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ORGANIC TRACER ANALYSES AND RECEPTOR MODELING OF PM$_{2.5}$ IN FAIRBANKS, ALASKA

By

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Thesis

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Abstract

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Organic Tracer Analyses and Receptor Modeling of $PM_{2.5}$ in Fairbanks, Alaska

Chairperson: Christopher Palmer

Co-Chairpersons: Garon Smith, Tony Ward

Ambient particulate matter (PM) levels are of great importance to many areas around the world for both environmental and health concerns. It is well known that many sources of PM are anthropogenic in nature, including sources such as the combustion of petroleum products and wood. As per the Clean Air Act of 1970, the US EPA has established a National Ambient Air Quality Standard (NAAQS) of $35 \mu g/m^3$ for a 24 hour average and $15 \mu g/m^3$ for an annual average of ambient $PM_{2.5}$ to improve the quality of air and reduce occurrences of respiratory illness resulting from exposure to high levels of $PM_{2.5}$.

Fairbanks, the largest city in the interior of Alaska, experiences harsh winters with prolonged temperature inversions and calm winds. Due to these factors, there is an accumulation of PM in the valley, resulting in regular violations of the 24 hour NAAQS during the winter and thus in the Fairbanks North Star Borough area being considered a nonattainment area for $PM_{2.5}$ by the US EPA. Previous chemical mass balance (CMB) studies have shown that the majority of the Fairbanks wintertime $PM_{2.5}$ is from residential wood combustion. But these CMB studies also identified a relatively high fraction (up to 20%) of sulfate of unspecified origin.

The goal of this work is to paint a clearer picture of the sources of the $PM_{2.5}$ problem in Fairbanks, AK with a focus on the potential sources of sulfate. This is achieved by quantifying select organic species (hopanes, steranes, picene, and thiophenes) in Fairbanks $PM_{2.5}$. These compounds have been reported to be found in emissions from combustion of various fossil fuels. The measured chemical composition of Fairbanks $PM_{2.5}$ is compared to reported composition for $PM_{2.5}$ in other air sheds and to published source profiles. Several fuels received from Fairbanks were analyzed as well for the selected chemical markers in an effort to identify potential sources of these markers.

Fairbanks $PM_{2.5}$ was found to contain relatively high levels of all of the markers analyzed. Comparisons of the chemical composition of Fairbanks $PM_{2.5}$ to other air sheds and to source profiles revealed that Fairbanks $PM_{2.5}$ is heavily impacted from fossil fuel use. Thus, while it remains clear that Fairbanks $PM_{2.5}$ is impacted predominantly by wood smoke from residential heating, it is now also clear that fossil fuel combustion is a major contributor. High levels of picene indicate a significant contribution of coal combustion, while high levels of thiophenes very likely indicate a significant contribution from no. 2 fuel oil combustion. High levels of select organo-sulfur compounds in no. 2 Fuel oil suggest that this fuel used in Fairbanks for residential heating and power production is very likely a significant source of the sulfate.

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List of Acronyms

AA	abietic acid
BNT	2,3-benzo-[b]-naphtho[1,2d]-thiophene
BSTFA	N,O-bis (trimethyl-silyl) trifluoro-acetamide
CMB	chemical mass balance
DBT	dibenzo-thiophene
DEC	Department of Environmental Conservation
DHAA	dehydro-abietic acid
DRI	Desert Research Institute
EPA	Environmental Protection Agency
EtOAc/TEA	3.6mM triethyl-amine in ethyl acetate solution
GC-MS	gas chromatography mass spectroscopy
HSDF	high-sulfur diesel fuel
ICP-AES	inductively coupled plasma atomic emission spectroscopy
LSDF	low-sulfur diesel fuel
NAAQS	National Ambient Air Quality Standard
OC/EC	organic carbon to elemental carbon ratio
PAH	poly-cyclic aromatic hydrocarbons
PCA	principle components analysis
PM	particulate matter
ppm	parts per million
SASS	spiral ambient speciation sampler
TMCS	trimethyl-chloro-silane
TMSI	trimethyl-silyl-imidazole

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Chapter 1: Introduction

Chapter 1 Contents

1.1 Project Overview

Ambient particulate matter (PM) levels are of great importance to many areas around the world for both environmental and health concerns. Some consequences of high PM levels include upper respiratory illnesses (Slaughter 2003). It turns out that the majority of the health concern with PM is with the presence of fine particles that are 2.5µm in diameter or less ($PM_{2.5}$).

It is well known that many sources of PM are anthropogenic in nature (Section 2.5). Such anthropogenic sources include the combustion of petroleum products and wood. As such, it has been observed in numerous air sheds that the ambient PM levels are increased in areas that have heavy automobile traffic, significant coal burning as well as residential heating amongst other sources. Considering that residential heating is a significant source of PM, it is expected that PM levels are greatly increased during the winter months. Indeed, this is the case in areas that experience cold winters where use of wood and/or fuel oil for residential heating is abundant.

Fairbanks, the largest city in the interior of Alaska and second largest in the state behind Anchorage, experiences winters with temperature averages as low as $-28^{o}C$ ($-19^{o}F$) during the months of December and January. Fairbanks also sits in a mountain valley that experiences prolonged temperature inversions and calm winds during these months. Due to these factors, Fairbanks exhibits very high levels of ambient $PM_{2.5}$ during the winter months. As discussed later, Fairbanks often exceeds the 24 hour National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ of $35µg/m^3$ during the winter months. It is believed that the major source is residential wood combustion. Studies are currently underway to identify and quantify the most influential sources of PM to the total PM in Fairbanks, AK. If these sources can be correctly identified a plan may be put into place to decrease the $PM_{2.5}$.

The goal of this work is to paint a clearer picture of the sources of the $PM_{2.5}$ problem in Fairbanks, AK by quantifying select organic species in the $PM_{2.5}$ reported to be found in emissions from anthropogenic sources. This is done by comparing the $PM_{2.5}$ components in Fairbanks to those found in other air sheds. Several fuel samples received from Fairbanks were also analyzed for select chemical markers, and the implications of levels of select markers to that found in Fairbanks PM is discussed.

1.2 Chapter Summaries

The following sections in the remainder of this chapter are brief descriptions of the content of each chapter found in this thesis.

1.2.1 Chapter 2: PM Overview, Summary

Chapter 2 is an overview of PM related topics. The chapter begins by discussing the health effects of PM, which are the main reasons for concern regarding ambient PM levels. Next, PM composition is discussed and why PM is classified by size rather than composition. The effects of weather on PM concentrations, especially how extended inversion events during the winter months result in elevated levels of $PM_{2.5}$, are presented. This is followed by a presentation of air quality regulations, specifically the Clean Air Act. The remainder of the chapter focuses on the anthropogenic sources of PM and specific chemical markers that can be utilized for source apportionment.

1.2.2 Chapter 3: Fairbanks Background, Summary

Chapter 3 discusses some of the details of the town of Fairbanks, AK. Particularly, geographical details, meteorological statistics, population size and why $PM_{2.5}$ is of such concern to Fairbanks.

1.2.3 Chapter 4: Fairbanks PM and Comparisons, Summary

Chapter 4 is considered to be the “heart” of this thesis; some of the $PM_{2.5}$ work that has already been conducted in Fairbanks is discussed. Within Chapter 4 $PM_{2.5}$ sampling methods and locations as well as the types of analyses that were conducted are described. The chemical mass balance (CMB) model and how it uses inorganic PM data coupled with source profiles and how it assists in source apportionment work as well as supplemental information obtained from select organic marker analyses is discussed.

The chapter then presents comparisons of Fairbanks PM composition to that found in various source profiles as well as other air sheds in order to possibly further illustrate what exactly is causing the high levels of $PM_{2.5}$ during the winter months in Fairbanks. Next, the analyses performed on various fuel samples received from Fairbanks and the results are discussed. Lastly, conclusive remarks, based upon the comparisons of Fairbanks $PM_{2.5}$ to source profiles and PM compositions in other airsheds and the sulfur content of the fuel samples, are presented.

1.2.4 Chapter 5: Analysis of $PM_{2.5}$ for Select Markers: Method Development, Summary

Chapter 5 discusses the methods developed by the author for select organic chemical markers based upon those previously reported in the literature as well as the analyses performed on the fuels received in Fairbanks in detail. Lastly, instrument parameters and how quantification is achieved by using the described solvent extraction gas chromatography mass spectroscopy (GC-MS) method and the use of deuterated standards is discussed.

1.2.5 Chapter 6: Future Directions, Summary

Chapter 6 discusses possible future directions that may be informative in the determination of the sources of the relatively high levels of $PM_{2.5}$ in Fairbanks, specifically two alternate models as well as additional source profiles to be employed in current models. Both of the alternate models correlate various meteorological parameters to Fairbanks $PM_{2.5}$ data. The first model is a principle components analysis (PCA) approach that groups various meteorological parameters into categories that may or may not have physical significance which can then be correlated to individual source markers found in Fairbanks $PM_{2.5}$. The second model investigates the adiabatic lapse rates of a parcel of air that may contain $PM_{2.5}$ and compared to the actual temperature gradient in Fairbanks as a means to determine the height of an inversion boundary.

Chapter 2: Particulate Matter Overview

Chapter 2 Contents

2.1 Health Effects of PM

PM can have a significant impact on communities in areas which have increased level of PM in the ambient air. PM is generally categorized as being either coarse or fine; however we are not as concerned with the coarse particles as the fine particles. Coarse particles (PM_{10}) are not typically associated with long term health effects from PM and often act as irritants to the eyes, nose and throat. These symptoms are easily remedied by going indoors if there is sufficient ventilation (Hystad 2009). However, fine particles ($PM_{2.5}$) can have serious health effects; they can reach fully into the lungs where they can instigate systemic inflammatory and oxidative stress responses and where chemical components may eventually make their way into the bloodstream. It has been shown that $PM_{2.5}$ can affect both the heart and lungs. Those of who are at the greatest risk are children (developing lungs, higher activity levels), elderly (may have undiagnosed heart or lung disease) and those who have diagnosed lung or heart diseases (Slaughter 2003). $PM_{2.5}$ can act as a serious agitator for coronary heart disease, congestive heart failure and asthma to name a few (Slaughter 2005), which can lead to decreased lung function. Short-term exposure can lead to asthma attacks, acute bronchitis and increased susceptibility to respiratory illness.

2.2 PM composition and classifications

PM is a mixture of compounds that become suspended in the air in a condensed phase. PM can originate from either a natural or anthropogenic source, giving rise to a complex chemical mixture. This mixture is composed of numerous inorganic and organic components.

The inorganic components include varying oxidative states of nitrates, sulfates (Section 4.2.1) and, generally crustal-derived, species such as phosphate, sodium, potassium, calcium, magnesium and silicon (Schlesinger 2007). The organic components consist of numerous involatile and semi-volatile compounds (sVOC). The organics cover a very broad spectrum of organic species such as poly-cyclic aromatic hydrocarbons (PAHs), alkanes, olephins, carboxylic acids, alcohols, amines and sulfides (Amador-Munez 2007). Many who have performed analyses of the organic composition have categorized the individual compounds into fractions separated by solubility properties (Murillo-Tuvar 2010). The exact inorganic and organic species composition of the $PM_{2.5}$ can give information on the sources if source profiles are available.

Because of this complexity as well as the health consequences of the fine particulate, it is often convenient to categorize PM by size rather than composition. The 2 categories that are of interest are the following: fine particles which are less than 2.5 µm in diameter ($PM_{2.5}$) and coarse particles which include all PM that is 10 µm or less in diameter (PM_{10}). In this work the $PM_{2.5}$ fraction is of particular interest primarily for its health consequences and regulations imposed by the US EPA. It should be noted that only the $PM_{2.5}$ data was of concern to this work and that $PM_{2.5}$ was selectively collected (Section 4.1.1).

2.2.1 Sulfate Aerosols

As discussed later in detail in Section 4.1.2, a CMB model was used to assist in the source apportionment of Fairbanks $PM_{2.5}$. The CMB model returned the result of sulfate being a significant contributor to the total mass of Fairbanks $PM_{2.5}$, up to 20% in the downtown area. It is now relevant to discuss the possible sources of sulfate that can be found in PM.

Sulfate aerosols have numerous sources in the environment, both natural and anthropogenic. Sulfate aerosols are commonly referred to as “secondary sulfate”, implying that they were formed from some precursor gas or particulate within the atmosphere. Sulfates are common in the PM in areas that have high levels of air pollution from fossil fuel usage. Natural sources of precursor gases that oxidize to sulfate aerosols include di-methyl sulfide from marine life, hydrogen sulfide from various bacteria and sulfur dioxide from volcanic activity (Chimonas 2007), none of which are applicable to Fairbanks.

Sulfur dioxide, a precursor gas to secondary sulfate (Devitofrancesco 1987), is characteristic of fossil fuel combustion, particularly that of coal (Hinneburg 2009; Wen 2009). It is not suspected that sulfate aerosols in Fairbanks originate from gasoline and diesel fuel emissions because these fuels are treated for the removal of sulfur content before consumer use.

2.3 Clean Air Act

It has been recognized for more than half a century that many anthropogenic pollutants in the air can have detrimental effects to human health (Section 2.1). In order to reduce the influence of such pollutants, the Clean Air Act was established in 1970 and has been amended several times since; 1977, 1990 and 2008 (epa.gov). The Clean Air Act is the comprehensive federal law that regulates air emissions from stationary and mobile sources. Among other things, this law authorizes EPA to establish National Ambient Air Quality Standards (NAAQS) to protect public health and public welfare and to regulate emissions of hazardous air pollutants.

The Clean Air Act has established two sets of air quality standards, primary and secondary standards. Primary standards are intended to reduce the pollutants shown to be harmful to human health, especially those at elevated risk; asthmatics, children and elderly. Secondary standards are intended to protect public welfare such as visibility, damage to buildings, animals and vegetation. Furthermore, individual pollutants must meet NAAQS for different sampling time frames, such as 1 hour, 24 hours or annual average (epa.gov).

Of particular interest to this work, and similar $PM_{2.5}$ studies in the United States, are the primary NAAQS for $PM_{2.5}$ which are currently 15.0 $\mu g/m^3$ for the annual average standard and 35$\mu g/m^3$ for the 24 hour standard. Other regulated air-borne pollutants include carbon monoxide, lead, nitrogen dioxide, ozone and sulfur dioxide. The full Clean Air Act document and revisions can be found as public information on the US EPA's website (epa.gov).

2.4 Weather effects on PM concentrations

On inspection of the anthropogenic sources discussed later in Section 2.5, one might expect the levels of PM to increase in the winter due to residential heating, and indeed this is often the case. As expected for such cases, the PM levels are at their maximum during winter months. These issues can then be further compounded by weather effects, such as inversions.

Temperature inversions, which are common to mountain valleys, are characterized by an increase in air temperature with height above the surface. An inversion layer is the air mass above the surface in which the temperature inversion persists. Temperature inversions can act as a "cap" above the ground that result in the trapping and accumulation of pollutants, such as PM, in the stagnant air below the inversion boundary throughout their duration. This can then lead to these areas repeatedly exceeding the threshold established by the NAAQS (i.e. nonattainment area). Some examples of areas that experience inversions and are (or have been) above the annual or 24hr NAAQS for $PM_{2.5}$ (Section 2.3) are Libby, MT (Bergauff 2009) as well as more densely populated areas such as Missoula, MT and Fairbanks, AK.

Typically, temperature decreases with an increase in altitude at the rate of approximately $-6.4^{o}C$ per kilometer ($-3.5^{o}C$/1000 feet) in a stable air mass. Stable air masses allow for air parcels to disperse and if the parcel contains any pollutants, such as PM, the pollutants will disperse as well (Gymer 1977). A temperature inversion occurs when a warm body of air rests over a cool body of air, thus reversing the temperature gradient. Inversions are common to mountain valleys where winds can push down cold air from mountain tops into the underlying valley where the more dense cold air is trapped below less dense warm air for long periods of time. Also, in areas of high latitude, such as Fairbanks, due to the low angle of the sun on the horizon in the winter months the majority of heat from sunshine is conferred to the upper atmosphere and the surface is not warmed much, if at all (Bourne 2010; Rosenberg 2011). Additionally, cold air can sink into the valley at night. This can further increase the temperature differential of an inversion event.

As mentioned previously, the warm air can effectively restrict the movement of the cold air below during an inversion event. Pollutants emitted from sources such as wood smoke and fossil fuel combustion can be trapped in the valley resulting in an increase in their ambient concentrations (Figure 2.1). Areas that experience long inversion events and very little wind, such as Fairbanks, experience elevated pollution and PM levels during the winter months, when inversions are likely to occur (Section 3.2).

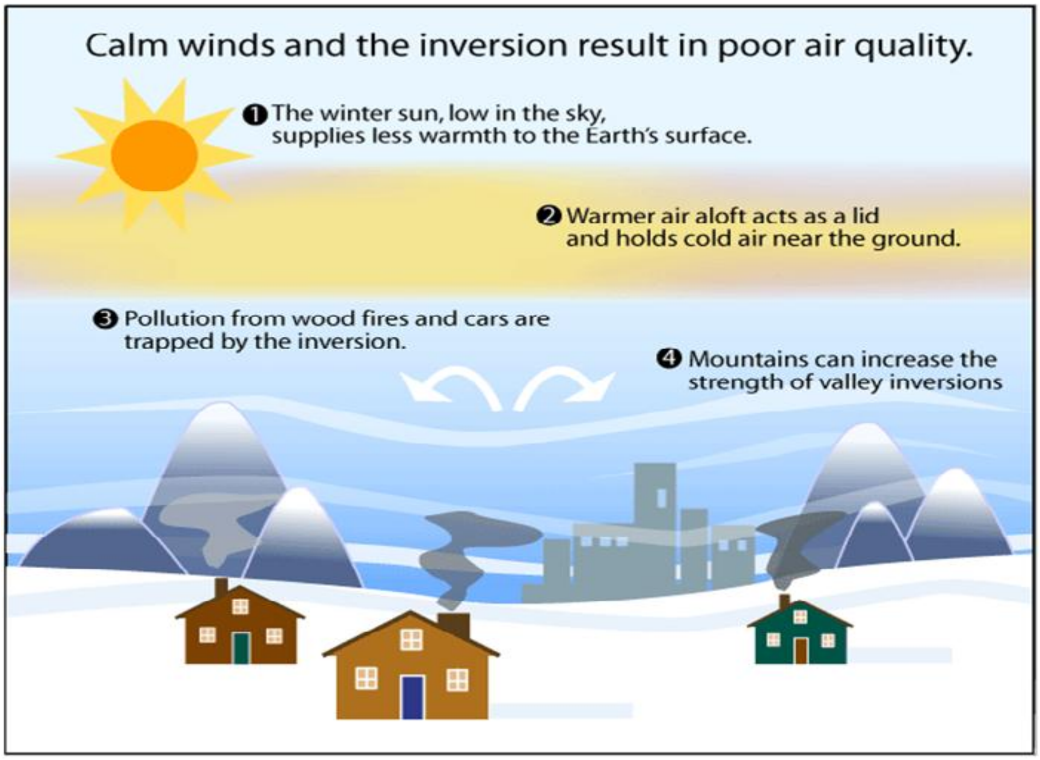


Figure 2.1: Effects of Inversion Events on Ambient Pollution
wrh.noaa.gov

2.5 Anthropogenic Sources of PM and Organic Chemical Markers

It is a well-known fact that the combustion of carbonaceous materials leads to measureable quantities of particulate matter (PM) in the atmosphere (Hays 2005). It is also known that the presence of PM in our local communities may have a significant impact to the health of the residents over time, particularly respiratory related illness (see Section 2.1). Natural sources such as dust in areas with limited vegetation, smoke from wild fires, volcanic activity and sea spray are known to have significant contribution to the total PM (Chimonas

2007). Nonetheless, we cannot expect to have full control on natural contributions to PM and, for regulatory purposes, place our concerns on anthropogenic sources.

Since the numerous mechanical advancements made during the Industrial Revolution, our society has become completely dependent on a cheap and reliable source of fuel for a vast number of processes (Haelssig 2011). With current technology, fossil fuels fit this role perfectly, despite the impacts to the environment resulting from their use. Because of these economic consequences, the consumption of carbonaceous materials has become an absolute necessity for our society to function. Many are investigating alternative means for energy generation but none have come close to both the cost and accessibility of fossil fuels.

However, industrial uses of carbonaceous fuels are not the only anthropogenic PM source; another source of PM that plays a significant role in PM concentrations found in the atmosphere is residential heating. The four main fuels employed for residential heating are no.2 fuel oil, wood, electricity and natural gas. However, neither electric heating devices nor natural gas heaters are significant a source of local PM (Steiber 1991) and therefore were not investigated in this work. The emissions from combustion of both wood and petroleum products (including no. 2 fuel oil) are well known for producing significant quantities of PM (Schauer 2002; Rogge 1997).

Upon investigation of various PM source emission profiles it becomes clear that certain organic species may be useful in the source apportionment of $PM_{2.5}$ (Schauer 1999, Schauer 2002, Hays 2002). It is useful to categorize the numerous species investigated by their chemical classification and source.

The sources of each chemical species used as a chemical marker and industrial uses of similar/related materials are discussed below in their corresponding sections.

2.6 Wood Composition and Chemical Markers for Wood Smoke

Unprocessed wood is a substance consisting of a lignin matrix containing various celluloses, waxes, resins, tannins and terpenes (Steiber 1991). Of interest to PM source marker analyses are lignin, cellulose and resins and their associated combustion products. In this section the sources of each chemical marker (from the un-combusted fuel) found in PM emissions, their usefulness as a chemical marker, as well as industrial applications of materials is briefly discussed.

2.6.1 Lignin: Methoxy-Phenols

Lignin, being one of the most abundant organic polymers on earth, does not have a distinct structure and reported structures of lignin are often theoretical. Below in Figure 2.2 is the proposed structure for lignin found in European beech (Tiaz 2011).

Looking at this particular structure of lignin it is apparent that there are many methoxy-phenolic groups present. Upon combustion, the mass is decomposed and its components are released and often oxidized.

Consequently, some methoxy-phenols, such as vanillin below in Figure 2.3, may be useful in source marker analyses for wood smoke. Indeed vanillin has been used in analyses of PM found in areas that contain large amounts of biomass burning such as wood (Bergauff 2009).

