establish whether there is a direct connection between the molecules identified in the biomass burning aerosols and those present in other sources.
REFERENCES


Matos, J., Freire, S., Duarte, R., and Duarte, A.: Natural organic matter in urban aerosols: Comparison between water and alkaline soluble components using excitation–
emission matrix fluorescence spectroscopy and multiway data analysis, Atmos. Environ., 102, 1-10, 2015.


APPENDIX A

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# APPENDIX B

## ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H NMR</td>
<td>Proton nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>AImod</td>
<td>Aromaticity index (modified)</td>
</tr>
<tr>
<td>ASOM</td>
<td>Acetonitrile-soluble organic matter</td>
</tr>
<tr>
<td>BC</td>
<td>Black carbon</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CCN</td>
<td>Cloud condensation nuclei</td>
</tr>
<tr>
<td>CRAM</td>
<td>Carboxylic-rich alicyclic molecules</td>
</tr>
<tr>
<td>CTO-375</td>
<td>Chemothermal oxidation at 375°C</td>
</tr>
<tr>
<td>D</td>
<td>Deuterium</td>
</tr>
<tr>
<td>Da</td>
<td>Daltons</td>
</tr>
<tr>
<td>DBE</td>
<td>Double bond equivalent</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
</tr>
<tr>
<td>EEMs</td>
<td>Excitation emission matrix spectroscopy</td>
</tr>
<tr>
<td>Em</td>
<td>Emission wavelength</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray ionization</td>
</tr>
<tr>
<td>Ex</td>
<td>Excitation wavelength</td>
</tr>
<tr>
<td>FTICR</td>
<td>Fourier transform ion cyclotron resonance</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HULIS</td>
<td>Humic-like substances</td>
</tr>
<tr>
<td>KM</td>
<td>Kendrick mass</td>
</tr>
<tr>
<td>KMD</td>
<td>Kendrick mass defect</td>
</tr>
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</table>
LAC: Light-absorbing carbonaceous aerosols
MACR/MVK: Methacrolein and methyl vinyl ketone
MS: Mass spectrometry
m/z: Mass-to-charge ratio
N: Nitrogen
NMR: Nuclear magnetic resonance spectroscopy
NOx: Nitrates
O: Oxygen
OA: Organic aerosols
OC: Organic carbon
OM: Organic matter
P: Phosphorus
PAH: Polycyclic aromatic hydrocarbons
PC: Principal component
PCA: Principal component analysis
PPL: A solid-phase extraction resin
ppm: parts per million
PSOM: Pyridine-soluble organic matter
QM/A: Quartz microfiber filter
RU: Raman units
S: Sulfur
S/N: Signal-to-noise ratio
SOA: Secondary organic aerosol
SOx: Sulfates
TC: Total carbon
TSP: Total suspended particulates
UHR: Ultrahigh-resolution
US EPA: United States Environmental Protection Agency
UV: Ultraviolet radiation
WIOM: Water-insoluble organic matter
WIOM$_{acen}$: Water-insoluble organic matter, acetonitrile-soluble
WIOM$_{pyr}$: Water-insoluble organic matter, pyridine-soluble
WSOC: Water-soluble organic carbon
WSOM: Water-soluble organic matter
WSOM$_{PPL}$: Water-soluble organic matter that has been PPL extracted
Figure S1. Kendrick mass defect (CH$_2$) plot for formulas identified at $m/z=427$ in Fig. 2, Chapter II. The different colors represent the different solvents, and the different shapes represent different formula types. A vertical line is drawn to highlight $m/z=427$. 
**Figure S2.** The percentage of molecular formulas sorted by measured mass defect (the decimal value of the measured $m/z$) for each of the solvents.
Table S1. Percent area contributions from the major proton regions and calculated H/C ratios in $^1$H NMR spectra for aerosol PSOM.

<table>
<thead>
<tr>
<th>Aerosol source (Collection date)</th>
<th>Functional group region (chemical shift)</th>
<th>H-C-O (3.2 – 4.4 ppm)</th>
<th>H-C-C= (1.95 – 3.2 ppm)</th>
<th>H-C (0.7 – 1.95 ppm)</th>
<th>Calculated H/C</th>
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</thead>
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<tr>
<td>Mixed source (16 – 17 August 2011)</td>
<td></td>
<td>2.5</td>
<td>18.3</td>
<td>78.8</td>
<td>1.98</td>
</tr>
<tr>
<td>Mixed source (24 – 25 June 2013)</td>
<td></td>
<td>2.5</td>
<td>21.0</td>
<td>76.0</td>
<td>1.98</td>
</tr>
<tr>
<td>Mixed source (25 – 26 June 2013)</td>
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<td>6.4</td>
<td>25.5</td>
<td>67.0</td>
<td>1.94</td>
</tr>
<tr>
<td>Biomass burning (21 August 2011)</td>
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<td>1.5</td>
<td>15.8</td>
<td>82.7</td>
<td>1.99</td>
</tr>
<tr>
<td>Biomass burning (24 – 25 August 2011)</td>
<td></td>
<td>2.6</td>
<td>17.3</td>
<td>80.2</td>
<td>1.98</td>
</tr>
<tr>
<td>Urban (4 – 5 August 2014)</td>
<td></td>
<td>5.4</td>
<td>19.5</td>
<td>75.1</td>
<td>1.95</td>
</tr>
<tr>
<td>Urban (5 August 2014)</td>
<td></td>
<td>4.7</td>
<td>22.7</td>
<td>72.5</td>
<td>1.96</td>
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<tr>
<td>Urban (5 – 6 August 2014)</td>
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<td>5.5</td>
<td>22.2</td>
<td>72.2</td>
<td>1.95</td>
</tr>
<tr>
<td>*Urban (6 August 2014)</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Urban (6 – 7 August 2014)</td>
<td></td>
<td>5.0</td>
<td>22.5</td>
<td>72.6</td>
<td>1.96</td>
</tr>
</tbody>
</table>

*Not determined.
**Figure S3.** Raw UV-visible spectra for aerosol WSOM. Absorbance units are carbon normalized and line color varies by aerosol source, indicated by the legend.
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