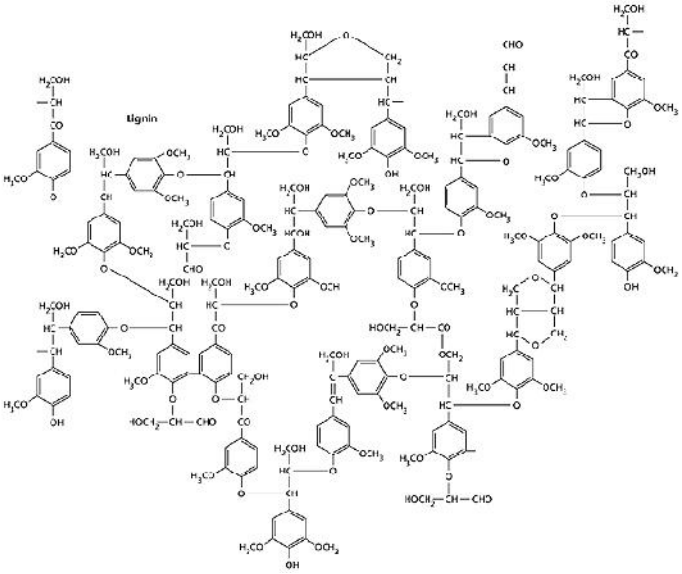


Figure 2.2: Hypothetical Structure of Lignin in European beech
http://5e.plantphys.net

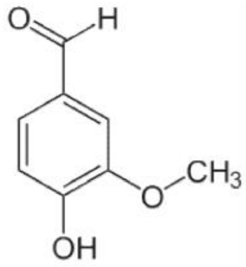


Figure 2.3: Vanillin

However, it should be noted that the presence of lignin is not unique to wood and is present in all plant life. Lignin is an integral part of the cell walls of plants and some algae; it serves to fill the spaces between cellulose, hemicellulose and pectin components. It is covalently cross-linked to different polysaccharides conferring mechanical strength to the cell walls of plant cells, thus to the entire plant mass (Lebo 2001). Because vanillin is not unique to wood, vanillin and any other methoxy-phenols should not be used as the sole marker for wood smoke, and should only serve as additional information to be used in conjunction with additional, preferably more unique, markers.

2.6.2 Cellulose: Sugar Anhydrides

Cellulose, the most abundant organic compound in the world, composes approximately 33% of all plant matter. Cellulose is most commonly used industrially in paper production and is often extracted from either wood pulp or cotton (Xu 2011). It also has many other industrial applications such as the production of cellophane and has also been used as an alternate fuel source to fossil fuels.

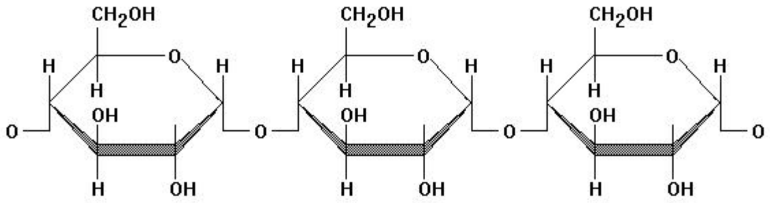
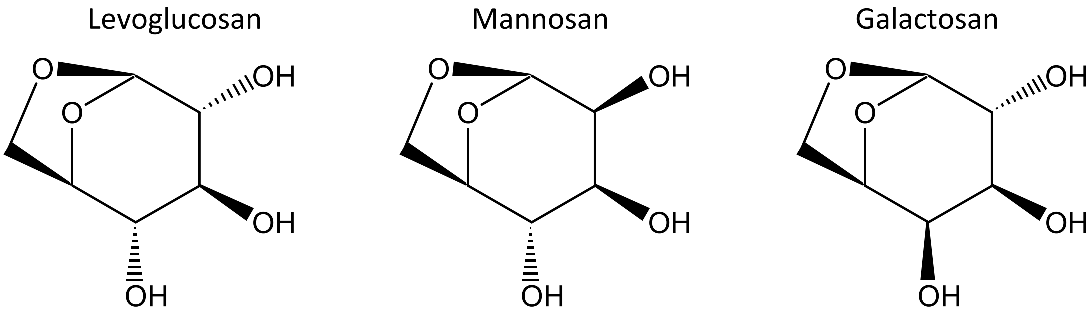


Figure 2.4: Cellulose Structure
Ohio-state.edu

Unlike lignin, the structure of cellulose is well known due to the fact that there is only one monomer unit present. Cellulose is a large organic polymer consisting of up to 10,000 β,D-glucose monomer units and is highly chiral. Cellulose is a straight chain polymer; however it tends to be crystalline due to the large number of hydrogen bonds that occur upon stacking individual polymer chains. The exact identity of various different cellulose crystals, as well as physical properties, is determined by the degree of polymerization as well as the locations and the number of hydrogen bonds present. Upon combustion of cellulose the β,D-glucose monomer units are released and oxidized to several possible sugar anhydrides.


Levoglucosan Mannosan Galactosan

<u>Figure 2.5</u>: Sugar Anhydrides

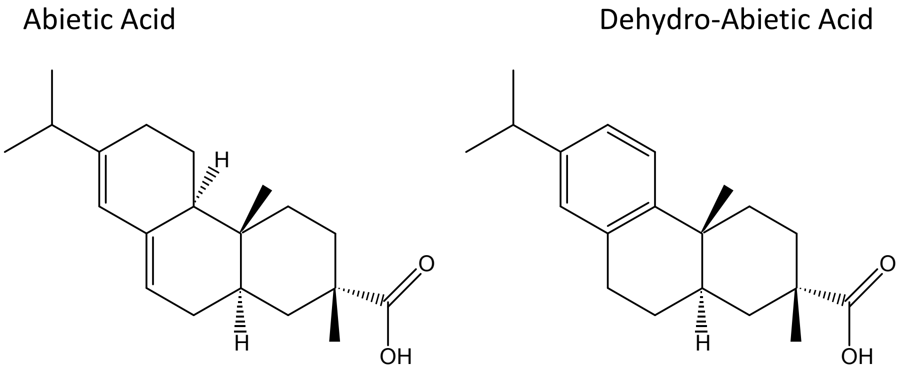
The term sugar anhydrides used here does not imply the presence of anhydride functionality. It is instead referring to the loss of a hydrogen atom from a hydroxyl group upon formation of the ether linkage in the bridgehead of the structure. Note that each of the sugar anhydrides shown above has the exact same absolute structure. Thus they all share the IUPAC name of β,D-glucopyranose and have very similar physical and chemical properties. However, the main difference between them is in the orientation of the chiral hydroxyl groups making them diastereomers. Conveniently, this difference in chirality confers slight differences in net dipole moments to each sugar anhydride allowing for separations on a GC column.

Similar to vanillin, sugar anhydrides are not unique to wood smoke and are found in all biomass burning emissions. However, levoglucosan tends to be found in significant levels in wood smoke compared to the other diastereomers mannosan and galactosan (Kuo 2011). Therefore, levoglucosan is often used as the primary marker for wood smoke emissions because it is fairly unique to wood smoke and is in much larger abundance then the unique wood smoke markers (see below) abietic acid and dehydro-abietic acid.

2.6.3 Resin Acids

The last group of interest concerning wood composition is resins. Resin is a hydrocarbon secretion of many plants, particularly coniferous trees (Hafizoglu 1997). It is used widely industrially in the production of a large variety of materials such as varnishes, adhesives, incense, perfume and food glaze. Resins are also used as a source of raw materials for various organic syntheses. The word resin is commonly incorrectly used for materials that have similar physical characteristics, viscous, sticky liquids that readily solidify.

Unlike lignin and cellulose, resins are not a distinct class of compounds but rather a homogenous mixture usually containing terpenes. Resin act as a preservative for the wood, protecting it from decay and weather elements. Upon combustion, the PM from wood resin emissions contains quantitative amounts of the unique resin acids abietic acid (AA) and dehydro-abietic acid (DHAA) (Fine 2002). The structures of these two resin acids can be seen below in Figure 2.6.


Abietic Acid

Dehydro-Abietic Acid

<u>Figure 2.6</u>: Resin Acids

2.6.4 Levoglucosan as the Primary Marker for Wood Smoke

Initially, it may seem that a resin acid would be a better marker for wood smoke emissions because it is a more unique marker than either sugar anhydrides or methoxy-phenols. Unfortunately, they do not occur in all woods and occur in significantly lower concentrations; 1-10ppb for AA and 100-1000ppb for DHAA, where in comparison levoglucosan is found at the 50-100ppm level in areas below the NAAQS for $PM_{2.5}$ and as high as 3000ppm in non-attainment areas primarily impacted by wood smoke (Bergauff 2009). Like methoxy-phenols, the resin acids serve as supporting information on identifying wood smoke as a PM source and contribution to the total PM mass.

2.7 Fossil Fuel Composition and Chemical Markers

Fossil fuels are fuels formed by anaerobic decomposition of long dead organisms buried within the earth's crust. Fossil fuels include coal, petroleum products and natural gas (methane) and are considered a non-renewable energy source because they take upwards to 650 million years to form (Mann 2009). Since the beginning of the Industrial Revolution in the 1700s fossil fuels have become the primary method of energy production in the world, accounting for approximately 90% of the total energy production in the US (eia.gov).

Of interest to this work are the composition and sVOC emission markers for possible sources of sulfate. Thus, the composition and chemical markers of coal and petroleum products (diesel and gasoline fuels) are of interest. Similar to Section 2.6, the sources of selected chemical marker found in PM emissions from fossil fuel combustion, their usefulness as chemical markers, as well as industrial applications of materials is discussed.

2.7.1 Hopanes and Steranes

Because all fossil fuels essentially come from the same source there are significant similarities in the PM emissions from all fossil fuel sources. An example of these similarities is the presence of hopanes and steranes in all fossil fuel emissions (Andreou 2008).

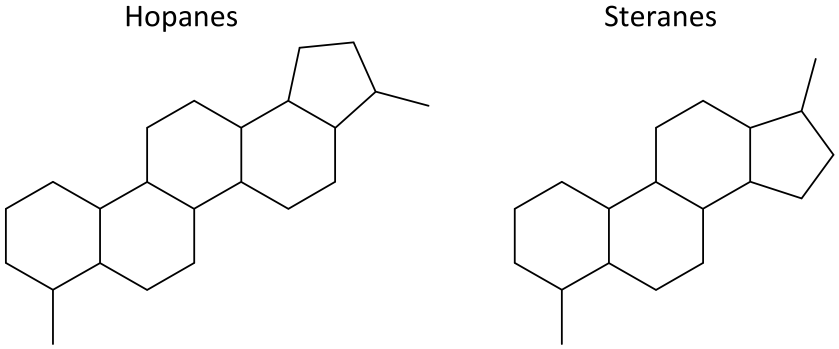


Figure 2.7: Hopanes and Steranes

Hopanes are penta-cyclic organic compounds that result from the combustion of hopanoids. Hopanoids serve several functions in the plasma membrane of cells in both prokaryotic and eukaryotic organisms such as conferring cellular rigidity and thus limiting the amount of oxygen that can permeate through the plasma membrane (Moreau 1997).

Steranes are buta-cyclic organic compounds that result from the combustion of steroids. Steroids serve an extremely vast amount of biological functions, specifically hormonal responses and metabolic processes. In any given plant, animal or fungi there is up to 100 different varieties of steroids present. Since hopanoids and steroids serve such a large variety of biological functions their associated combustion products, hopanes and steranes, are always found when analyzing the PM emissions from any fossil fuel source.

On a side note, it is likely that hopanes and steranes are precursors for the formation of PAHs in fossil fuel combustion reactions. PAHs are found in the PM from the combustion of most carbonaceous fuels and hopanes and steranes are found in the PM emissions of all fossil fuels (Andreou 2008). Reduction of the structures above in Figure 2.7 would result in PAHs.

2.7.2 Diesel Products: Thiophenes

In general, diesel fuel is any combustible liquid that can be used to operate a diesel engine. While it is not suspected that commercial diesel fuels are a large contributor to PM their PM emissions were investigated due to the similar compositions of diesel fuels and residential fuel oil (Perry 1984). However, in this work the PM emissions from biodiesel and synthetic diesel fuels were not investigated and the primary focus is placed on diesel products (commercial fuel and residential fuel oil) and gasoline as a source of thiophenes. Thiophenes are also of particular interest as they contain sulfur and may possibly be directly correlated to the sulfate content of $PM_{2.5}$.

In the past, diesel fuel contained very high levels of sulfur, but in more recent years it has been mandated in many nations that oil refineries dramatically lower the sulfur content of the commercial diesel fuels they produce. As a result, as of 2007 nearly all diesel fuels used for autos in the US, Canada and Europe are ultra-low sulfur diesel fuel. In fact, it was reported by the Alaska Department of Environmental Conservation that currently the commercial diesel fuel as well as gasoline used in Alaska contains less than 15ppm total sulfur (dec.state.ak.us).

Diesel distillate fractions are also commonly used for residential heating by means of an oil burner in place of a furnace in homes and are very similar in chemical composition to the fraction used for diesel fuel for automobiles. In fact, the words “diesel fuel” and “heating oil” are often used interchangeably. In particular, the fraction used for residential heating is number 2 fuel oil, where the fuel number is a grade based on viscosity and volatility. Both no. 2 oil and diesel fuel come from close fractions in the distillation of crude oil; diesel fuel is the 300^{o}C fraction and no. 2 oil is the 370^{o}C fraction (Perry 1984). Differences in molecular weight, alkane branching and functionality result in differences in volatility and viscosity. However, these differences can be summed up into one key difference, the number of carbon atoms found in the individual species of the distillate fraction. As expected, diesel fuel and no. 2 oil components have a similar amount of carbons; the diesel fuel fraction ranges from 8-21 carbon atoms and the no. 2 oil fraction ranges from 14-20 carbon atoms. It has been suggested (Steiber 1991) that the type of fuel combusted could possibly be identified by looking at both the smallest and the largest alkanes found in the emissions from an oil burner.

Since diesel fuel and no. 2 oil have similar properties they can be used interchangeably in diesel engines and oil burners. However, it is illegal in most areas to use no. 2 oil in place of diesel fuel for transportation for several reasons (Timkovich 2000). No. 2 oil is not taxed in the same manner as diesel fuel for transportation. Also, no. 2 fuel oil is not treated for consumer use in the same ways as diesel fuel, particularly regarding sulfur removal. To ensure both fuels are being used for their intended purposes, dyes are added to no. 2 oil. Often red or yellow/orange dyes are used giving rise to the term “red diesel” for no. 2 oil. Because of the decrease in taxation of red diesel it is authorized in many areas for agricultural use in farm vehicles/equipment as well as diesel autos as long as the diesel auto remains on the farm property and off any public roads or highways (Harvey 2011).

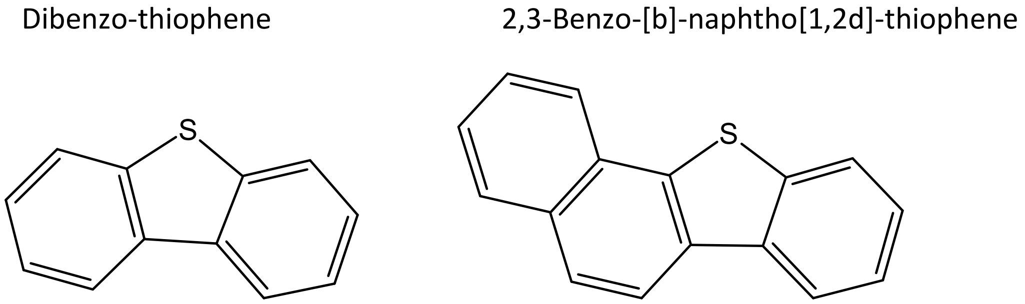
Even though diesel fuel and no. 2 oil have similar physical properties, the methods for combustion are vastly different. In an oil burner, the fuel is compressed under high pressures (by means of a pump) and forced through a spray nozzle (often mixed with air as well) into the combustion chamber where it is ignited by either a high voltage spark or a glow bar. It has also been shown (Steiber 2001) that no matter how well tuned an oil burner is there is always some of the raw fuel found in the emissions. It is believed that this raw fuel escapes when it is mixed with the air in the combustion chamber.

In contrast, diesel engines make use of high pressure. Air is first introduced into a cylinder where it is compressed by a piston. It is heated by high compression; the fuel is then introduced by a fuel injection system. The fuel is vaporized by the hot air and is ignited by the high temperatures rather than the spark plug found in most gasoline motors.

Sulfur emissions from fossil fuel combustion are of concern for health and environmental consequences (Su 2005). In fact, many efforts have been made to reduce sulfur emissions from automobiles (Shimizu 2011). As such, it may be useful to investigate the possibility of an organo-sulfur compound as a chemical marker. It was shown that a large fraction of the sulfur content, up to 30%, in the particulate of residential heating oil (Huffman 2000) as well as the un-combusted fuel (Hays 2008) is thiophenic. While it is known that there is a significant amount of thiophenic sulfur in all fossil fuels, there is a minimal amount of work in the literature regarding the speciation of thiophenic sulfur in both the particulate and the un-combusted fuel.

Thiophenes are not found in a large abundance in nature and they do not serve many industrial applications and are often found as contaminants of benzene and concentrated sulfuric acid solutions. Thiophenes in fossil fuels are likely to have formed from the alkylation of hydrogen sulfide gas emitted as part of the anaerobic decomposition of proteins within the earth's crust. Thiophenes exhibit a variety of applications as building blocks in agrochemicals and pharmaceuticals such as the NSAID lornoxicam (Swantson 2006).

The thiophenes that are found in the PM emissions of diesel products are often highly aromatic with several fused benzene rings and can be categorized as hetero-PAHs. Dibenzo-thiophene (DBT) and benzo-naphtho-thiophenes (3 possible isomers) and their alkylated derivatives have been shown to be a component of both the raw fuel and the combustion emissions PM of gasoline, diesel fuel and no. 2 oil (Huffman 2000, Liang 2006, Schauer 1999, Schauer 2002).


Dibenzo-thiophene

2,3-Benzo-[b]-naphtho[1,2d]-thiophene

<u>Figure 2.8</u>: Select Thiophenes

Because of the similarities in the composition of the PM and raw fuel it is difficult to distinguish between diesel fuel and no. 2 oil in regards to their contribution to the total PM. The contributions from gasoline can muddle the results further as DBT is found in the PM emissions as well. However, comparing multiple studies (Schauer 1999 and 2002, Liang 2006) suggests that 2,3-benzo-[b]-naphtho[1,2d]-thiophene (BNT) may be unique to diesel fuel or no. 2 oil emissions only (see Section 4.3.1B).

As mentioned previously, commercial diesel fuel contains less than 15ppm total sulfur. Therefore, it is unlikely that diesel fuel is a significant source of thiophenes.

2.7.3 Coal: Picene

Upon combustion of coal, as well as most carbonaceous fuels, significant amounts of poly-cyclic aromatic hydrocarbons (PAH) are found in the resultant particulate (Zhang 2008). While many of the PAHs found are not unique to coal and found in many carbonaceous fuels PM emissions, picene, in particular, is unique to coal emissions (Oros 2000). Picene is a 5-ring PAH and can be seen below in Figure 2.9.

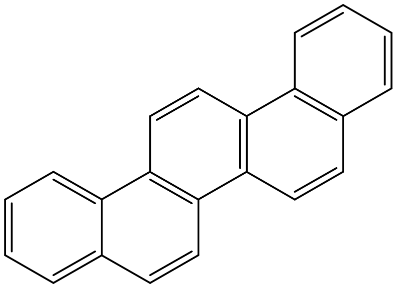


Figure 2.9: Picene

Given that picene is unique to coal, it is an ideal candidate for use as a chemical marker to assist in the source apportionment of PM. Interestingly, however, it has been reported that picene is notably absent in emissions from brown and mixed coal emissions from residential boilers (Zhang 2008). Additionally, it has been reported that C_2 substituted picenes are more specific markers for coal combustion than the un-substituted analogs (Oros 2000).

Even though picene does not contain a sulfur atom it can still be possibly linked to the sulfate content of $PM_{2.5}$ in areas where a significant amount of coal combustion occurs. It is well known that coal contains sulfur, albeit it is most likely elemental (Goodarzi 2002), which can result in sulfur dioxide emissions and the formation of secondary sulfate (Section 2.2.1). It has also been found in this work that the coal used in Fairbanks power production contains a significant amount of sulfur (Section 4.4.2).

Also, picene is believed to be formed during the combustion of coal, possibly from a hopane or sterane precursor, and is not found in the un-combusted fuel. As such, picene currently has no industrial applications.

2.8 Summary of Organic PM Source Markers

The compounds of interest to this work are several solvent extractable organic chemical markers and are believed to be markers for various anthropogenic sources of carbon and sulfur in our atmosphere. The chemical markers of interest can be classified into groups by sources and chemical classifications as indicated below in Table 2.1

Table 2.1: Summary of Organic Chemical Markers of PM Sources

PM Emission Source	Class	Identity
Wood	Sugar Anhydrides Methoxy-Phenols Resin Acids	Levoglucosan, Mannosan, Galactosan Vanillin Abietic Acid, Dehydro-abietic Acid
Fuel Oils	Thiophenes	DBT, BNT
Coal	PAH	Picene

Chapter 3: Fairbanks, Alaska Background

Chapter 3 Contents

3.1 Fairbanks, Alaska Overview

Fairbanks is the largest city in the interior of Alaska and second largest in the state behind Anchorage and has a population approximately 31,000 within the city limits and 98,000 in the Fairbanks North Star Borough (2009 US Census). The population of Fairbanks, AK has been increasing at the rate of 1,000-1,500 residents per year since 1980. Fairbanks is located in the Tanana Valley along the Chena River near its confluence with the Tanana River. North of the city there is a chain of hills that gradually rise to the White Mountains. South from the city is the Tanana River and the Tanana Flats. The Tanana Flats is a marsh land that extends for 100 miles and rises into the Alaska Range. These two mountain ranges (White Mountains and Alaska Range) result in Fairbanks sitting in a partially enclosed mountain valley, which can be seen below in Fig. 3.1.

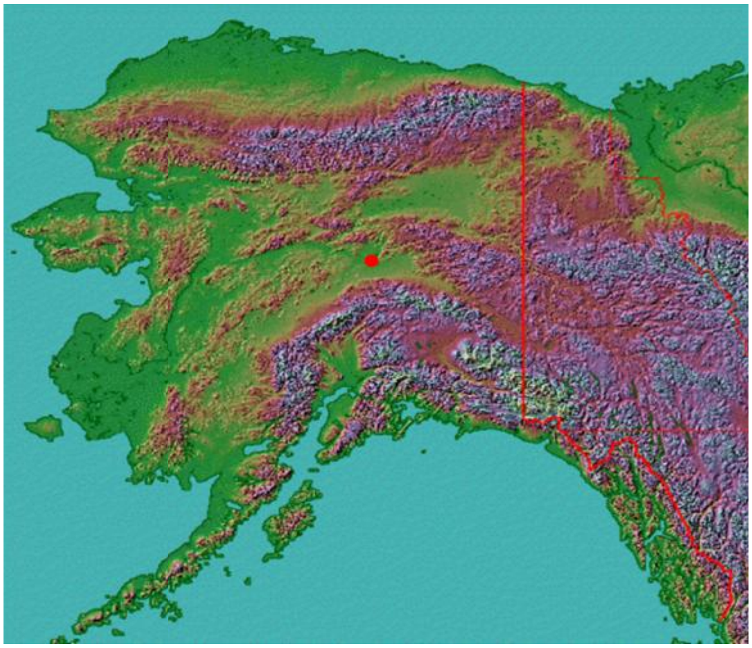


Figure 3.1: Alaska Topography
Fairbanks is indicated by the red dot found in central Alaska
workingnet.com

3.2 Fairbanks Weather

The climate in Fairbanks has been classified as subarctic (Murray 2009) with long and extremely cold winters and brief, but warm, summers. Winters typically last from late September to early May. Of particular interest are the abnormal lows found in Fairbanks during the winter months. Average winter low temperatures range from -15^{o}F (-26^{o}C) to -25^{o}F (-32^{o}C) with record lows of -60^{o}F (-51^{o}C) (Mowry 2009). Fortunately for the people of Fairbanks, there are little to no winds within the city itself. Several factors lead to the extreme cold conditions found in Fairbanks. Cold air accumulates in the Tanana Valley while warm air is pushed upwards towards the White Mountains. Also, heating from the sun is limited during the winter months due to its high-latitude position, Fairbanks experiences 21 hours of direct daylight between May 10th and Aug. 2nd each summer, and less than 4 hours of daylight between Nov. 18th and Jan. 24th each winter (Wendler 1975).

Because of these factors, and various other meteorological anomalies, it is believed that Fairbanks experiences some of the harshest temperature inversions in the world (Rozel 2004). Often times Fairbanks experiences high levels of PM as well as ice fog (fog that contains suspended fine particles of ice). An example of a typical inversion in Fairbanks can be seen below in Fig. 3.2. Notice how the sky is practically clear of clouds and that there is a significant amount of haze settling in the valley. Also notice that it appears that the emissions from a coal-powered plant are being emitted above the low-lying inversion. Low-lying inversions are typical in Fairbanks and for this reason it has been argued that coal emissions from tall stacks are of minimal contribution to Fairbanks $PM_{2.5}$. However, it is shown later in this work (Section 4.3.2C) that this may not be the case.

Figure 3.2: **Fairbanks Winter Temperature Inversion**

3.3 Residential Heating and Diesel Products

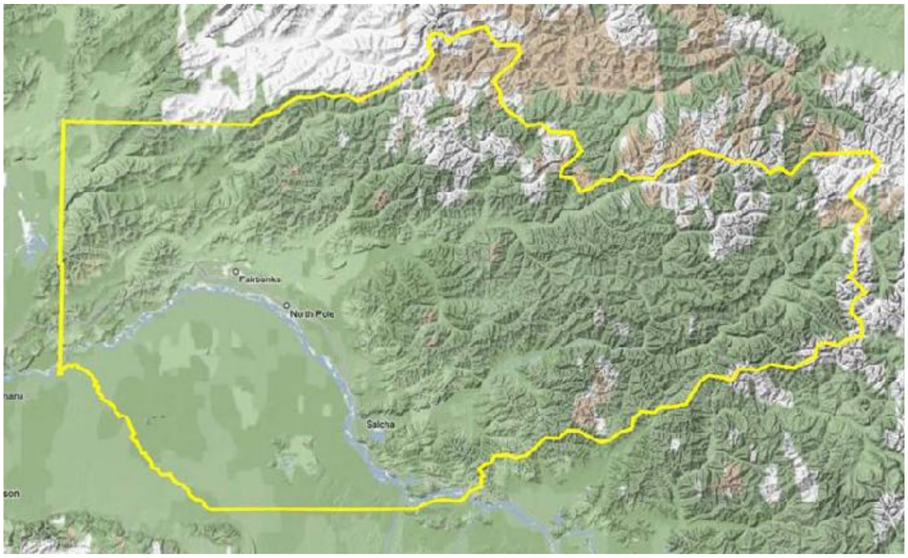
Since Fairbanks experiences such harsh winter conditions; residential and commercial heating are of great concern to the people of Fairbanks. One of the most abundantly used sources of residential heating is the burning of wood in homes through the use of wood burning stoves and fireplaces. It is shown later in Section 4.1.2 that wood smoke is indeed the largest contributor to Fairbanks $PM_{2.5}$, up to 63% by mass. Residential heating is also achieved through the use of residential fuel oil using oil burners/furnaces to supplement the use of wood combustion. Lastly, it should be noted that there are no natural gas lines in Fairbanks, so residential heating by any natural gas source is impossible until such lines are established.

3.4 Particulate Matter Levels in Fairbanks

Strong temperature inversions often lead to a stagnation of the air in Fairbanks, and this leads to the accumulation of PM and other pollutants in the valley. Because of this, Fairbanks is often found to exceed the 24 hour NAAQS for $PM_{2.5}$ of $35\mu g/m^3$ during the winter months making Fairbanks a non-attainment area for $PM_{2.5}$. The interest is placed solely on the winter months because Fairbanks does not exceed the annual NAAQS $PM_{2.5}$ standard of $15\mu g/m^3$ but often exceeds the 24 hour standard of $35\mu g/m^3$ during the winter. The boundary of the non-attainment area can be seen below in Figure 3.3. To correct this issue, it has been mandated by the EPA that a State Implementation Plan be set in place during the winter of 2011/2012 such that Fairbanks, AK no longer exceeds this 24 hour standard for extended periods of time.

Studies are currently underway to identify the most influential sources of PM to the total PM in Fairbanks, AK such that an effective Implementation Plan can be developed. As expected, the major contributor to the total $PM_{2.5}$ in Fairbanks is wood smoke; however, it is impacted significantly by sulfate as well (see Section 4.2).

The Alaska Department of Environmental Conservation (DEC) is diligent with the measurement of various toxic gaseous pollutants. These pollutants include, but are not limited to, sulfur dioxide, nitrogen oxide and nitrogen dioxide. These gases are measured hourly from a sampling station on top of the State Building in downtown Fairbanks for purposes of compliance and regulation (Alaska DEC 2011). Monthly averages of ambient levels of sulfur dioxide can be seen below in Table 3.1.



<u>Figure 3.3</u>: North Star Borough PM Non-Attainment Boundary

<u>Table 3.1</u>: Ambient Sulfur Dioxide Levels in Fairbanks (ppb), State Building

Month	SO2
Oct 08	7.087
Nov 08	15.741
Dec 08	18.176
Jan 09	8.055
Feb 09	6.995
Mar 09	3.345

As discussed previously in Section 2.2.1, sulfur dioxide is a precursor for the formation of sulfate particulate in the atmosphere. Note that the levels of sulfur dioxide are increased during the months of November and December relative to the other months. These increased levels do not necessarily imply that there is an increased production of sulfur dioxide during these months (it is, however, still a possibility); it is likely this is a consequence of the stronger inversions that Fairbanks experiences during these months. However, it is expected that sulfate levels in Fairbanks $PM_{2.5}$ are increased during these months.

Table 3.2: Reported Emissions (2005) from Major Facilities in Non-Attainment Boundary (tons/year)

Facility	VOC	NO x	SO2	PM10	CO
Aurora Energy LLC Chena Power Plant	0	629	**248**	353	459
Flint Hills Resources Alaska, LLC North Pole Refinery	35	215	**13**	15	33
Golden Valley Electric Association, North Pole Power Plant	2	3604	**3019**	50	14
Golden Valley Electric Association, Zehinder facility	1	28	**24**	0	1
US Air Force Eielson Air Force Base	21	367	**281**	8	125
US Army Fort Wainwright	6	471	**697**	14	262
University of Alaska Fairbanks Campus Power Plant	2	509	**280**	7	187
Wilder Construction Company Asphalt Plant	0	6	**3**	13	6
Total Point Source Emissions	67	5829	**4565**	460	1087

Currently, model studies are being conducted in Fairbanks by the Alaska DEC to further understand the effects of point source emissions to the levels of ambient sulfur dioxide and the resultant sulfate particulate. Unfortunately, these model studies were not completed at the time of this writing. However, inspection of previous Alaska emissions inventories may be instructive in identifying likely sources for the high levels of sulfate found in Fairbanks $PM_{2.5}$.

While the reported emissions inventory in Table 3.2 may be from four years prior the winter investigated in the CMB model discussed later in Section 4.1, it is expected that the emissions were roughly equivalent. It should also be noted that the Wilder Construction Company Asphalt Plant does not operate during the winter months when violations of the NAAQS occur. On inspection of Table 3.2 it appears that the major source of sulfur dioxide emissions during the winter months is from power generation. However, this does not rule out residential heating or automobiles as being equivalent or greater sources of sulfate particulate than the power plants.

Chapter 4: Fairbanks PM Analyses and Comparisons

Chapter 4 Contents

4.1 Prior Studies

Previous studies conducted on $PM_{2.5}$ apportionment in Fairbanks and in Libby, MT demonstrate that Fairbanks is unique with respect to the high levels of sulfate in the $PM_{2.5}$. The search for the source of the sulfate in Fairbanks $PM_{2.5}$ was the driving force behind this work. Organic chemical markers were identified and quantified in Fairbanks $PM_{2.5}$ in order to develop a clearer picture of other potential sources of PM that would contribute to sulfate. Eight quartz filters collected during the time when CMB analyses were performed were analyzed for 89 different suspected chemical markers for various PM sources by the Desert Research Institute (Section 4.3). Results were compared to source profiles found in the literature and to the results of similar analyses conducted on PM in other communities. Un-combusted fuels from Fairbanks were analyzed for picene, DBT and BNT (Section 4.4.1). The thiophenes were of particular interest because they have been shown to be found in significant levels in residential heating oil (Huffman 2000), a widely used heat source in Fairbanks (Section 3.3). Picene is of particular interest because it is recognized as an organic marker for coal combustion (Oros 2000), which could also be a significant source of sulfate in Fairbanks $PM_{2.5}$.

Several model studies were conducted in Fairbanks, AK to shed some light on the causes of the high $PM_{2.5}$ levels during the winter months. Of interest to this work is the CMB model, ^{14}C analyses and anthropogenic PM organic carbon marker analyses. Each method gives different, but complementary information on the source of the PM. The CMB model tells us what sources are contributing to the PM by looking at elemental composition, organic carbon to elemental carbon ratio (OC/EC) and ionic compositions (Section 4.1.2). ^{14}C analyses tell us what fraction of the PM comes from biomass burning versus a fossil fuel combustion source (Section 4.1.3). Lastly, organic carbon marker analyses tell us additional information about the source (Section 2.5-2.8 and 4.4).

4.1.1 Fairbanks $PM_{2.5}$ Sampling

A CMB model study, ^{14}C analyses and wood smoke marker analyses were conducted in the winter of 2008/2009 by Tony Ward's group with assistance from the Alaska Department of Environmental Conservation (Ward 2009). The current study was done to complement the $PM_{2.5}$ source apportionment work already done with additional strategies. A map of the city of Fairbanks, AK with the sampling locations marked can be seen below in Figure 4.1.

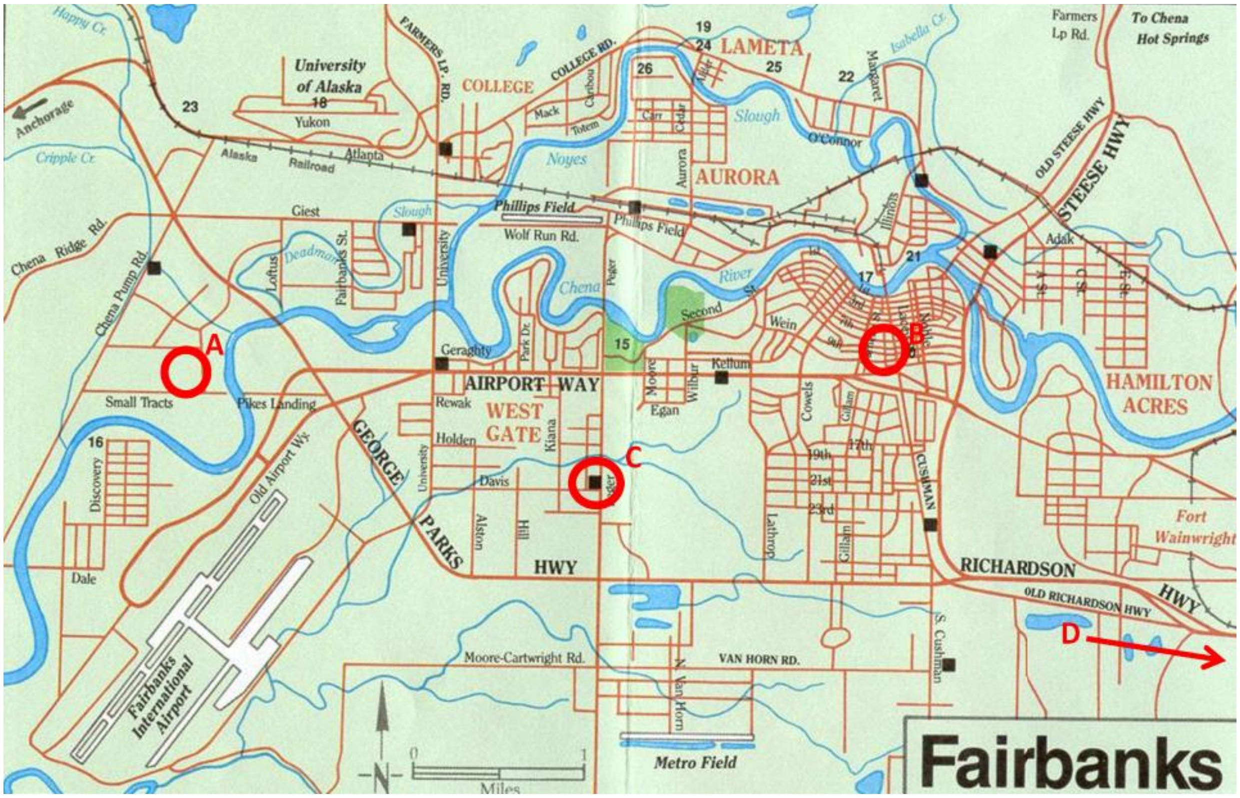


Figure 4.1: City of Fairbanks, AK and PM Sampling Locations

Alaskais.com

Site A is the mobile RAMS station and was located at the Woodriver Elementary school; this site is well outside of the downtown area located between the University of Alaska and the Fairbanks International Airport. Site B is located on top of the State Building in the heart of downtown. Site C is a mobile collection station on top of a trailer and was located at Peger road. Lastly, site D is located in the nearby town of North Pole, AK, approximately 14 miles south-east of Fairbanks along interstate AK-2 E. The town of North Pole is a small rural town with a population of approximately 2,200 (US Census 2009).

The $PM_{2.5}$ sample collection is achieved by means of a Met One spiral ambient speciation sampler (SASS) at each site. A Met One SASS sampler can be seen in Figure 4.2.

Figure 4.2: Met One SASS Sampler
akrulogic.com

The Met One SASS sampler is a multi-channeled $PM_{2.5}$ collection device. The ambient $PM_{2.5}$ samples are collected on filters inserted by the user; multiple filter types are used for different types of analyses. The Met One SASS sampler is the most widely used sample collection device for EPA $PM_{2.5}$ speciation work (epa.gov). The filters are inserted into canisters which are then inserted into the sample head in the lab before going to the field, preventing risk of contamination on the field. These canisters are designed to exclude PM larger than 2.5µm and can be fitted with a denuder to remove contamination gases that may lead to erroneous results. This device also has a convection solar radiation shield around the sample head to maintain the temperature of the samples at or near ambient temperature (akrulogic.com).

Table 4.1: PM Sampling Filters and Methods for Analysis

Filter Type	**Analyses**	**Method**
Teflon	Mass	Microbalance
	Elements	X-ray fluorescense
Nylon	Ions	Ion Chromatography
Quartz	OC/EC	Thermal Optical Reflectance
	Carbon-14	Accelerator Mass Spectroscopy
	Organic Markers	Gas Chromatography-Mass Spectroscopy

Fairbanks $PM_{2.5}$ samples were collected on three different filter types: Teflon for mass and elemental analyses, nylon for ionic species analyses, and quartz for organic carbon, elemental carbon, ^{14}C and organic carbon marker analyses. Research Triangle Institute performed the analyses for mass, elements, ions and OC/EC. University of Arizona analyzed the quartz filters for ^{14}C and University of Montana analyzed for the organic markers (Ward 2009). A summary of the filter types used as well as the methods for analyses can be seen above in Table 4.1.

4.1.2 Chemical Mass Balance Model

The CMB model is widely used and extremely useful in the source apportionment of PM in communities (Ward 2010). It is one of many receptor models applied to air quality problems (particularly PM non-attainment areas) for the last two decades, and has proven itself to be highly useful in localized studies (epa.gov). The CMB model is supported by the EPA and is used as a regulatory planning tool in areas which have problems with PM being above either the annual or 24-hour average non-attainment standards.

The CMB model requires speciated profiles of all of the suspected contributing PM sources in the area as well as the data corresponding to the particular location. These speciated profiles, the CMBv8.2 software and sample data sets are available from the EPA's website.

The CMB model accepts inputs such as PM total mass collected, elemental and ionic species as well as organic to elemental carbon ratios (Ward 2010). The model's outputs are presented as solutions to a system of linear equations where each chemical receptor is a linear sum of the products of source abundances and contributions, as indicated by the equation below.

$$C_i = \sum_{j=1}^{p}(a_{ij}S_j), i = 1, n.$$

Where C_i is the concentration of species *i*, a_{ij} is the fractional concentration of species *i* from the source *j* and S_j is the total mass concentration contributed by the source (Ward 2009).

The source profiles used for the Fairbanks CMB were taken from SPECIATE 4.0 and a Missoula County CMB source library. These source profiles included the following: street sand and road dust, pure secondary emissions (sulfate, ammonium sulfate and ammonium nitrate), gasoline and diesel exhaust emissions, tire and brake wear, wood combustion, meat cooking

Table 4.2: Chemical Mass Balance Results Summary for Fairbanks Winter 2009/2010

	State Building **11/8/08–4/7/09**	**North Pole** **1/25/09–4/7/09**	**RAMS** **1/25/09–4/7/09**	**Peger Road** **1/25/09–4/7/09**
$PM_{2.5}$ Mass ± Std Deviation	25.3±15.3	18.9±14.3	8.2±2.1	16.8±10.3
Sample Days	47	21	23	26
Ammonium Nitrate	2.1±0.7 8.10%	1.0±0.2 5.10%	0.9±0.1 10.50%	1.5±0.4 8.90%
Sulfate	5.1±0.6 20.00%	1.9±0.2 9.80%	1.1±0.1 13.00%	2.8±0.3 16.70%
Diesel Exhaust	0.3±0. 1 1.10%	0.2±0.05 0.80%	N.D.	1.2±0.5 7.30%
Automobile Exhaust	1.7±0.7 6.80%	0.7±0.3 3.70%	N.D.	0.7±0.2 3.90%
Woodsmoke	16.0±2.3 63.10%	15.0±2.0 79.80%	6.3±0.8 76.00%	10.6±1.6 62.70%
Unexplained	0.2 0.80%	0.2 0.80%	0.04 0.50%	0.08 0.50%

Mass quantities are reported in $\mu g/m^3$

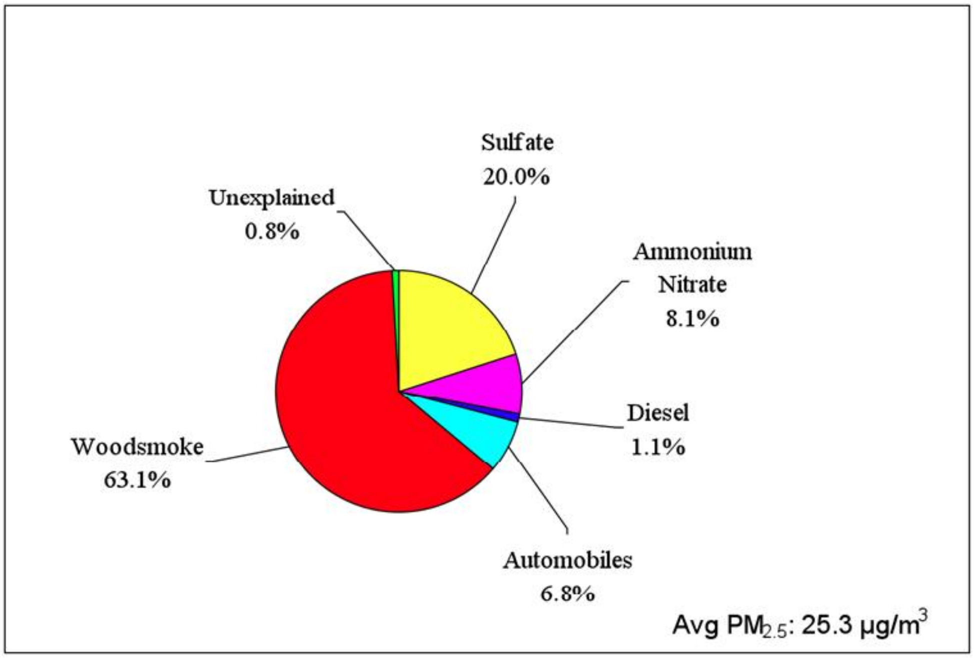


Figure 4.3: Graphical Representation of CMB Results – State Building Site

and distillate / residual oil combustion (Ward 2009). A summary of the CMB results for Fairbanks, AK for the winter of 2009/2010 can be seen above in Table 4.2 and Figure 4.3.

The total $PM_{2.5}$ mass was found to range between 8.2-25.3µg/m^3 within Fairbanks, the North Pole site was an intermediate value of 18.9µg/m^3. As expected, the largest contributor to the Fairbanks and North Pole $PM_{2.5}$ is from wood burning; wood smoke particulate was shown to be 63-76% in Fairbanks and 79.10% in North Pole of the $PM_{2.5}$ identified by the CMB model. This is due to the large amount of residential heating during the winter, as mentioned previously. The contribution from auto mobile exhaust (3-7%) appears to be only a fraction of that reported in more populated industrial areas (El Haddad 2011). Contribution from diesel exhaust appears to be minimal at the State Building downtown site (1.10%) and not detected at the RAMS site. In contrast there is a significant increase in the contribution from diesel exhaust at the Peger Road site (7.3%). This sampling site is near the Borough's Motor Pool and a trucking company, and thus the results may be impacted by a relatively high level of local diesel powered traffic. The contribution from ammonium nitrate appears to be fairly constant across all three Fairbanks sites (8.10-10.50%) and approximately half this amount was found at the North Pole site (5.10%). The unexplained portion of the PM detected in all four sites appears to be fairly constant (<1%).

Note that neither sulfate nor ammonium nitrate were identified as primary sources, but instead were identified as secondary particulates formed from sulfur oxide (SO_x) and nitrogen oxide (NO_x) emissions, respectively. In the CMB model they are used as fitting parameters and thus always appear in the results.

One striking feature of these results for Fairbanks $PM_{2.5}$, is the relatively high contributions from sulfate identified by the CMB model. The sulfate was found to be as high as 20% of the Fairbanks $PM_{2.5}$ at the State Building site which was more than double of that found at the North Pole site (9.80%). The RAMS site and the Peger road site are intermediates between those two extremes (13.00% and 16.70%, respectively).

The Fairbanks North Star Borough area does not contain any of the natural or industrial sources of sulfate mentioned previously in Section 2.2.1. Other possible sources of sulfate are the formation of secondary sulfate from sulfur dioxide emissions or from diesel fuel/fuel oil particulate. It is not believed that the high levels of sulfate in Fairbanks $PM_{2.5}$ are from diesel fuel particulate because diesel fuels are treated such that they have very low levels of sulfurous compounds (thiophenes), typically found at the ppb levels in most commercial fuels (Section

2.7.2). While there may be a minimal amount of sulfate found in diesel fuel particulate, it does not account for the high levels of sulfate found in Fairbanks $PM_{2.5}$.

4.1.3 ^{14}C Analyses

^{14}C is the smallest fraction of the naturally occurring carbon isotopes and accounts for approximately 1 part per trillion of atmospheric carbon (Kamen 1963) and can be used as a means to determine the fraction of the organic carbon present in the PM that is from a biomass burning source or a fossil fuel source. This is fundamentally based on the fact that ^{14}C is radioactive and will decay to the stable ^{14}N through beta decay over time (half life ≈ 5800 years). While alive, plants incorporate ^{14}C from the atmosphere through photosynthesis. The carbon in fossil fuels was incorporated up to 650 million years ago, and has essentially decayed entirely given the amount of time that has passed since it was incorporated compared to the half-life. Therefore, if ^{14}C is found in PM at modern atmospheric levels it must have come from combustion of recently harvested plant biomass combustion.

During the analyses for ^{14}C the carbon was extracted and combusted in an oxygen rich environment and then analyzed by accelerator mass spectroscopy. The fraction of modern carbon found in the sample (F_m) is determined by the analysis and it is also defined by the following equation (Ward 2010);

$$F_m(total) = \frac{mass(wood)}{mass(total)} F_m(wood) + \frac{mass(coal)}{mass(total)} F_m(coal) + \frac{mass(blank)}{mass(total)} F_m(blank)$$

In this model, F_m(coal) is assumed to be zero. It is also safe to assume that contributions from other fossil fuels are contained within this term because the concentration of ^{14}C is essentially zero. Also, the mass(blank) is set equal to zero. With these two considerations the above equation reduces to the following;

$$\%Wood = \frac{F_m(total)}{F_m(wood)} x100\%$$

The results from the ^{14}C analyses of the Fairbanks $PM_{2.5}$ from the winter of 2008/2009 can be seen below in Table 4.3.

<u>Table 4.3</u>: Fairbanks $PM_{2.5}$ ^{14}C Results and Comparison to CMB Model

Date	$PM_{2.5}$ Mass ($\mu g/m^3$)	% $PM_{2.5}$ Resulting from Woodsmoke	% Woodsmoke $PM_{2.5}$ Identified by CMB Model
12/14/2008	39	59.6-71.8	70.8
12/17/2008	34.9	49.8-60.0	62.8
12/23/2008	47.5	43.6-52.5	82.3
12/29/2008	66	45.3-54.5	63.9
1/7/2009	63.7	42.2-50.8	62
1/25/2009	26.7	53.2-64.1	69.3
2/9/2009	12.3	42.5-51.1	72
2/15/2009	29.6	41.7-50.3	47.3

As mentioned previously, the ^{14}C analyses serve as complementary information to the CMB model. While the percent contributions to the $PM_{2.5}$ from wood smoke may not fully agree, they are within acceptable variations to each other. These differences can be explained by the uncertainties in each model.

4.1.4 Organic Marker Analyses

As described in Section 2.7, levoglucosan is the most useful chemical marker for wood smoke. Levoglucosan analyses (along with analyses for other wood smoke markers) were performed by the method described in Section 5.4 for samples collected during the winter of 2008/2009. As indicated below in Table 4.4, there is a significant amount of levoglucosan found in the Fairbanks $PM_{2.5}$, which further supports the CMB model and ^{14}C analysis that wood smoke is a significant contributor to the PM.

Table 4.4 **Fairbanks Levoglucosan (ng/m^3)**

Month	State Building	Peger Road	RAMS	North Pole
Dec 2008	1085			
Jan 2009	832	544	696	1209
Feb 2009	451	315	341	1017
Mar 2009	459	239	228	444
Apr 2009	101	159		261

Levoglucosan was found to be the most abundant in Fairbanks $PM_{2.5}$ during the month of December, when it is the coldest and residential heating is at the maximum, and decreases as the months go by and temperatures in Fairbanks increase. Comparing the levels found at the State Building and North Pole sites roughly mirrors the results found by the CMB for contribution of wood smoke to both areas, North Pole is a rural area that is predominantly impacted by wood smoke.

The other supplemental wood smoke markers (methoxy-phenols and resin acids) did not appear to follow a trend relative to levoglucosan or with time. In many cases, the methoxy-phenols were not detected and the resin acids follow a seemingly random trend.

4.2 Libby, MT Comparisons to Fairbanks, AK

Libby, Montana is located in north-western Montana in Lincoln County. It is a small rural town with a population size of approximately 2,600 (US Census 2000). The town sits in a forested mountain valley along the Kootenai River with the Purcell Mountains to the north and the Cabinet Mountains to the south. The geographical similarities, similar cold winters that exhibit long inversion events (Figure 4.4), as well as the fact that Libby's $PM_{2.5}$ is impacted primarily by wood smoke make it an ideal comparison to the conditions found in Fairbanks. There has been interest in the air quality of Libby because of the fact it was found to be a non-attainment area by the NAAQS for $PM_{2.5}$ during the winter months.

A large scale wood stove change-out project was conducted during 2005-2007 as a partnership between the USEPA, Montana DEQ and the Hearth, Patio and Barbeque Association as an effort to lower the ambient $PM_{2.5}$ in the Libby area. Up to 1200 wood stoves were changed-out or modified to more current technology that met the 1988 EPA emissions standards (7.5g/hr). This was the largest change-out ever conducted in the US (Ward 2010; Bergauff 2009).

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Figure 4.4: Libby, MT Inversion Event

Table 4.5: CMB (µg/m^3) Results for Libby, MT Wood Stove Change-Out

	2003-2004		2007-2008			
Source	**CMB**	**Percent Contribution**	**CMB**	**Percent Contribution**		**Percent Difference**
PM2.5 Mass	28.2		20.1			-25.6
Street Sand	0.02 ± 0.01	0.1	0.04 ± 0.01	0.2		145
Sulfate	0.6 ± 0.1	2.1	0.5 ± 0.07	2.2		-23
Ammonium Nitrate	1.5 ± 0.2	5.2	1.3 ± 0.1	6.3		-13
Automobile Exhaust	2.1 ± 0.8	7.4	0.9 ± 0.3	4.5		-56
Diesel Exhaust	1.0 ± 0.3	3.6	1.1 ± 0.3	5.3		5
Wood Smoke	22.8 ± 3.0	81.0	16.4 ± 2.3	81.3		-28
Unexplained	0.19	0.7	0.03	0.2		-83

Similar $PM_{2.5}$ studies to those done Fairbanks were conducted in Libby. A CMB model study was conducted on the $PM_{2.5}$ in Libby during the winters of 2003/2004 and once again following a wide-scale wood stove change-out in 2007/2008. A summary of the CMB results before and after the wood stove change-out can be seen in Table 4.5.

The wood stove change-out project was found to be successful in decreasing the ambient $PM_{2.5}$ in Libby. The total ambient $PM_{2.5}$ decreased from 28.2μg/m^3 to 20.1μg/m^3. However, the percent contribution of wood smoke to the total ambient $PM_{2.5}$ mass remained constant at approximately 81%. This further supports the fact that that wood smoke is indeed the primary source of $PM_{2.5}$ in Libby.

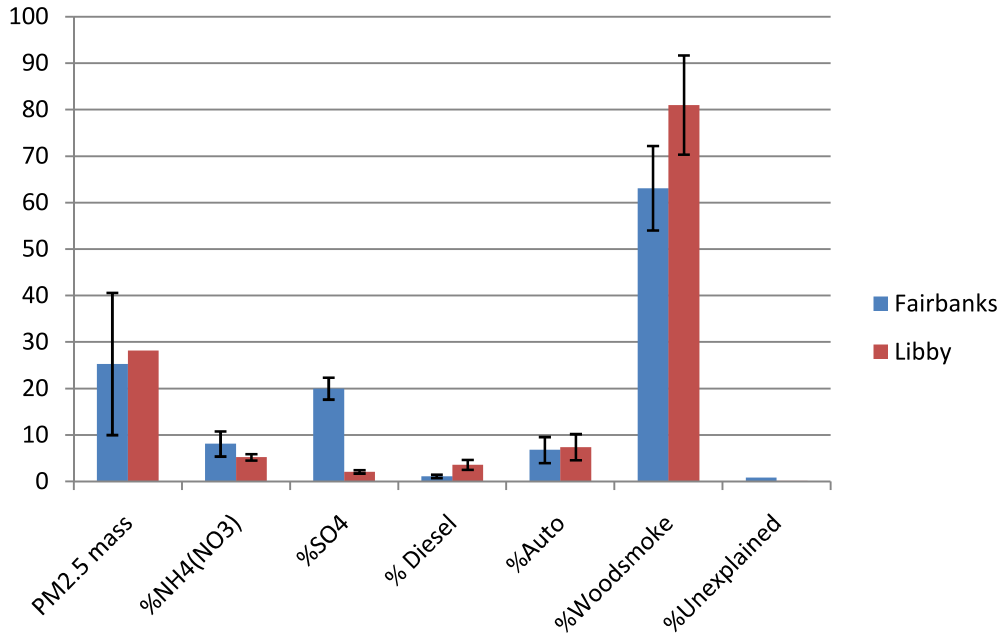
4.2.1 Organic Marker Analyses of Libby, MT $PM_{2.5}$

In addition to the CMB model studies, analyses for organic wood smoke markers were also conducted to investigate the impact of the wood stove change-out program on Libby, MT $PM_{2.5}$ (Bergauff 2009). The organic markers analyzed were the following; the sugar anhydride levoglucosan; the methoxy-phenols guaiacol, 4-ethyl guaiacol, vanillin and aceto-vanillone; and the resin acids DHAA and AA (Section 2.6). Levoglucosan was found to decrease by 50% over the course of the change-out. Resin acid levels, however, remained essentially constant. No quantitative pattern or trend could be observed with the methoxy-phenols. No analysis of organic markers associated with fossil fuel emissions was conducted in Libby.

4.2.2 Comparisons of Libby to Fairbanks

While Fairbanks may have a significantly larger population to that of Libby, it is still meaningful to make comparisons between the two. Both locations have near equivalent levels of $PM_{2.5}$ during the years investigated in this work and primarily impacted by wood smoke. However, as shown previously, wood smoke does not contribute as much to the Fairbanks $PM_{2.5}$ as it does to the Libby $PM_{2.5}$. Wood smoke contributes up to 63% in the industrial/business portions of town and up to 76% in the rural parts of town, where Libby is predominantly rural and wood smoke contributes up to 81%. This difference is crucial in the comparisons being made between the two locations because it implies that if a wood stove change-out program were conducted in Fairbanks if it may not be enough to consistently bring Fairbanks $PM_{2.5}$ below the 24 hr NAAQS.

A direct comparison of the CMB results from Libby prior to the wood stove change-out to that of Fairbanks, AK in the winter of 2007/2008 can be seen below in Figure 4.5. A few notable differences in the $PM_{2.5}$ compositions are readily apparent upon investigation of Figure 4.5. The total $PM_{2.5}$ mass, the contribution from automobiles and the unexplained portion are approximately equivalent between both towns. Libby $PM_{2.5}$ is significantly more impacted by wood smoke than Fairbanks $PM_{2.5}$ and Fairbanks $PM_{2.5}$ is slightly more impacted by ammonium nitrate than Libby $PM_{2.5}$. The greatest difference is seen in the sulfate levels. Fairbanks $PM_{2.5}$ has a significantly higher level of sulfate than Libby PM. The relatively low levels of sulfate in Libby, which is heavily impacted by residential wood combustion, demonstrate that sulfate is not associated with this source.



<u>Figure 4.5</u>: CMB Comparison between Fairbanks and Libby (Prior Wood Stove Change-out)

It does not seem likely that a wood stove change-out in Fairbanks would be sufficient to consistently address Fairbanks' non-attainment status. To help explain this, a crude comparison of the reduction in the $PM_{2.5}$ in Libby from the change-out was compared to the levels of $PM_{2.5}$ found in Fairbanks. Recall that the Libby wood stove change-out showed a decrease of 28% in the mass associated with wood smoke PM in Libby. Applying this decrease to the mass found at the State Building from wood smoke in Fairbanks gives a decrease of $16ug/m^3$ to $11.52ug/m^3$. Adding this to the remainder of the PM found at the State Building gives a net reduction of about 17% (26.3 to $20.9ug/m^3$). Thus, either a separate approach or additional efforts would be needed to achieve attainment.

It is not clear from the Libby results that any significant decrease in sulfate can be expected from a wood stove change-out program. The minimal reduction in levels of sulfate in

Libby following the change-out further demonstrate the fact that wood smoke is not a significant source of sulfate.

4.3 Organic Marker Analysis of Fairbanks $PM_{2.5}$

In an effort to identify other sources for the sulfate that could account for the high sulfate contributions to the CMB model (Section 4.1.2), source profiles for various anthropogenic organic carbon sources were investigated. The source organic profiles that were investigated were; residential oil burners (Rogge 1997), diesel vehicles (Liang 2006; Schauer 1999), gasoline vehicles (Schauer 2002), and bituminite coal (Oros 2000; Zhang 2008). Potential organic markers can be classified as follows; hopanes and steranes for all fossil fuels PM, thiophenes for residential fuel oil or diesel fuels PM, and PAH for coal PM (Section 2.7).

The Desert Research Institute (DRI) in Reno, NV was contracted for a comprehensive analysis of eight Fairbanks $PM_{2.5}$ samples from the winter of 2009-2010 and one laboratory blank. The eight $PM_{2.5}$ samples, selected in consultation with the Alaska DEC, were chosen to be representative of typical to high $PM_{2.5}$ days. In total, eighty-nine compounds were selected for analysis, including sixty-six PAH and related compounds and twenty-three hopanes and steranes. The analytical results included levels for the thiophenes DBT and BNT as they are known to be found in the emissions of residential oil burners (Huffman 2000) as well as diesel emissions (Schauer 1999; Zhang 2008). The analyses included hopanes and steranes which are found in all fossil fuel emissions. Among the PAH compounds determined is picene which is reported to be a unique marker for coal combustion (Oros 2000). The full data set returned by DRI can be seen in Appendix A.1.

The Fairbanks $PM_{2.5}$ samples selected from the winter of 2009-2010 can be seen below in Table 4.6. Notice that 3 of the days chosen are above the 24 hr NAAQS for $PM_{2.5}$.

<u>Table 4.6</u>: Date and $PM_{2.5}$ level of samples selected for DRI analysis

Date	$PM_{2.5}$ level (µg/m^3)
11-15-2009	15.7
11-27-2009	20.9
12-10-2009	54.4
12-13-2009	44.4
12-27-2009	24.1
1-11-2010	38.5
1-17-2010	15.8
2-10-2010	22.1

The raw data returned from DRI are difficult to interpret without some context. These data were investigated and are discussed in the context of comparisons of the composition of Fairbanks $PM_{2.5}$ to that of the source profiles (Section 4.3.1) and later as comparisons to other PM impacted air sheds discussed in the literature (Section 4.3.2).

4.3.1 Comparisons of Source Profiles to Fairbanks PM

Many of the source profiles found in the literature were reported in variable units relative to how Fairbanks $PM_{2.5}$ was reported in this work. As such, all of the values reported were converted to be consistent with the units used for Fairbanks $PM_{2.5}$; each individual species is reported as a fraction of the PM (ppm). Below in Table 4.8 is a summary of source profiles compared to the observed Fairbanks $PM_{2.5}$.

While it has been shown previously that thiophenes can be found in both the un-combusted fuel (Rogge 1997) as well as the resultant particulate of diesel products (Rogge 2000) as well as gasoline particulate (Schauer 2002), the amount of data on the thiophenes found in the PM of other sources, particularly coal emissions ,is severely limited. This is possibly due to the difficulty in the detection and resolution of hetero-organic species and may require specialized detectors; where many of the PAHs, hopanes/steranes, etc. are more readily resolved by more standard GC-MS methods or GCxGC methods (Frysinger 2003).

When compared to the analysis performed by DRI for the 8 selected $PM_{2.5}$ samples, many of the source profiles for organic species in the literature only contain a small subset of those analyzed. As such, a blank cell in Table 4.7 indicates that the compound was not mentioned in the literature source, where an entry of “nd” indicates that the compound was analyzed for but was below the method’s detection limit.

Table 4.7: Levels of selected organic markers as a fraction of PM (ppm)

	Compound	Residential Oil Burner (1)	Diesel Vehicles (2,3)	Gasoline Vehicles (4)	Bituminite Coal (5)	Bituminite Coal (6)b	Fairbanks Median (Maximum)
Hopanes and Steranes	**17α(H)-22,29,30-Trisnor Hopane**		5.3		0.4	67	16.6 (90.6)
	17α(H), 21β(H)-29- Nor Hopane	2.22	14.8	2.5		85	41.3 (152)
	17α(H), 21β(H)-Hopane	3.53	61.6	4.4	1.4	45	26.0 (79.8)
	22S-17α(H), 21β(H)-30-Homo Hopane	1.02		nd	1.1	10	17.7 (55.9)
	22R-17α(H), 21β(H)-30-Homo Hopane	0.64		nd	0.2	17	23.5 (129)
	22S-17α(H), 21β(H)-30,31-Bishomo Hopane	0.58		nd	nd	11	8.5 (34.5)
	22R-17α(H), 21β(H)-30,31-Bishomo Hopane	0.40		nd	nd	16	15.9 (39.5)
	20R-5α(H), 14β(H), 17β(H)-Cholestane	2.03					39.2 (45.7)
	20S-5α(H), 14α(H), 17α(H)-Ergostane	4.53	4.2				4.43 (4.97)
	20R-5α(H), 14β(H), 17β(H)-Stigmastane	1.87	17.0				4.89 (6.36)
Thiophenes	**Dibenzo-thiophene**		12.6; 10.7(a)	43(a)			49.0 (65.8)
	2,3-Benzo-[b]-naphtho[1,2d]-thiophene		23.8				15.8 (29.7)
PAHs	**Picene**				nd	94	36.2 (69.3)
	Retene				4.6	nd	44.2 (68.0)

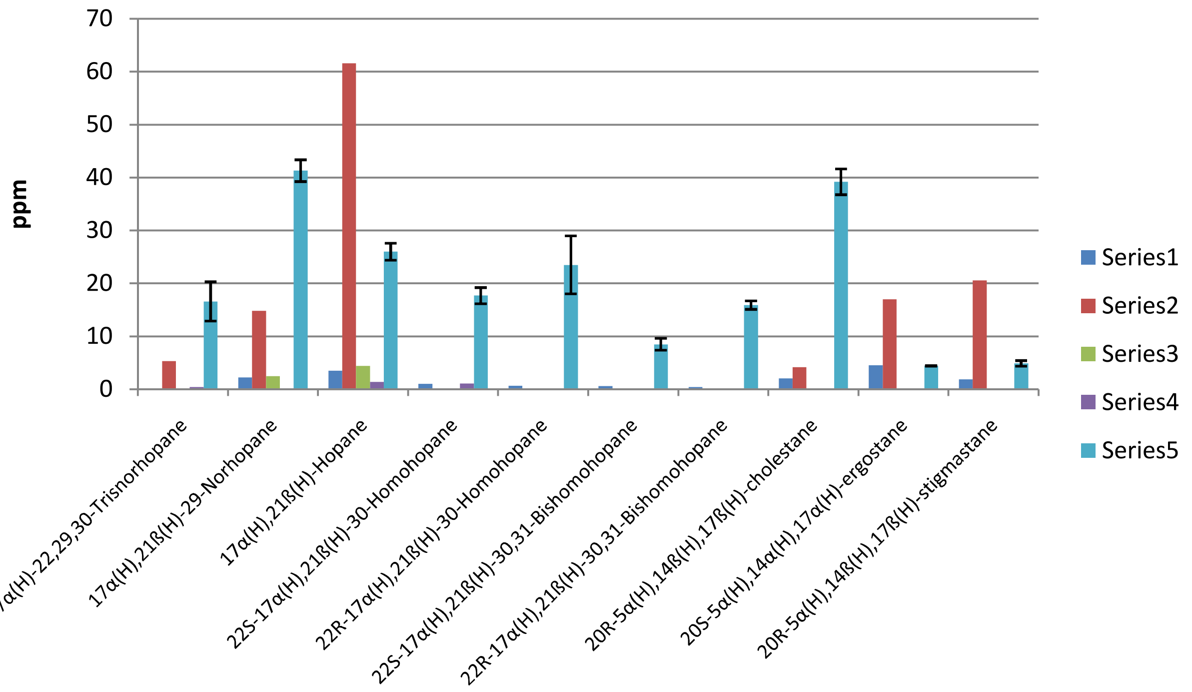
(a) Gas phase only, (b) Emission factors in mg/kg fuel, (1) Rogge 1997, (2) Liang 2006, (3) Schauer 1999, (4) Schauer 2002, (5) Zhang 2008, (6) Oros 2000

4.3.1A Hopanes and Steranes

As discussed in Section 2.7, hopanes and steranes should not be used as a unique marker for any particular $PM_{2.5}$ source. Instead, hopanes and steranes are indicative of the presence of any fossil fuel source of $PM_{2.5}$ and are not present in biomass burning emissions. Therefore, hopanes and steranes can give an idea as to the extent to which a particular air shed is impacted by fossil fuel emissions.

Below in Figure 4.6 is a graphical representation of a portion of the data shown in Table 4.8 to further illustrate the comparisons of hopanes and steranes from various sources to the amount found in the Fairbanks $PM_{2.5}$. In almost all of the cases, the fraction of hopanes and steranes found in Fairbanks $PM_{2.5}$ is higher than that found directly from a source. The most notable exception is when comparing source PM emissions of some hopanes from diesel combustion to that of Fairbanks $PM_{2.5}$.

It has been suggested that the ratios of the hopanes17α(H), 21β(H) hopane to 22R-17α(H) 21β(H) homo hopane can give additional information to the identity of the fossil fuel source (Oros 2000; Zhang 2008). Unfortunately, Oros and Zhang have conflicting values reported for coal emissions, 0.1-2.6 and 4.28-9.19 respectively. The median value for Fairbanks PM is 1.2, which may imply that the Fairbanks PM is heavily impacted by coal emissions if using the Oros 2000 results for this type of analysis. However, due to the conflicting reports it is impossible to draw this conclusion. In general, it is not possible to determine the primary fossil fuel PM source from hopanes and steranes alone and additional information is required.



<u>Figure 4.6</u>: Hopanes and Steranes as a Fraction of $PM_{2.5}$
(1) Residential Oil Burner, (2) Diesel, (3) Gasoline, (4) Bituminous Coal (5) Fairbanks Median

4.3.1B Thiophenes

Thiophenes were investigated as a means to identify the possible sources of the high levels of sulfate in Fairbanks $PM_{2.5}$ as identified in the CMB model. As discussed in Section 2.7, thiophenes have been shown to be present in the PM emissions of gasoline, diesel products and residential fuel oil. Fuels that contain thiophenes are a possible source of sulfate aerosols as they may form sulfur dioxide, which can then lead to sulfate in the atmosphere (Section 2.2.1), upon combustion.

Similar to the comparisons made to source profiles with the select hopanes and steranes in the previous section, comparisons were made between the levels of the select thiophenes DBT and BNT in Fairbanks $PM_{2.5}$ and reported emissions profiles (Schauer 1999 and 2002, Liang 2006). A summary of these comparisons can be seen below in Figure 4.7.

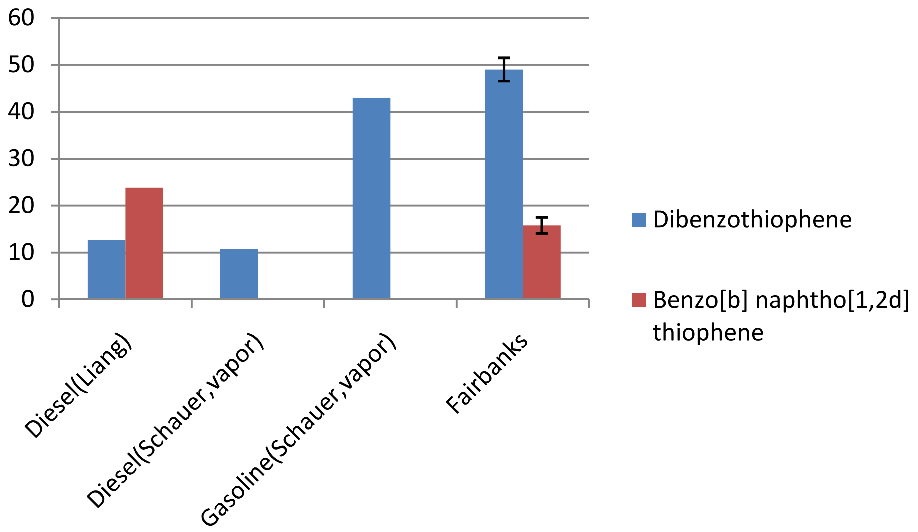


Figure 4.7: Select Thiophenes as a Fraction of $PM_{2.5}$

Fairbanks $PM_{2.5}$ has elevated levels of DBT relative to reported source profiles, nearly equivalent to gasoline PM emissions and approximately five times that found in diesel PM. BNT appears to be a more useful chemical marker in distinguishing between gasoline and diesel/fuel oil PM emissions, DBT was not found in gasoline PM emissions. Fairbanks $PM_{2.5}$ is impacted by BNT approximately half of that of diesel PM as reported by Liang.

4.3.1C Poly-cyclic Aromatic Hydrocarbons

As shown in Table 4.8, there is a significant quantity of the select PAH picene found in Fairbanks $PM_{2.5}$ (36.2ppm median, 69.3ppm maximum as a fraction of the PM). Recall, that picene has been reported to be a unique marker for coal combustion (Section 2.7). These levels are not as high as those reported for residential coal burners in China but are much higher than those expected in commercial boilers (Zhang 2008).

4.3.2 Comparisons of Fairbanks PM to other Air Sheds

Comparisons were made between various air sheds to what was seen in Fairbanks during the winter of 2009/2010 using the results from the DRI analysis of the 8 Fairbanks $PM_{2.5}$ samples and reports found in the literature. Unfortunately, it appears that across the US in $PM_{2.5}$ studies there is not much interest in the levels of thiophenes in the PM. It seems that the focus of many studies in the US was on alkanes, hopanes, steranes, PAH, and various carbonyl compounds (acids, ketones, aldehydes). However, data was found for thiophenes in a study done on the PM in 6 urban sites across Europe (Section 4.3.2B) (Saarnio 2008).

4.3.2A Southeastern US

A summary of the comparisons of air sheds in Southeastern US (Zheng 2002) to what was found in Fairbanks can be seen below in Table 4.9. A blank entry indicates that the particular compound was not analyzed for and an entry of “nd” means the compound was below the method’s detection limit. The type of air shed is also indicated.

On inspection of Table 4.9 it becomes clear that the levels of hopanes and steranes found in the Southeastern US PM is much higher in the urban areas than that in the rural and residential areas. As mentioned previously, hopanes and steranes are indicative of fossil fuel combustion. This is expected because there is less traffic and little to no industrial processes occurring in the rural/residential areas compared to the urban areas.

In comparison to Fairbanks, all of the urban areas investigated in the study by Zheng have a much larger population. Birmingham, AL has a population of 1.2 million (US Census 2010). Atlanta, GA has a population of 5.2 million in the metropolitan area (US Census 2010) and is the ninth most populated city in the nation. Recall (Section 3.1) that Fairbanks has a population of only 99,000 (US Census 2009). In population versus PM level comparisons, it is expected that the levels of hopanes and steranes would be much higher in Birmingham and Atlanta than Fairbanks simply due to the fact there is significantly more automobile traffic and industry; however, this is not the case. Fairbanks has 1.5 to 5 times the amount of selected hopanes and steranes in its PM as indicated in Table 4.8.

It is suspected that the differences may be due to the differences in weather and topography. Neither Atlanta nor Birmingham are enclosed by mountains, experience winters as cold or experience extended inversion events when compared to Fairbanks. Also, the values reported for the hopanes and steranes for the Southeastern US air sheds are an average value observed throughout the year, where the Fairbanks values are only for the winter months. As shown in the Zheng report, the PM is most effected by diesel and gasoline exhaust primarily during the month of October for Birmingham and Atlanta. Lastly, the Southeastern US has significantly more retene contributing to the $PM_{2.5}$ than what was seen in Fairbanks. The Fairbanks $PM_{2.5}$ has less retene than the lowest found in the Southeastern US PM.

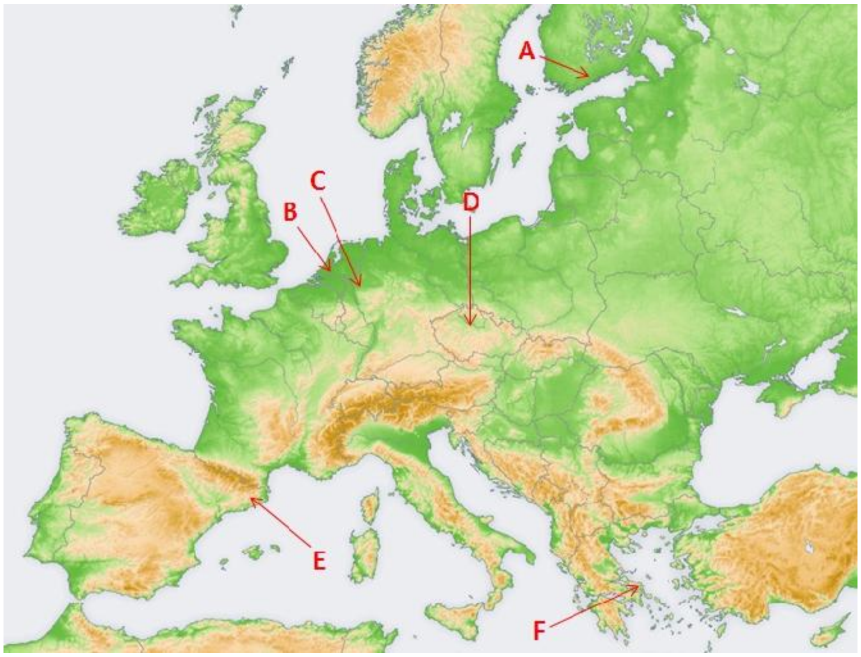
<u>Table 4.8</u>: Levels of Select Markers found in Southeastern US and Fairbanks PM (ng/m^3)

		Centreville, AL (rural)	N. Burningham, AL (urban)	Yorkville, GA (rural)	Jefferson Street, Atlanta, GA (urban)	Oak Grove, MS (rural)	Gulfport, MS (residential, commercial)	OLF#8, FL (suburban)	Pensacola, FL (residential)	Fairbanks Median (Maximum)
Hopanes and Steranes	**17α(H)-22,29,30-Trisnor Hopane**	nd	0.10	nd	0.10	nd	nd	0.01	0.01	0.53 (2.18)
	17α(H), 21β(H)-29- Nor Hopane	0.01	0.56	0.02	0.57	nd	0.11	0.04	0.21	1.26 (3.67)
	17α(H), 21β(H)-Hopane	0.01	0.59	0.03	0.56	0.01	0.12	0.04	0.23	0.72 (1.92)
	22S-17α(H), 21β(H)-30-Homo Hopane	nd	0.30	0.01	0.31	nd	0.06	nd	0.12	0.47 (1.92)
	22R-17α(H), 21β(H)-30-Homo Hopane	nd	0.29	0.01	0.26	nd	0.05	nd	0.12	0.61 (3.11)
	22S-17α(H), 21β(H)-30,31-Bishomo Hopane	nd	0.19	nd	0.19	nd	0.01	nd	0.05	0.38 (0.72)
	22R-17α(H), 21β(H)-30,31-Bishomo Hopane	nd	0.14	nd	0.15	nd	0.01	nd	0.04	0.45 (0.95)
	20R-5α(H), 14β(H), 17β(H)-Cholestane	nd	0.24	nd	0.25	nd	0.05	0.03	0.07	0.88 (2.49)
	20S-5α(H), 14α(H), 17α(H)-Ergostane									0.082 (0.086)
	20R-5α(H), 14β(H), 17β(H)-Stigmastane									0.12 (0.24)
Thiophenes	**DibenzoThiophene**									0.93 (2.92)
	2,3-Benzo [b] Naphtha [1,2d] Thiophene									0.45 (0.72)
PAHs	**Picene**									0.76 (1.67)
	Retene	4.99	1.84	1.45	1.44	16.4	1.8	3.44	3.14	1.08 (2.58)

Zheng2002

4.3.2B Europe

In the Saarnio 2008 study, the PM was analyzed for 32 PAHs and hetero-PAHs in sites located in Duisburg, Germany; Prague, Czech Republic; Amsterdam, The Netherlands; Helsinki, Finland; Barcelona, Spain; and Athens, Greece (Figure 4.8). This approach focused on levels of select PAH and hetero-PAH markers in 6 sites across Europe to evaluate contributions of point sources and PM toxicity.

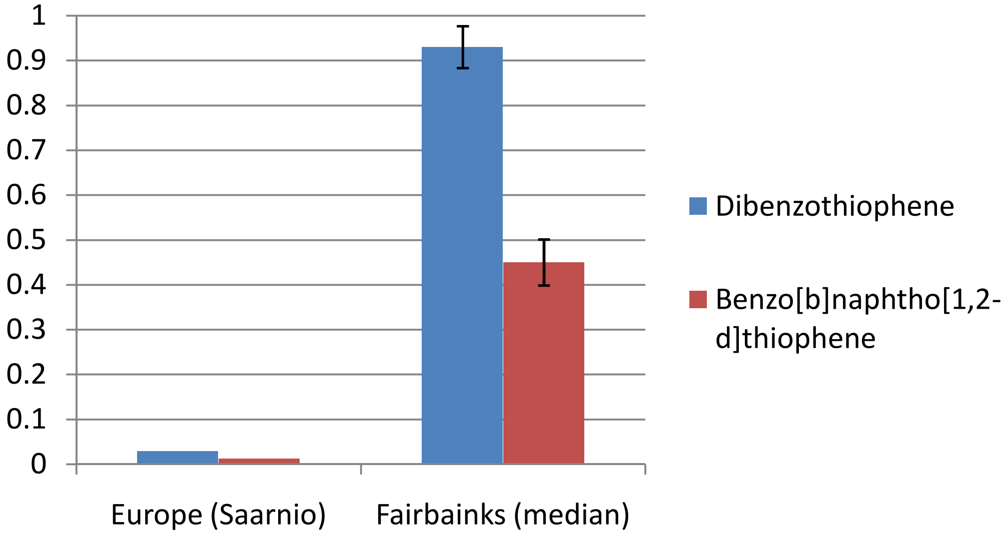


<u>Figure 4.8</u>: European Sites Sampled in Saarnio 2008 PM Study
(A) Helsinki, (B) Amsterdam, (C) Duisburg, (D) Prague, (E) Barcelona, (F) Athens

Comparison was made between DBT and the BNT from the Fairbanks $PM_{2.5}$ DRI results and the levels observed in the Saarnio 2008 study and can be seen below in Figure 4.9.

Diesel powered engines are more popular in Europe than in the USA; 50% of the automobiles in Europe contain diesel powered engines (Webster 2011). As such, it is expected that the contribution to PM from diesel emissions in Europe should be greater than that of the

US. However, the DRI results for Fairbanks $PM_{2.5}$ indicate the levels of the select thiophenes are much greater than those found in Europe during the Saarnio 2008 study. Also, considering that it is now standard to treat commercial diesel fuels used in automobiles for sulfur content in the US since 2006 (<500ppm total sulfur) (epa.gov), and all transportation diesel fuel in Fairbanks is low sulfur fuel, it is unlikely that diesel fuels are the source of the thiophenes.



<u>Figure 4.9:</u> Ambient Thiophenes in Fairbanks and Average European $PM_{2.5}$ (ng/m^3)

4.3.2C Mingo Junction, OH

Mingo Junction, OH is a small industrial town with a population of 3,600 (US Census 2000). Mingo Junction is impacted predominantly by coal combustion PM due to the increased amount of industry when compared to towns of similar size. The heavy influence of industry on the town can be seen below in Figure 4.10.

Figure 4.10: Mingo Junction, OH
coalcampusa.com

Studies have been conducted in Mingo Junction, OH investigating the PAHs in the PM, specifically the PAH picene (Section 2.7). A comparison of the organic carbon levels found in Mingo Junction PM to that of Fairbanks $PM_{2.5}$can be seen below in Figure 4.11.

The Mingo Junction PM contains 0.3µg/m^3 organic carbon, where 3-10% has been identified as being contributed from coal combustion emissions. The median value of picene levels found in Fairbanks $PM_{2.5}$ is 69.3µg/m^3 (Table 4.8), more than three times the levels found in Mingo Junction, OH. This provides very strong evidence that the Fairbanks PM is heavily impacted by contributions from coal combustion emissions as well.

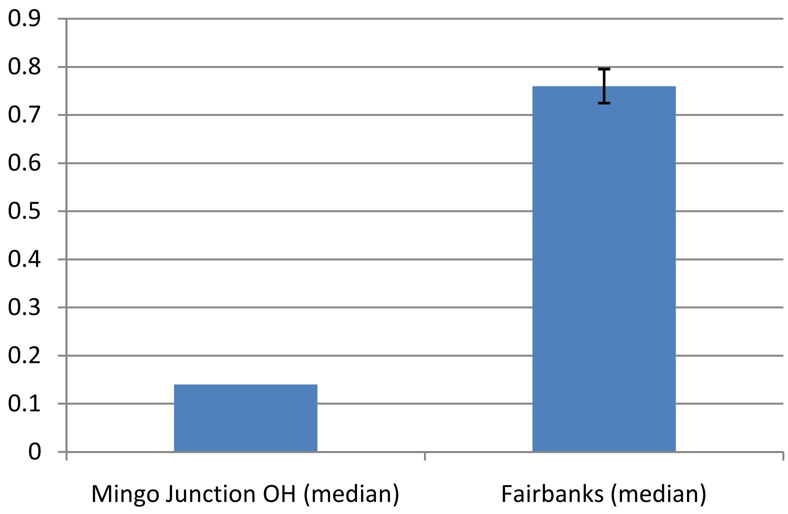


Figure 4.11: Ambient Picene in Mingo Junction and Fairbanks PM (ng/m^3)

4.4 Fairbanks, AK Fuels Analyses

Four fuel samples were received from Fairbanks, AK for analysis; three of which were liquid samples of Fuel #1, Fuel #2, and waste oil. The remaining fuel was a coal sample of the type used in the coal-fired power plant in downtown Fairbanks. The liquid fuels were analyzed by the GC-MS method described later in Chapter 5 for the select thiophenes; DBT and BNT (Section 2.7). The coal sample was analyzed for DBT, BNT and picene by a dichloro-methane extraction followed by a GC-MS method (Section 5.5). Additionally, the coal sample was analyzed for elemental composition by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (USEPA Method 200.7) following a digestion using a standard *aqua regia* digestion method (USEPA Method 3050B). This analysis was conducted at the Environmental Biogeochemistry Laboratory in the University of Montana Geosciences Department.

4.4.1 Liquid Fuels Results

The results of the liquid fuels analysis is below in Table 4.9, with values reported earlier for DBT in high-sulfur diesel fuel (HSDF) and low-sulfur-diesel fuel (LSDF) (Liang 2007). DBT was found in all 3 fuel samples and NBT was not found in any of the samples. The levels of DBT found in Fuel #1 is comparable to reported levels for LSDF (Liang 2007) as well as levels of speciated sulfur content in fuels designated ultra-low sulfur diesel by US EPA, assuming that DBT is the most abundant organic sulfur compound in the fuel. The levels of DBT in Fuel #2 is approximately five times that of reported levels for HSDF (Liang 2007), however it is still in line with the levels approved by the EPA for commercial use, assuming that all the sulfur content in the fuels is thiophenic (<1000ppm total sulfur) (epa.gov).

Table 4.9: Dibenzo-thiophene Concentrations in Liquid Fuels

Fuel Sample	[DBT] (ppm)
Fuel #1	15.5
Fuel #2	441.2
Waste Fuel	11.5
LSDF	15.2
HSDF	84.0

4.4.2 Coal Sample Results

The coal was analyzed for DBT, BNT picene by the dichloro-methane extraction GC-MS method described in detail in Section 5.5. as well as for elemental composition by ICP-AES. The

ICP-AES method showed that sulfur comprises up to 0.119% (1188mg/kg) of the coal sample. Somewhat surprisingly, however, none of the organic species of interest were detected by the GC-MS method. High levels of thiophenes were not necessarily expected due to the high levels of total sulfur observed by the ICP-AES method. It is known that the sulfur content in coal may be elemental (Goodarzi 2002). The complete results for the elemental composition analysis can be seen in Appendix A.2.

4.4.3 Implications to Fairbanks $PM_{2.5}$ Composition

Based on the results from the liquid fuels analysis, it is expected that if Fuel #2 is used for residential heating and/or to complement the coal used for energy production then it serves as a significant source of the thiophenes DBT and BNT found in Fairbanks $PM_{2.5}$. Although BNT was not found in the liquid fuel samples, it is known to be formed during combustion of fuels that contain DBT (Martin 2000). The high levels of sulfur in the coal could also generate significant levels of particulate borne secondary sulfate through release of gaseous SO_2.

4.5 Concluding Remarks

While there has been an extensive amount of work done on the source apportionment of Fairbanks $PM_{2.5}$, it is still not well understood as to what is the major contributing source of the high levels of sulfate identified by the CMB model. Based on the comparisons of the CMB model and organic carbon composition of Fairbanks $PM_{2.5}$ it is likely that the sources of the sulfate aerosols are (in no particular order) the combustion emissions of coal, and residential fuel oil.

It is not suspected that commercial diesel fuels or gasoline are a significant source of the high levels of sulfate due to their low levels of total sulfur. In particular, the diesel fuels used in Fairbanks are below 10ppm total sulfur content and is virtually absent in gasoline (Alaska DEC 2011). The analyses of the liquid fuels revealed that Fuel #2 has more than 40 times of sulfur content, in looking at the levels of DBT alone (441.2ppm), compared to the levels found in diesel fuels. This suggests that Fuel #2 used in residential oil burners for heating may be a significant source of the sulfate. Lastly, comparisons of levels of picene in Fairbanks PM to that reported to be found in commercial boiler emissions (Zhang 2008) and the relative contribution to the PM in a community heavily impacted by coal emissions (Mingo Junction, OH), provides very strong evidence that Fairbanks PM is impacted greatly from coal emissions.

Chapter 5: Analysis of $PM_{2.5}$ for Select Markers: Method Development

Chapter 5 Contents

5.1 Overview

Particulate matter generated during combustion of various fuels is a complex mixture of inorganic and organic constituents (Section 2.2). Typically, source apportionment through CMB approaches relies on the inorganic composition of the PM and inorganic source profiles. However, this chemical mass balance approach is not able to satisfactorily apportion the sulfur and sulfate content of Fairbanks $PM_{2.5}$ to specific sources (Section 4.1).

An alternative approach to source apportionment is to utilize the organic composition of the PM (Schauer 1999; 2002; 2008). This approach requires a comprehensive quantitative analysis of hundreds of organic compounds in the PM and comparison to published organic profiles for various sources. This is a very expensive approach, and its utility can be limited by the lack of representative source profiles.

Still, there is a great deal of useful information that can be obtained from selective quantitative analysis of the organic composition of PM, especially when this is combined with source apportionment through chemical mass balance methods based on inorganics analysis. An example of this targeted analytical approach is the method developed by Megan Bergauff (Bergauff 2008) and used in the wood smoke and woodstove change-out studies conducted in Libby, MT (Section 4.2). In those studies, seven known chemical markers of wood combustion found in $PM_{2.5}$ were selected and a simplified method developed to allow for cost effective analysis of a large number of filters. The results of those analyses were utilized to confirm or verify that wood combustion was a significant contribution to the $PM_{2.5}$ in Libby and to provide a quantitative measure of the reduction in wood combustion related $PM_{2.5}$ as a result of the woodstove change-out program.

In the current study, organic markers have been selected in order to better understand the possible sources of high levels of sulfate found in Fairbanks, AK. These markers were chosen based on alternative sources of $PM_{2.5}$ instead of wood, being that wood alone could not generate the levels of sulfate observed in Fairbanks, AK (Figure 4.3). The following markers were chosen for method development: the unique coal PM marker picene and the suspected diesel and residential heating oil PM markers DBT and BNT (Section 2.5). Levoglucosan was also selected as a marker of wood combustion.

A new method was thus needed to allow for the cost effective and sensitive analysis of these compounds. A goal of this method development project was to perform a single extraction for all of the analytes of interest, since this would keep analytical costs down and would allow for more sensitive extraction and analysis of entire filter halves. This presented a challenge, however, because the various compounds of interest have differences in solubility and because levoglucosan must be derivatized before GC-MS analysis. Two separate methods for levoglucosan and for coal and fuel oil PM markers would require the filter sample to be divided before analysis. This would have definite negative effects on the levels that could be seen in the filter samples.

The target concentration ranges for the analysis of the select markers DBT, BNT and picene were based upon the average ng/sample found in the results returned by DRI for the analysis of the eight filters that contained Fairbanks $PM_{2.5}$ (Appendix A.1). The average ng/sample of DBT, BNT and picene can be seen below in Table 5.1.

<u>Table 5.1</u>: Levels of Select Markers in Fairbanks $PM_{2.5}$ and Target Concentration Ranges

	Average (ng/sample)	ppm (whole filter)	ppm (1/2 filter)
Dibenzo-thiophene	13.46	0.0269	0.0135
2,3-Benzo-[b]-naphtho[1,2d]-thiophene	4.74	0.0095	0.0047
Picene	9.64	0.0193	0.0096

The concentrations in Table 5.1 correspond to what is expected if the reported ng/sample for each marker were in a solution of a total volume of 500µL, which is the final volume of the solution following the method described later in Section 5.4. Since only half of the filter is analyzed for the select organic markers, the concentration ranges in the method developed would have to have to be at or below those reported above in Table 5.1 for the ½ filters.

In addition to the analysis of PM, a method was needed for the analysis of fuel samples from Fairbanks for the presence and concentration of the selected marker compounds. Thiophenes are typically found at detectable concentrations in diesel fuel and residential heating oil, but their concentrations are significantly reduced in low sulfur diesel fuel (Liang 2007).

5.2 Previous Results

The GC method most commonly employed for the analysis of thiophenes in the literature utilizes an atomic emission detector (AED) (Frysinger 2003). This element-specific detector allows the detection of sulfur containing compounds within the unidentified complex mixture (UCM) portion of diesel fuels. An example of the complexity of these mixtures can be seen below in the sulfur GC-AED chromatogram of residential oil burner particulate in Figure 5.1 (Hays 2008).

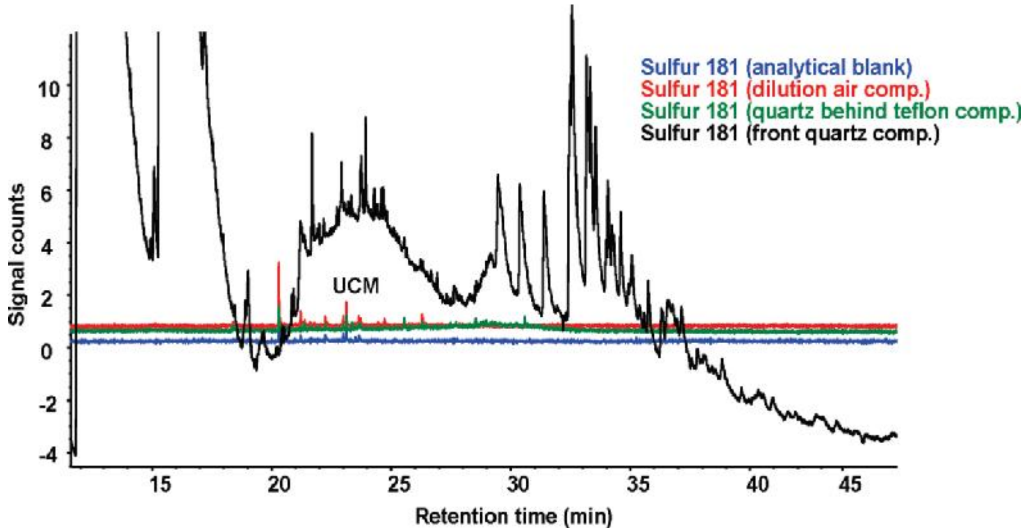


Figure 5.1: Sulfur GC-AED Chromatogram of Residential Oil Burner Particulate

Several different varieties of thiophenes are also found in diesel PM (Huffman 2000). These UCMs in all fossil fuels and their PM are highly complex, containing dozens of different organic species that are very difficult to resolve by standard GC methods.

As mentioned previously in Section 2.7.2, the sugar anyhydride levoglucosan is the optimal choice as the organic marker for PM from wood smoke to assist in the source apportionment of $PM_{2.5}$. A method was developed and optimized previously for the analysis of levoglucosan which is comparable to other methods found in the literature (Bergauff 2008). However, this alternate method employs a relatively safe ethyl acetate solution as the extraction solvent instead of the more toxic benzene or dichloro-methane. The use of ethyl acetate also allowed for the simultaneous extraction of several other wood smoke markers. This method is described in detail later in Section 5.4. The conditions of Bergauff's levoglucosan method were pursued in this such that it would confer the convenience of a single extraction method for the select markers of wood smoke, fuel oils and coal emissions.

5.3 Experimental

This section describes the instrumentation employed as well as any reagents used.

5.3.1 Equipment

The instrument employed in this work was an Agilent model 6890N GC with an Agilent 5973 Network MS detector. The column was a Supelco SLB-5ms fused silica capillary column of the dimensions 30m length, 0.25mm diameter and a 0.25µm film thickness. Ultra high purity helium was used as the carrier gas. The software used for the data analysis was Agilent ChemStation software and associated NIST library database. Column flow was regulated with an electronic pressure control system and was set to maintain a temperature independent linear carrier gas velocity of 40 cm/sec and flow rate of 1.0 mL/min.

5.3.2 Reagents and Chemicals

Standards: dibenzo-thiophene 99% (Acros), 2,3-benzo-[b]-naphtho[1,2d]-thiophene 99+% (Aldrich), d8-dibenzo-thiophene 98 atom% D (Aldrich), picene 50µg/mL in toluene

(AccuStandard), semi-volatile internal standard mix that contained D10-acenaphthene, D12-chrysene, D4-1,4-dichloro-benzene, D8-naphthalene, D12-perylene, and D10-phenanthrene; 2000µg/mL each in dichloro-methane (Supelco).

Derivatization reagents: N-O-bis(trimethyl-silyl)-trifluoro-acetamide derivatization grade 99+% (Sigma), trimethyl-chloro-silane 97% (Aldrich), trimethyl-silyl-imidazole derivatization grade 99+% (Supelco).

Solvents: ethyl acetate HPLC grade (EMD), dichloro-methane HPLC grade (EMD), triethyl-amine 99.5% (Aldrich).

5.4 Methods

This section describes the methods employed for the extraction of quartz filters containing $PM_{2.5}$ and their analysis.

5.4.1 Filters

Upon receiving quartz filter samples containing $PM_{2.5}$, they are placed into frozen storage at $0^{O}C$ until analyses are performed. This is done to prevent any semi-volatile or volatile compounds from being lost during storage.

The quartz filter is removed from the plastic container and cut into two equal portions. The scissors used for cutting the filters are rinsed with hexane and ethyl acetate and then air dried between samples to prevent cross-contamination. One filter portion is returned to the container and frozen storage to be sent for ^{14}C analysis while the other is placed into a cleaned and oven-dried 30mL glass vial.

5.4.2 Extraction

The filter portion is spiked with a volume of 3.6mM triethyl-amine in ethyl acetate (EtOAc/TEA) containing a known amount of a deuterated internal standard. The spiked filter is allowed to sit in the capped vial at room temperature until the solvent has evaporated and the internal standard has adhered to the filter, typically 10 minutes. Recovery standards are prepared by spiking clean filters with a known amount of analyte and allowing the solvent to evaporate in the same manner.

Approximately 20mL of EtOAc/TEA is added to the vial; the vial is then recapped and sonicated and heated at 30^{o}C for 30 minutes. Upon removal from the sonicator, the solution is filtered through a 0.45µm syringe filter to remove insoluble particulates, usually from the filter being broken apart as indicated by the cloudy solution. The solvent is then evaporated in an oil bath at 45^{o}C with a gentle stream of air until the total volume is less than 400µL and transferred to a 1mL eppendorf tube for derivatization.

5.4.3 Trimethyl-silyl Derivatization

The analyte and standards for levoglucosan were converted to their TMS derivatives following extraction. This derivatization is done to increase the volatility of the compounds and allow efficient separations. In a fume hood, 75µL N,O-bis (trimethyl-silyl) trifluoro-acetamide (BSTFA), 10µL trimethyl-chlorosilane (TMCS) and 10µL trimethyl-silyl-imidazole (TMSI) are added. The vials are capped and heated in an oil (or sand) bath at 70^{O}C for 1 hour. The vials are then removed from the bath, allowed to cool to room temperature, and then diluted to 500µL with EtOAc/TEA. The solution is then transferred to a GC vial insert (500µL capacity) in a 2mL GC vial for GCMS analysis.

5.4.4 Calibration Standards

Calibration standards were prepared by adding a constant amount, corresponding to the concentration at the middle point in the calibration curve and to a final internal standard concentration matching that for the filter extracts, of the deuterated internal standards to six vials. Five solutions of increasing concentration of each analyte and one blank were prepared in the vials. The calibration standards were then derivatized to their TMS derivatives as described in Section 5.4.3. The low end calibration points were analyzed 3 times on the GC-MS to determine an accurate value for the detection limit of the instrument for the particular compounds.

5.5 Method Development

A published method for the filter extraction and GC-MS analysis of the select wood smoke marker levoglucosan (Bergauff 2008) was modified and optimized for the simultaneous extraction and analysis of the selected markers DBT and BNT. The development of a method for picene was attempted but not successful.

In methods reported in the literature, the solvent most commonly used for the thiophenes were dichloro-methane (Leary 1987) or hexanes (Schauer 1999), where the solvent used in the detection of wood smoke markers was ethyl acetate (Bergauff 2008). It is expected that the solvent used for the extraction of the highly non-polar picene would have to be non-polar, such as dichloro-methane, hexanes or benzene. For the current method, ethyl acetate was investigated as an extraction solvent for all analytes, and the solution was sonicated and heated slightly above room temperature (30°C) for 30 minutes.

Levoglucosan requires derivatization to the trimethyl-silyl derivative before GC analysis. In the current study, it was investigated whether the derivatization method required for the analysis of levoglucosan has any significant impact on the analysis of the thiophenes or picene, which it did not. These observations allowed for the simultaneous extraction of levoglucosan, picene and the thiophenes, followed by derivatization of the levoglucosan and analysis by GC-MS.

5.5.1 GC-MS of Thiophenes

The temperature program used in previous methods for the analysis of levoglucosan, which can be seen below in Table 5.2, was found to provide suitable separation of the thiophenes.

Table 5.2: GC-MS method temperature profile

	C/min	Next C	Hold	Runtime
initial		40	1.5	1.5
Ramp 1	30	190	0.0	6.5
Ramp 2	20	210	0.0	7.5
Ramp 3	50	300	1.5	10.8

Calibration standards were prepared for DBT in the range of 0.001-1.000ppm and analyzed by GC-MS employing a splitless injection method to increase sensitivity. Each standard within the 0.001-0.010ppm range was analyzed three times each to access the sensitivity and reproducibility at this range. A constant amount of the deuterated standard D8-DBT was added to each to be used as an internal standard. Initially, the GC-MS data are presented as a total ion chromatogram as seen below in Figure 5.2. We can filter the data to only show specific extracted ions to ensure any peaks integrated are from only one or more particular ions (Figure 5.5).

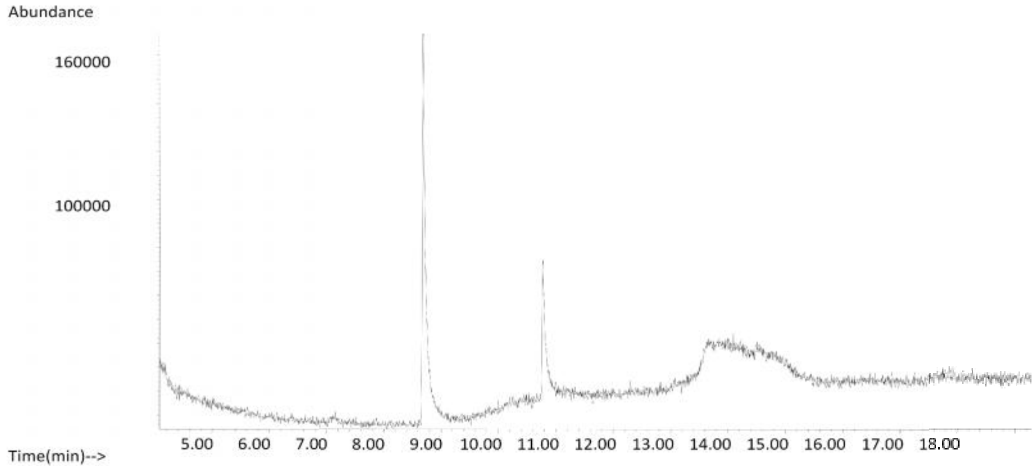


Figure 5.2: Total Ion Chromatogram: Dibenzo-thiophene (1.00ppm)

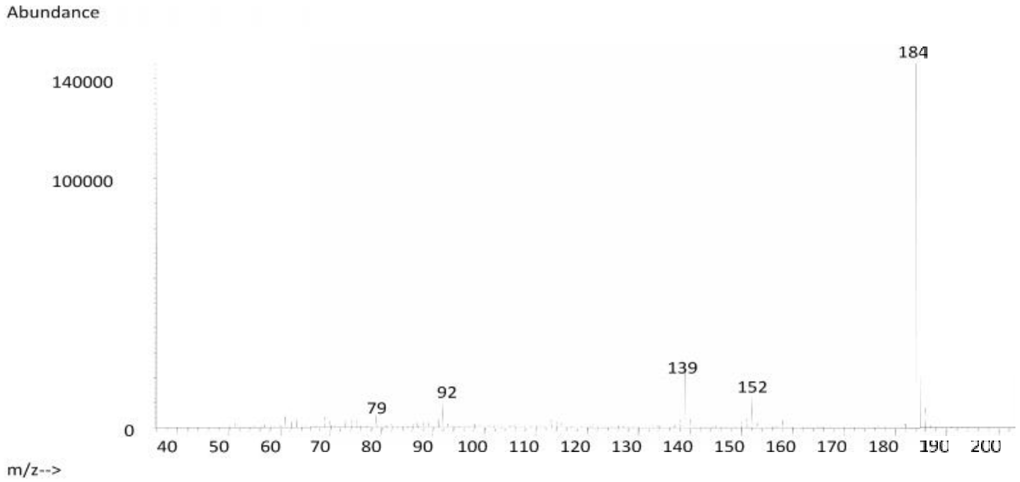


Figure 5.3: Mass Spectrum of Dibenzo-thiophene

The values for the areas used for DBT and D8-DBT were extracted from the total ion chromatogram by filtering the data to only show the select ions m/z=184 (DBT) and m/z=192 (D8-DBT). These ions were selected because they represent the major ions in the mass spectra for these species as seen in Figure 5.3 and Figure 5.4.

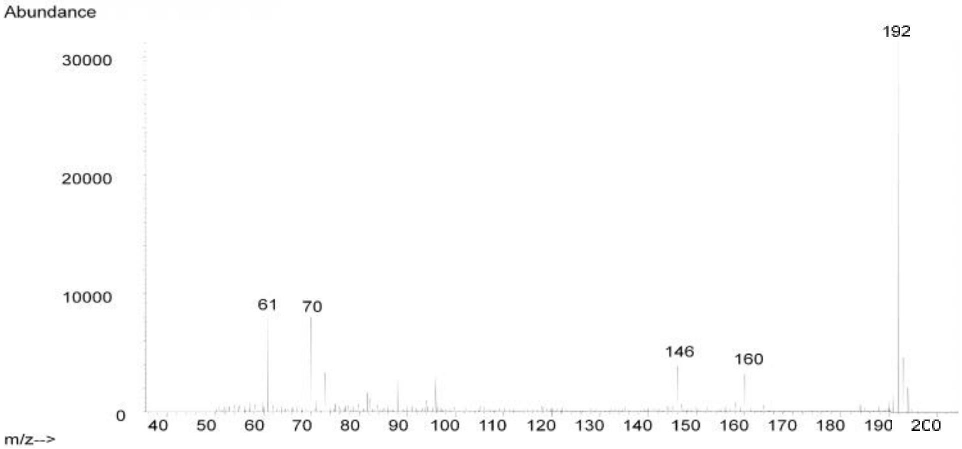
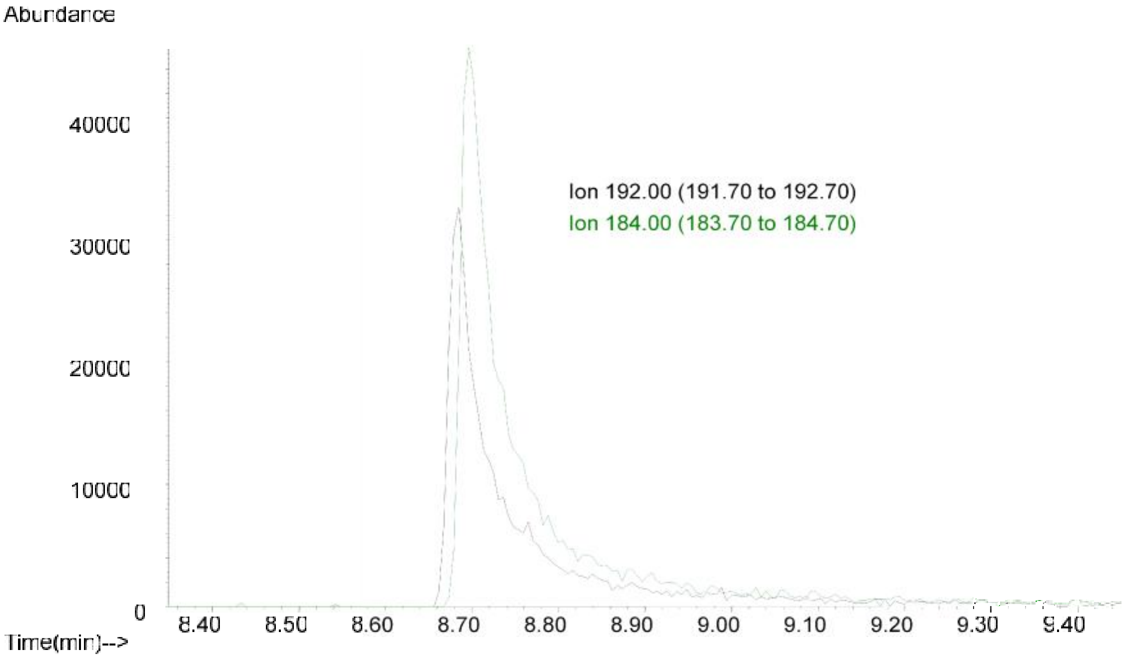


Figure 5.4: Mass Spectrum of D8-Dibenzo-thiophene

The mass spectrum for DBT was confirmed by a comparison to the spectrum in the NIST library data base, which can be seen in Appendix A.3. Confirmation of DBT was based upon the ions at m/z=139, 152 and 184 where the only suitable mass to be used for quantification was m/z=184. There was not a mass spectrum available in the NIST library database for the internal standard D8-DBT. However, due to their similar structures (identical except for the exchange of hydrogen with deuterium) it was expected that the fragmentation pattern in the observed mass spectrum of D8-DBT to be similar to DBT. The ions found at m/z=160 and 192 correspond to an increase of 8 m/z to that of the ions m/z=152 and 184 in the spectrum for DBT, respectively. Similarly to DBT, the ion found at 192 was the only ion used for quantification for D8-DBT.

The total ion chromatogram is then converted to an extracted ion chromatogram only displaying ions m/z=184 and 192, as can be seen below in Figure 5.5.



<u>Figure 5.5</u>: Extracted Ion Chromatogram: Dibenzo-thiophene

Typically, integration of the extracted ion peaks was performed automatically with the Chemstation integrator. However, at the low end of 0.001ppm manual integration was required. It is believed this manual integration method may have been part of the cause of the relatively high value for the percent relative standard deviation (%RSD) at 0.001ppm. The raw GC-MS data can be seen below in Table 5.3.

Regression analysis of the calibration data returned acceptable results for all ranges investigated. Below in Table 5.4 is a summary of correlation coefficients with respect to particular concentration ranges.

<u>Table 5.3</u>: Dibenzo-thiophene Calibration Data

	DBT (184)					D8 DBT (192)				
Vial	[DBT] (ppm)	Tr (min)	Area	stdev	Area %RSD	Tr (min)	Area	stdev	Area %RSD	RATIO
BLK	0.000	nd	0			13.651	1067667			0
A	0.001	13.671	14261	6129	42.98	13.652	1063146	166273	15.64	0.01341
B	0.003	13.678	35827	9512	26.55	13.653	970689	113586	11.70	0.03691
C	0.005	13.677	61659	4098	6.65	13.653	984210	78291	7.95	0.06265
D	0.007	13.674	104310	25233	24.19	13.653	1024263	43167	4.21	0.10184
E	0.010	13.678	124066	18090	14.58	13.652	1085340	171495	15.80	0.11431
F	0.050	13.673	529424			13.652	982066			0.53909
G	0.100	13.671	1537504			13.648	1237210			1.24272
H	1.000	13.664	11202263			13.644	1297228			8.63554

Often times, when working at the low end of the calibration with the recover standards, the calculated values for the concentrations would result in a negative concentration if the Y-intercept in the calibration curve was large. To avoid this, these calibration plots were forced to have a zero Y-intercept. Investigating Table 5.4 indicates that this correction had a minimal impact on the correlation coefficient.

In order to evaluate the method, several recovery standards were prepared by adding known amounts of DBT as well as D8-DBT to a blank filter. This spiked filter was then solvent extracted using the method described previously in Section 5.4. Known amounts of both DBT and D8-DBT standards were spiked onto blank quartz filters such that a particular known concentration was reached following the extraction and dilution to 500µL as indicated in Table 5.5 below.

Table 5.4: Calibration Correlation Coefficients

Range	Corr	Corr (zero Y-int)
0.001-1.000	0.9982	0.9975
0.001-0.010	0.9977	0.9945
0.001-0.100	0.9954	0.9953
0.010-0.100	0.9940	0.9916

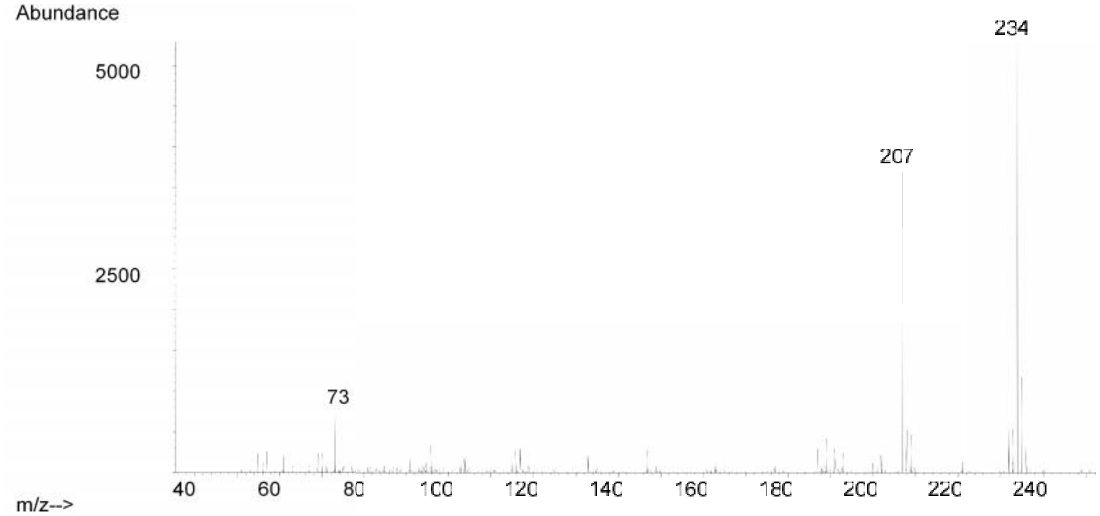
Table 5.5: Dibenzo-thiophene Extraction Method Validation

Sample	expected [ppm]	calc [ppm]	expected [ppm]	Percent recovery	%RSD
BK	0	0.00563			
R1	0.010	0.01132	0.01	107.9	4.2
R2	0.010	0.01041	0.01	100.4	5.3
R3	0.020	0.02286	0.02	121.8	5.4
R4	0.020	0.02813	0.02	118.7	18.2
R5	0.200	0.24366	0.2	119.8	1.8
R6	0.200	0.21306	0.2	106.2	4.0

All of the calculated concentrations above in Table 5.5 were blank corrected (sample BK). Note that all of the percent recoveries were greater than 100%, which is likely resulting from the use of a deuterated standard. In all but one case, the recoveries were within one standard deviation of 100%, and are thus not significantly greater than 100%. It was suspected that, in this case, the deuterated standards are slightly more volatile than their non-deuterated analogs and the areas for the deuterated standards is used as the denominator in the ratios used in the calibration to calculate the concentrations. It is likely that slightly more of the deuterated standard is lost relative to the non-deuterated standard during the extraction process.

Recall that from Table 5.1 that the target concentration range for DBT was at or below 0.0135 ppm, this concentration corresponded to the average amount of DBT report to be in Fairbanks $PM_{2.5}$ by the analysis done by DRI. Samples R1 and R2 indicate that the method for the extraction of DBT using a similar method as that for levoglucosan was successful for the average concentration returned from DRI with a detection limit of approximately 0.010 ppm. However, the minimum amount of DBT in the DRI results was 4.209 ng/sample (Appendix A.1) which results in a final expected concentration of 0.004 ppm if the previously described method is employed. Thus, further optimization of this method is needed to be useful for the minimum DBT range.

A GC-MS calibration of the select marker BNT was performed in a similar manner as was done for DBT. However, at the lower end of the calibration (0.001-0.010ppm) there was a large amount of variability in the signal. Typically, as was done for levoglucosan and DBT, the GC-MS results are returned as a total ion chromatogram (TIC) and the relevant data is obtained by extracted ion analysis. In order to improve the signal to noise ratio for BNT a GC-MS method was programmed for single ion monitoring (SIM). During select time periods chosen to encompass the retention times for BNT as well as for the internal standard D8-DBT, only selected ions were monitored. For extracted ion and SIM analyses, the molecular ion m/z=234 was used as the selected ion because it is the most abundant ion in the MS spectrum as seen below in Figure 5.6. Notice that there was a significant ion found at m/z=207, however this ion was not used for quantification because this ion is not seen in the mass spectrum for BNT in the NIST library database, which can be seen in Appendix A.3. While this alteration to the GC-MS method did indeed increase the sensitivity of BNT and D8-DBT it did not decrease the variability at the low end of the calibration.



<u>Figure 5.6</u>: Mass Spectra of 2,3-Benzo-[b]-naphtho[1,2d]-thiophene

In order to access the feasibility of the ethyl acetate extraction method for BNT a calibration was performed in the 1-10ppm range, and analyzed by using a standard split GC-MS method. A sample extracted ion chromatogram in this concentration range can be seen below in Figure 5.7. The results of this BNT calibration can be seen below in Table 5.6.

The resultant linear regression of the data below in Table 5.4 resulted in a correlation coefficient of 0.99. Setting the Y-intercept to be equal to zero resulted in a significant decrease in the correlation coefficient to 0.980. Therefore, the Y-intercept correction was not used.

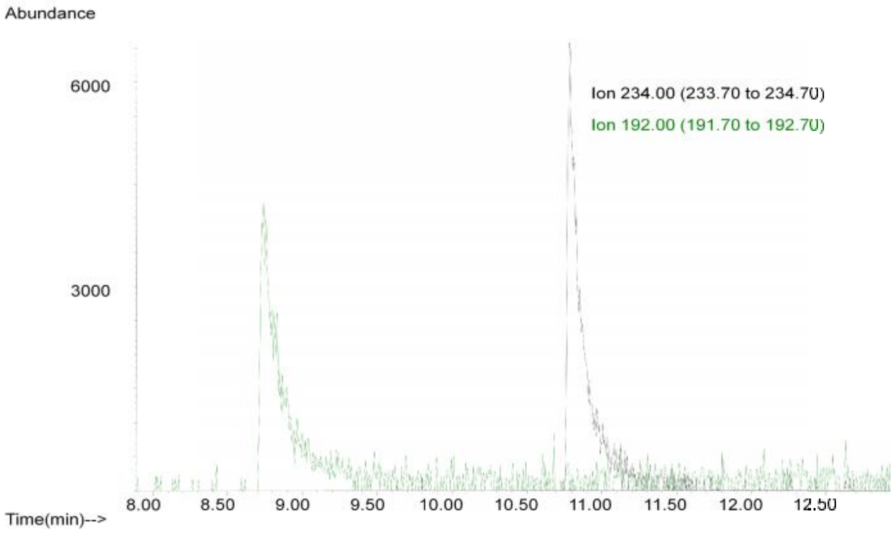


Figure 5.7: Extraction Ion Chromatogram: 2,3-Benzo-[b]-naphtho[1,2d]-thiophene

Table 5.6: 2,3-Benzo-[b]-naphtho[1,2d]-thiophene Calibration

		BNT (234)				D8-DBT (192)				
Vial	[BNT] ppm	Tr (min)	Area	stdev	Area %RSD	Tr (min)	Area avg	Area std	Area %RSD	Ratio
BLK	0.00					8.747	676055	364	0.05	0
A	1.00	10.831	99589	9563	9.60	8.726	900372	54754	6.08	0.1104
B	3.00	10.820	258408	10446	4.04	8.728	929035	28546	3.07	0.2782
C	7.00	10.788	567435	42338	7.46	8.747	560110	25374	4.53	1.0140
D	10.00	10.781	878006	16097	1.83	8.756	614492	12026	1.96	1.4290

Blank filters were then spiked with known amounts of BNT and D8-DBT, allowed to dry for 1 hour and then extracted and analyzed by GC-MS in a similar fashion as was done for DBT as a means to validate the method. Results of the validation can be seen below in Table 5.7.

The method for BNT appears to have similar percent recoveries as seen with DBT at this concentration. It should be noted that sample E2 was accidentally brought to dryness during the evaporation step in the extraction process. The seemingly elevated percent recovery is likely due to the increased volatility of the D8-DBT relative to BNT, resulting in an increased calculated percent recovery if more D8-DBT was lost in the extraction compared to BNT. This illustrates that the recoveries for BNT are more sensitive to being brought to dryness than is the case with levoglucosan, which shows little to no change if brought to dryness during the evaporation step.

<u>Table 5.7</u>: 2,3-Benzo-[b]-naphtho[1,2d]-thiophene Extraction Method Validation

Sample	Expected [ppm]	Calc [ppm]	Percent recovery	%RSD
BK	0.00	0.00		
E1	5.00	4.99	99.80	0.57
E2	5.00	6.60	132.03	0.56
E3	5.00	5.67	113.48	0.71

Based on these preliminary results at this increased concentration range for BNT it appears that the extraction method using an ethyl acetate solution is viable. However, more studies need to be conducted at reduced concentration ranges (0.001-0.010ppm) if it is to be used for Fairbanks $PM_{2.5}$ analysis.

5.5.2 GC-MS Analysis of Picene

A calibration of picene using a splitless GC-MS method for the range of 0.100-1.000ppm was attempted in a similar fashion as was described for DBT and BNT. However, it is not likely that the internal standard D8-DBT is suitable for picene due to differences in volatility and polarity. Instead, a deuterated internal standard mixture containing D10-acenaphthene, D12-chrysene, D4-dichloro benzene, D8-naphthalene, D12-perylene, and D10-phenanthrene was used. Of the deuterated PAHs listed D12-chrysene is the best candidate to be used as an internal standard for picene due to similarities in their structures. The mass spectrum found in the NIST library database can be seen in Appendix A.3. Chrysene is a 4 ring PAH where picene is a 5 ring PAH and should exhibit similar physical properties and separations on the GC column.

Unfortunately, for reasons that are not well understood, picene has a significantly reduced sensitivity with the GC-MS method when compared to the thiophenes as well as D12-chrysene (m/z=240). The ion to be used for quantification for picene was determined to be m/z=278 by investigation of the mass spectrum in the NIST library database, as seen in Appendix A.3. The extracted single-ion chromatogram (m/z=278) for picene exhibited a very broad low intensity peak for picene of ~0.50min as can be seen in Figure 5.8. In fact, picene was only observed in the 0.700ppm and 1.000ppm calibration standards. Considering that picene was received as a 5.000ppm solution, a calibration at increased concentrations as was done for BNT was not possible.

Simultaneously with DBT, a GC-MS method was programmed for SIM. During select time periods chosen to encompass the retention times for DBT as well as for the internal standard D8-DBT, D12-chrysene and picene, only selected ions were monitored. The resultant SIM chromatogram can be seen below in Figure 5.8.

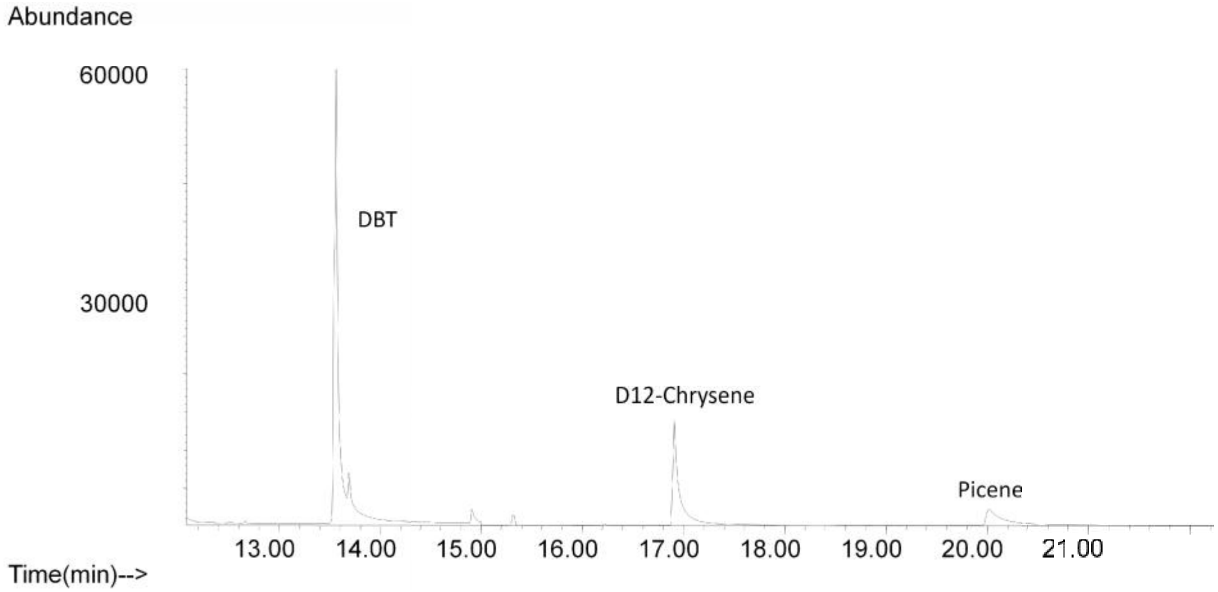


Figure 5.8: Single Ion Monitoring Chromatogram

The temperature ramp rate was adjusted several times to both increase the total run time as well as decrease it. Neither adjustment to the ramp rate appeared to have any effect on the peak shape or sensitivity of picene. The retention time shifted slightly but the broad peak remained.

In order to access if ethyl acetate would be a suitable solvent for the filter extraction of picene, an amount of picene corresponding to a final concentration of 1.000ppm when diluted to 500µL (100µL 5.00ppm picene) and a known amount of the internal standard mixture (similar to the calibration, 0.500ppm final concentration) were spiked onto a blank filter and extracted by the method described in Section 5.3.3. The result of this extraction revealed a ratio that was approximately 80% of the ratio observed with the 1.000ppm calibration standard. Because of this it appears that ethyl acetate could indeed be used as a filter extraction solvent, however it is not ideal.

Additional studies on the GC-MS parameters to increase the sensitivity of picene need to be conducted before this method can be used for the analysis of Fairbanks $PM_{2.5}$.

5.6 Fuel Samples Analyses

Three liquid fuels and solid coal fuel were obtained from Fairbanks for analysis. The liquid fuels were labeled as Fuel #1, Fuel #2 and Waste Fuel, and it was indicated that these fuels are used in residential oil burners. It was also indicated that the coal sample is of the same kind used in the coal-fired power plants and for limited residential heating in Fairbanks, AK.

Aliquots (10 and 20µL) of the liquid fuels were placed into GC vial inserts that contained a known amount of D8-DBT and internal standard PAH mixture. The resultant solution was then diluted to 500µL with EtOAc/TEA and analyzed by GC-MS. These samples were treated as if they were filter extract solutions and analyzed by the same GC-MS methods as described previously in this chapter except that split injection with a split ratio of 50:1 was used.

A portion of the coal sample was ground to a fine powder by a mortar and pestle and two portions of this fine powder (398.4mg and 801.7mg) were digested using a standard *aqua regia* digestion method (USEPA Method 3050B) and was analyzed for elemental composition by ICP-AES (USEPA Method 200.7). The thiophenes and picene content of the coal was analyzed by

GC-MS. From the portion of coal that was ground to a fine powder, 100mg was placed into 30mL dichloro-methane and sonicated and heated at 30°C for approximately 8 hours. Aliquots of the resultant solution were then placed into a GC vial insert containing a known amount of D8-DBT and internal standard mixture and diluted to 500µL with EtOAc/TEA and analyzed by GC-MS. The results of this fuels analyses can be seen in Section 4.4 and Appendix A.2.

Chapter 6: Future Directions

Chapter 6 Contents

6.1 Future Directions

As indicated in Chapter 4, the major sources of the high levels of sulfate in Fairbanks $PM_{2.5}$ are not yet completely understood and quantitative apportionment to various sources is not yet possible. In order to adequately apply source apportionment of the sulfate levels, additional studies need to be conducted. This Chapter describes additional work as well as alternative approaches that may shed some light on the sulfate levels in Fairbanks $PM_{2.5}$. As discussed in Section 5.4 additional work should be done on the filter extraction methods for the select markers BNT and picene to increase the sensitivity and reduce the variability of the low concentration ranges. The following sections are additional suggestions on future directions for this study.

6.1.1 Principle Components Analysis

It has been suggested by collaborator Robert Crawford that the levels of selected organics to be correlated with meteorological parameters, both raw parameters and meteorological factors obtained from a principle components analysis (PCA). Investigating the correlations in this fashion can give some insight into the conditions that lead to high levels of $PM_{2.5}$ from various sources, as well as the high levels of sulfate in the $PM_{2.5}$.

A principal component identified by Crawford's model (inversion strength) and actual meteorological data (temperature differentials at various altitudes) were correlated to levels of select chemical markers in the DRI analyses of eight PM samples from Fairbanks (Section 4.3). The principal component correlated to the masses of select chemical markers was the parameter "Met6", which can best be described as a measure of the inversion strength. The masses of chemical markers were also correlated with dT###, which are temperature differentials between the ground and the notated height in meters. A positive value for dT is indicative of a temperature inversion. The extent to which these positive temperature differentials extend to higher levels is an indication of the height and strength of the inversion layer in the valley. This is further illustrated in Figure 6.2, which shows average temperature profiles above Fairbanks for various months. The actual height of the inversion boundary in this figure is at the point where the rate of change of the temperature is equal to zero. On inspection of Figure 6.2 it becomes apparent that a relatively large value for dT at higher elevations implies a high inversion boundary. These correlations can be seen below in Table 6.1.

Table 6.1: Mass to Inversion Parameters Correlation Coefficients

	Met6	dT050	dT100	dT200	dT300	dT500
Dibenzo-thiophene	0.19	0.06	0.18	0.38	**0.60**	**0.67**
2,3-Benzo-[b]-naphtho[1,2d]-thiophene	**0.72**	-0.13	0.08	0.24	0.47	**0.73**
Picene	**0.79**	-0.28	-0.06	0.14	0.43	**0.74**

In this type of correlation analysis a correlation coefficient of 0.60 or greater is believed to be of significance. Interestingly, BNT and picene exhibited a relatively strong correlation to the inversion strength parameter Met6 while DBT did not. However, all 3 select chemical markers exhibited a correlation to the inversion height at 500m. Additionally DBT had a moderate correlation to inversion height of 300m. This preliminary analysis strongly indicates that the select markers DBT, BNT and picene are being emitted from a high source and are only trapped when the top of the inversion layer is also high. This is the case because if these compounds were emitted from a low source (residential) there would have been a strong correlation when the inversion layer was lower to the ground (dT050 and dT100). When the inversion layer is low, pollutants emitted from a high source are dispersed into the atmosphere above the inversion and are not trapped in the valley below. Pollutants emitted from a high source suggests that the select markers (fuel oils and coal) are being emitted from a smoke stack, possible that of a coal-fired power plant.

Additionally, mass to mass correlations were made for the select chemical markers DBT, BNT and picene. The results of these mass to mass correlations can be seen below in Table 6.2.

Table 6.2: Mass to Mass Correlations of Select Chemical Markers

	DBT	BNT	Picene
Dibenzo-thiophene	1	0.71	0.61
2,3-Benzo-[b]-naphtho[1,2d]-thiophene		1	0.94
Picene			1

These mass to mass correlations are relevant because they may suggest co-emission of positively correlated chemical markers. Of all the possible combinations of co-emission it appears that BNT and picene are emitted from the same source due to their strong correlation with each other. It is possible that the coal-fired power plants may use residential heating oil to supplement the use of coal in power production. If Fuel #2 is indeed the fuel being used as a supplement it is likely the source of the BNT (formed upon combustion) being co-emitted with the picene from the coal because of the high levels of DBT found in Fuel #2. . It should be noted, however, that many chemical components of Fairbanks PM are strongly correlated. This is probably because the levels of all contaminants are strongly correlated with inversion events.

Unfortunately, there is an insufficient amount of data used in the PCA for it to be conclusive enough to be used in source apportionment of Fairbanks $PM_{2.5}$. It was suggested by Crawford that a minimum of at least 22 more data points needed to be introduced to determine the significance of the correlations. It would also be instructive to include levoglucosan to confirm the validity of the temperature differentials influence. It would be expected that there would be a strong/moderate correlation at all of the temperature differentials because it is known that the majority of the levoglucosan in the PM is caused by residential heating.

6.1.2 Adiabatic Lapse Rate Modeling

Another type of model that may further strengthen the preliminary results from the PCA is an adiabatic lapse rate model. The adiabatic lapse rate is defined as the rate at which the temperature of a parcel of air changes as it descends or ascends in the atmosphere. It is expected that as a parcel of air rises in the atmosphere it will expand and result in a decrease in temperature with altitude and the reverse if the parcel of air is descending (the opposite is the case for a temperature inversion). The adiabatic lapse rate of a dry parcel of air can be seen in the equation below.

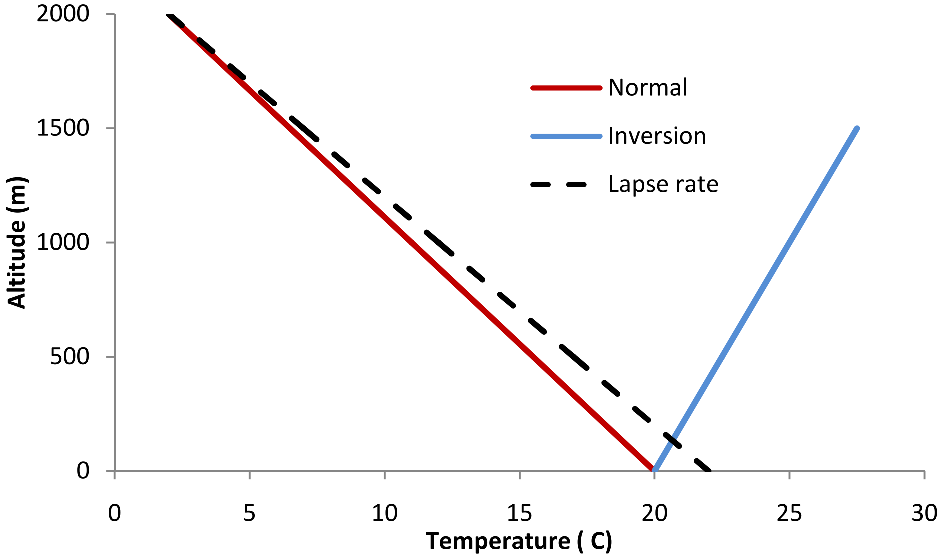
$$\Gamma_d = -\left(\frac{dT}{dZ}\right)_d = \frac{g}{c_{p,d}} = 9.760\ {}^{K}/_{km}$$

Where, dT/dz is the rate of change of the temperature with altitude, g is the gravitational constant for Earth (9.81m/s^2), and $c_{p,d}$ is the specific heat of dry air at constant pressure. Note that for a dry parcel of air this adiabatic lapse rate is constant.

For the derivation of the above equation, two assumptions are made and both are considered to be "good" assumptions for a dry parcel of air. First, it is assumed that the process is truly adiabatic, which is believed to be a good assumption because air is a poor thermal conductor. Secondly, the air parcel is considered to be at hydrostatic equilibrium, meaning that there is a constant mass in the parcel of air. This second assumption is good as long as there is not a high amount of wind present.

It is believed that if a plot is made of the actual temperature profile (temperature versus altitude) and compared to the adiabatic lapse rate plot then at the point of intersection the density of the rising air parcel will be equal to the surrounding air. At the point where the air densities are equal the parcel will not be able to rise further and any pollutants within the air parcel will be trapped at or below this altitude. A comparison of the dry adiabatic lapse rate to typical conditions as well as to an inversion event can be seen in Figure 6.1

Upon investigating Figure 6.1 it is apparent that if there is normal temperature conditions (decreasing temperature with altitude) that the point of intersection of the dry adiabatic lapse rate to the temperature profile occurs at a high altitude. In the case illustrated in Figure 6.1 this occurs at 2000m. However, in the case of a temperature inversion it is clear that the air is trapped at a much lower altitude (~100m) which implies that the pollutants would be trapped in the valley. This analysis also further supports the effects of pollutant trapping during inversion events as discussed previously in this work.



<u>Figure 6.1:</u> Dry Adiabatic Lapse Rate Comparisons to Normal and Inversion Conditions

Comparisons to the conditions in Fairbanks to a dry adiabatic lapse rate would be largely erroneous. Using a dry adiabatic lapse rate would only be applicable to an arid climate, which Fairbanks is not. As discussed previously in Section 3.2, Fairbanks experience ice fog during the winter which would imply that the air is saturated with water vapor during the winter. In this case, a wet adiabatic lapse rate would be more accurate for the conditions in Fairbanks. The equation for a wet adiabatic lapse rate can be seen below.

$$\Gamma_w = -\left(\frac{dT}{dZ}\right)_w = \frac{g}{c_{p,d}} + \frac{H_{vap}}{c_{p,w}}\left(\frac{dq_v}{dZ}\right)$$

Where H_{vap} is the enthalpy of vaporization of water, $c_{p,w}$ is the specific heat of wet air at constant pressure and dq_v/dZ is the rate of change of the mixing ratio of dry and wet air with altitude. Notice that the first term in the above equation is equivalent to the dry adiabatic lapse rate. The second term is warming due to the release of latent energy during condensation. The reason this is being considered a modeling project is due to the interdependent nature of the terms H_{vap} and dq_v/dZ to temperature and pressure. This is further complicated due to the fact that temperature and pressure are dependent on altitude.

Other considerations are the actual temperature profiles for Fairbanks as well as the conditions of a parcel of air coming from a smoke stack (possible significant source of $PM_{2.5}$ as discussed previously). Below in Figure 6.2 are monthly averages of temperature profiles in Fairbanks from 1957-2008 (Bourne 2010).

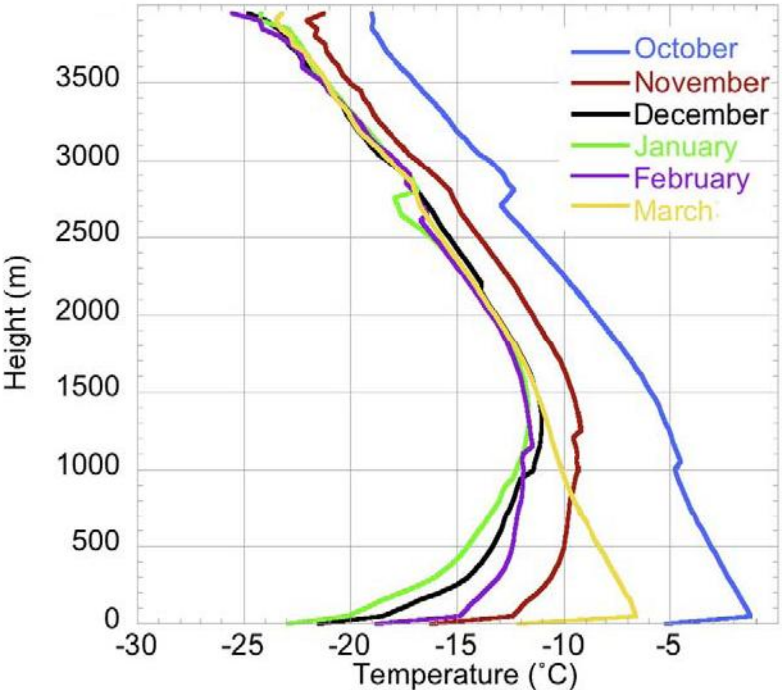


Figure 6.2: Average Temperature Profiles of Fairbanks

It appears that during the colder months (November to February) that the inversion boundary is at approximately 1200m. However, these are monthly averages and inversion height and thickness are highly variable from day to day. Therefore, meteorological data for each individual day used in the model would be needed. Also, notice that these temperature profiles are not linear; this would have to be taken into account in the model as well.

It is presently unclear how much information would be obtained from modeling what happens to a hot parcel of air (containing PM) as it leaves a smoke stack. The height of the smoke stack as well as the temperature of the air parcel would have to be considered. Since the air parcel leaving the smoke stack contains combustion products it is likely that it contains high levels of water vapor and is at significantly elevated temperatures relative to the ambient air. Due to the large difference in the temperature of the air parcel to the surrounding air it is likely that mixing occurs and this would have to be taken into account as well in the model.

6.3.3 Source Profiles

As discussed in Section 4.1.2, a CMB model analysis was conducted on Fairbanks $PM_{2.5}$. Recall, that the CMB model requires source profiles to be used as a basis for comparison for source apportionment of the $PM_{2.5}$. However, the profiles used for the Fairbanks CMB study were taken from other air sheds. While many of the air sheds are similar (such as Missoula) it is unlikely they are identical due to the uses of different fuels in both towns. It is recommended that source profile analyses be conducted for Fairbanks fuels. Profiles are needed for both the inorganic components for the CMB model as well as a thorough organic carbon speciation, specifically the select markers DBT, BNT and picene.

While it is unclear whether or not the CMB model will return different results with these Fairbanks specific profiles, the organic carbon speciation profiles will provide a significant amount of information due to the insufficient amount of information reported in the literature.

Appendix

A.1 Desert Research Institute $PM_{2.5}$ Analysis Results

A.1A DRI PAH sample IDs

field_name	compound	field_name	compound
A_MFLUO	A-Methylfluorene	BNTIOP	Benzonaphthothiophene
B_MFLUO	B-Methylfluorene	BZCPHEN	benzo(c)phenanthrene
M_1FLUO	1-Methylfluorene	BGHIFL	Benzo(ghi)fluoranthene
FL9ONE	9-fluorenone	CP_CDPYR	Cyclopenta(c,d)pyrene
DBTH	Dibenzothiophene	BAANTH	Benz(a)anthracene
PHENAN	Phenanthrene	CHRYSN	Chrysene
ANTHRA	Anthracene	BZANTHR	Benzanthrone
M_2PHEN	3-methylphenanthrene	BAA7_12	Benz(a)anthracene-7,12-dione
M_3PHEN	2-methylphenanthrene	M_3CHR	3-methylchrysene
M_2ANTH	2-methylanthracene	M_7BAA	7-methylbenz(a)anthracene
M_45PHEN	4,5-methylenephenanthrene	DMBAN712	7,12-dimethylbenz(a)anthracene
M_9PHEN	9-methylphenanthrene	BBFL	Benzo(b)fluoranthene
MPHT_1	1-methylphenanthrene	BJFL	Benzo(j)fluoranthene
M_9ANT	9-methylanthracene	BKFL	Benzo(k)fluoranthene
NAP2PHEN	2-phenylnaphthalene	BAFL	Benzo(a)fluoranthene
A_DMPH	A-dimethylphenanthrene	BEPYRN	BeP
B_DMPH	B-dimethylphenanthrene	BAPYRN	BaP
DM17PH	1,7-dimethylphenanthrene	PERYLE	Perylene
DM36PH	3,6-dimethylphenanthrene	M_7BPY	7-methylbenzo(a)pyrene
D_DMPH	D-dimethylphenanthrene	INCDFL	Indeno[123-cd]fluoranthene
E_DMPH	E-dimethylphenanthrene	IN123PYR	Indeno[123-cd]pyrene
C_DMPH	C-dimethylphenanthrene	DBAJAN	Dibenzo(a,j)anthracene
FLUORA	Fluoranthene	BBCHR	Benzo(b)chrysene
PYRENE	Pyrene	PIC	Picene
RETENE	Retene	BGHIPE	Benzo(ghi)perylene
BAFLUO	benzo(a)fluorene	ANTHAN	Anthanthrene
BBFLUO	benzo(b)fluorene	TRIPHEN	Triphenylene
C1MFLPY	1-MeFl+C-MeFl/Py	DBALPYR	Dibenzo(a,l)pyrene
M_13FL	1+3-methylfluoranthene	CORONE	Coronene
M_4PYR	4-methylpyrene	DBAEPYR	Dibenzo(a,e)pyrene
CMPYFL	C-MePy/MeFl	DBAIPYR	Dibenzo(a,i)pyrene
DMPYFL	D-MePy/MeFl	DBAHPYR	Dibenzo(a,h)pyrene
M_1PYR	1-methylpyrene	DBBKFL	Dibenzo(b,k)fluoranthene
A_MFLUOU=	A-Methylfluorene uncertainties (etc)		

A.1B DRI PAH results

site	strtdate	vol_m3	ug/m3	units	a_mfluo	a_mfluou	b_mfluo	b_mfluou	m_1fluo
510	11/15/2009	9.683	15.7	ng/sample	0.000	0.010	1.886	0.352	1.913
773	11/27/2009	9.683	20.9	ng/sample	0.000	0.010	1.344	0.251	0.632
772	12/10/2009	9.607	54.4	ng/sample	0.456	0.046	4.487	0.838	3.380
215	12/13/2009	9.659	44.4	ng/sample	4.550	0.463	7.341	1.371	7.681
721	12/27/2009	9.685	24.1	ng/sample	0.437	0.044	0.981	0.183	0.851
615	1/11/2010	9.671	38.5	ng/sample	2.710	0.276	4.402	0.822	5.396
753	1/17/2010	9.676	15.8	ng/sample	1.366	0.139	2.480	0.463	3.297
735	2/10/2010	9.673	22.1	ng/sample	0.000	0.010	1.240	0.232	0.310

site	m_1fluou	fl9one	fl9oneu	dbth	dbthu	phenan	phenanu	anthra	anthrau
510	0.260	31.583	1.579	7.533	0.377	19.692	0.985	3.012	0.384
773	0.086	52.742	2.637	3.906	0.195	4.807	0.240	0.501	0.064
772	0.459	71.832	3.592	25.343	1.267	72.640	3.632	13.284	1.694
215	1.044	93.130	4.657	28.218	1.411	143.375	7.169	25.982	3.313
721	0.116	43.762	2.188	9.405	0.470	13.805	0.690	1.099	0.140
615	0.733	79.808	3.990	20.971	1.049	135.573	6.779	18.501	2.359
753	0.448	47.755	2.388	8.684	0.434	35.232	1.762	3.085	0.393
735	0.042	20.197	1.010	4.209	0.211	4.304	0.215	0.490	0.062

site	m_2phen	m_2phenu	m_3phen	m_3phenu	m_2anth	m_2anthu	m_45phen	m_45phenu	m_9phen
510	6.068	0.319	7.619	0.733	0.352	0.056	0.000	0.010	3.225
773	2.313	0.121	3.761	0.362	0.896	0.141	3.839	0.192	1.058
772	19.153	1.006	23.457	2.257	5.507	0.869	7.987	0.399	10.840
215	25.450	1.336	36.484	3.510	7.496	1.182	5.012	0.251	15.512
721	8.267	0.434	9.282	0.893	1.956	0.309	0.000	0.010	5.099
615	23.861	1.253	28.530	2.745	6.451	1.017	0.000	0.010	11.646
753	8.195	0.430	11.723	1.128	1.536	0.242	0.000	0.010	4.791
735	2.294	0.120	2.477	0.238	0.462	0.073	0.000	0.010	1.053

site	m_9phenu	mpht_1	mpht_1u	m_9ant	m_9antu	nap2phen	nap2phenu	bntiopu	bzcphen
510	0.175	8.496	0.425	0.000	0.010	7.331	0.367	0.400	6.966
773	0.058	3.528	0.176	0.000	0.010	2.252	0.113	0.384	5.141
772	0.590	26.638	1.332	1.545	0.077	23.540	1.177	0.706	20.866
215	0.844	45.048	2.252	2.399	0.120	34.664	1.733	0.745	21.956
721	0.277	14.802	0.740	0.000	0.010	9.515	0.476	0.798	7.569
615	0.634	33.673	1.684	2.546	0.127	25.353	1.268	0.556	13.123
753	0.261	14.641	0.732	0.000	0.010	10.801	0.540	0.438	7.489
735	0.057	3.112	0.156	0.000	0.010	2.848	0.142	0.358	5.839

site	bzcphenu	bghifl	bghiflu	cp_cdpyr	cp_cdpyru	chrysn	chrysnu	baanth	baanthu
510	0.348	50.705	2.535	0.000	0.010	33.577	1.679	21.743	1.087
773	0.257	39.572	1.979	17.295	0.865	27.920	1.396	18.070	0.904
772	1.043	134.646	6.732	66.972	3.349	95.040	4.752	66.609	3.330
215	1.098	146.212	7.311	71.281	3.564	104.328	5.216	74.394	3.720
721	0.379	56.970	2.849	22.290	1.115	40.807	2.040	28.171	1.409
615	0.656	94.345	4.717	35.040	1.752	58.301	2.915	43.441	2.172
753	0.375	47.616	2.381	20.699	1.035	30.901	1.545	21.333	1.067
735	0.292	43.049	2.153	9.731	0.487	28.004	1.400	16.704	0.835
site	bzanthr	bzanthru	baa7_12	baa7_12u	m_3chr	m_3chru	m_7baa	m_7baau	dmban712
510	20.705	1.035	0.000	0.010	3.148	0.211	0.000	0.010	13.370
773	20.597	1.030	0.000	0.010	2.580	0.173	0.000	0.010	14.560
772	59.389	2.970	12.019	0.601	8.281	0.555	2.625	0.131	17.385
215	63.787	3.189	10.714	0.536	8.393	0.562	3.128	0.156	17.322
721	25.334	1.267	0.000	0.010	4.913	0.329	0.000	0.010	15.729
615	36.157	1.808	0.000	0.010	4.677	0.313	0.000	0.010	14.966
753	21.618	1.081	0.000	0.010	3.252	0.218	0.000	0.010	15.863
735	18.191	0.910	0.000	0.010	2.447	0.164	0.000	0.010	14.285

site	dmban712u	bbfl	bbflu	bjfl	bjflu	bkfl	bkflu	bafl	baflu
510	0.669	16.868	0.843	11.905	0.595	8.756	0.438	5.352	0.268
773	0.728	15.270	0.764	11.111	0.556	7.921	0.396	5.499	0.275
772	0.869	47.598	2.380	35.324	1.766	25.839	1.292	16.942	0.847
215	0.866	51.421	2.571	36.310	1.816	26.281	1.314	17.162	0.858
721	0.787	19.435	0.972	13.031	0.652	9.889	0.495	6.260	0.313
615	0.748	29.251	1.463	20.388	1.019	15.877	0.794	10.141	0.507
753	0.793	15.463	0.773	10.942	0.547	7.928	0.396	4.507	0.225
735	0.714	15.300	0.765	10.800	0.540	7.614	0.381	4.464	0.223

site	bepyrn	bepyrnu	bapyrn	bapyrnu	peryle	peryleu	m_7bpy	m_7bpyu	incdfl
510	13.065	0.666	20.871	1.044	3.252	0.163	1.050	0.152	1.561
773	12.005	0.612	19.394	0.970	3.993	0.200	3.344	0.483	2.039
772	36.149	1.844	64.273	3.214	9.824	0.491	2.454	0.354	4.310
215	38.263	1.951	67.734	3.387	10.325	0.516	0.000	0.010	4.232
721	14.586	0.744	23.442	1.172	4.956	0.248	1.569	0.227	1.713
615	21.672	1.105	38.917	1.946	6.337	0.317	1.548	0.224	2.679
753	11.406	0.582	19.741	0.987	3.329	0.167	1.372	0.198	2.248
735	12.801	0.653	16.902	0.845	3.324	0.166	0.000	0.010	1.312

site	incdflu	in123pyr	in123pyru	dbajan	dbajanu	bbchr	bbchru	pic	picu
510	0.180	13.662	0.930	2.456	0.491	2.060	0.339	5.525	0.559
773	0.235	12.168	0.829	2.241	0.448	2.170	0.357	7.321	0.741
772	0.497	39.635	2.699	4.154	0.831	5.892	0.968	14.160	1.433
215	0.488	40.045	2.727	5.063	1.013	5.562	0.914	15.668	1.586
721	0.198	16.276	1.108	1.968	0.394	2.652	0.436	16.172	1.637
615	0.309	23.580	1.606	3.264	0.653	3.331	0.547	7.386	0.748
753	0.259	12.158	0.828	1.989	0.398	1.098	0.180	6.397	0.647
735	0.151	13.675	0.931	1.806	0.361	1.440	0.237	4.470	0.452

site	bghipe	bghipeu	anthan	anthanu	triphen	triphenu	dbalpyr	dbalpyru	corone
510	22.154	1.108	5.155	0.469	0.000	0.010	1.597	0.251	4.114
773	21.977	1.099	5.407	0.492	0.000	0.010	0.000	0.010	6.310
772	59.461	2.973	18.292	1.665	0.000	0.010	4.622	0.725	16.394
215	59.604	2.980	16.079	1.463	0.000	0.010	1.574	0.247	12.964
721	23.000	1.150	5.793	0.527	0.000	0.010	0.000	0.010	6.917
615	38.057	1.903	9.526	0.867	0.000	0.010	2.062	0.324	9.980
753	18.031	0.902	5.132	0.467	0.000	0.010	0.980	0.154	4.853
735	24.762	1.238	3.555	0.324	0.000	0.010	0.000	0.010	7.588
site	coroneu	dbaepyr	dbaepyru	dbaipyr	dbaipyru	dbahpyr	dbahpyru	dbbkfl	dbbkflu
510	0.311	1.789	0.203	0.000	0.010	0.000	0.010	1.481	0.152
773	0.476	1.499	0.170	0.955	0.196	0.000	0.010	0.000	0.010
772	1.238	4.136	0.468	2.067	0.425	0.000	0.010	4.994	0.514
215	0.979	4.481	0.507	2.457	0.505	1.889	0.095	4.981	0.513
721	0.522	2.713	0.307	0.000	0.010	0.000	0.010	1.388	0.143
615	0.754	2.346	0.266	0.781	0.161	0.000	0.010	2.866	0.295
753	0.366	1.583	0.179	0.000	0.010	0.000	0.010	0.934	0.096
735	0.573	1.546	0.175	0.000	0.010	0.000	0.010	0.961	0.099

site	analdate	filename	blanksubtr
510	1/27/2011	P112M001I001-MS.TXT	Y
773	1/27/2011	P112M001I003-MS.TXT	Y
772	1/27/2011	P112M001I004-MS.TXT	Y
215	1/27/2011	P112M001I005-MS.TXT	Y
721	1/27/2011	P112M001I007-MS.TXT	Y
615	1/27/2011	P112M001I008-MS.TXT	Y
753	1/27/2011	P112M001I002-MS.TXT	Y
735	1/27/2011	P112M001I006-MS.TXT	Y

A.1C Hopanes and Steranes Sample IDs

field_name	compound
HOP15	17A(H),21B(H)-22,29,30-Trisnorhopane
HOP17	17A(H),21B(H)-30-Norhopane
HOP19	17A(H),21B(H)-Hopane
HOP20	17B(H),21A(H)-hopane
HOP21	22S-17A(H),21B(H)-30-Homohopane
HOP22	22R-17A(H),21B(H)-30-Homohopane
HOP23	17B(H),21B(H)-Hopane
HOP24	22S-17A(H),21B(H)-30,31-Bishomohopane
HOP25	22R-17A(H),21B(H)-30,31-Bishomohopane
HOP26	22S-17A(H),21B(H)-30,31,32-Trisomohopane
HOP27	22R-17A(H),21B(H)-30,31,32-Trishomohopane
STER42	C27-20S5A(H),14A(H)-cholestane
STER43	C27-20R5A(H),14B(H)-cholestane
STER44	C27-20S5A(H),14B(H),17B(H)-cholestane
STER45_40	C27-20R5A(H),14A(H),17A(H)-cholestane &20S-13B(H),17A(H)-diastigmastane
STER46	C28-20S5A(H),14A(H),17A(H)-ergostane
STER47	C28-20R5A(H),14B(H),17B(H)-ergostane
STER48	C28-20S5A(H),14B(H),17B(H)-ergostane
STER49	C28-20R5A(H),14A(H),17A(H)-ergostane
STER50	C29-20S5A(H),14A(H),17A(H)-stigmastane
STER51	C29-20R5A(H),14B(H),17B(H)-stigmastane
STER52	C29-20S5A(H),14B(H),17B(H)-stigmastane
STER53	C29-20R5A(H),14A(H),17A(H)-stigmastane
HOP15U=	17A(H),21B(H)-22,29,30-Trisnorhopane uncertainties (etc)

A.1D DRI Hopanes and Steranes Results

site	strtdate	vol_m3	ug/m3	units	hop15	hop15u	hop17	hop17u	hop19
510	11/15/2009	9.683	15.7	ng/sample	0.000	0.010	6.583	0.329	4.976
773	11/27/2009	9.683	20.9	ng/sample	4.609	1.036	13.669	0.684	12.224
772	12/10/2009	9.607	54.4	ng/sample	8.520	1.914	16.039	0.802	8.903
215	12/13/2009	9.659	44.4	ng/sample	7.140	1.604	16.830	0.842	8.243
721	12/27/2009	9.685	24.1	ng/sample	21.167	4.756	35.587	1.779	18.625
615	1/11/2010	9.671	38.5	ng/sample	5.601	1.258	8.076	0.404	5.571
753	1/17/2010	9.676	15.8	ng/sample	3.497	0.786	10.815	0.541	5.651
735	2/10/2010	9.673	22.1	ng/sample	0.192	0.043	7.876	0.394	4.109

site	hop19u	hop20	hop20u	hop21	hop21u	hop22	hop22u	hop23	hop23u
510	0.309	0.000	0.010	2.449	0.210	3.317	0.618	0.000	0.010
773	0.759	10.668	2.471	11.311	0.972	6.192	1.153	0.000	0.010
772	0.553	6.902	1.599	6.420	0.551	8.088	1.506	0.000	0.010
215	0.512	14.601	3.382	11.184	0.961	10.767	2.005	0.000	0.010
721	1.157	27.457	6.359	4.514	0.388	30.101	5.605	0.000	0.010
615	0.346	0.000	0.010	0.505	0.043	5.588	1.040	0.000	0.010
753	0.351	7.548	1.748	4.549	0.391	4.655	0.867	0.000	0.010
735	0.255	0.000	0.010	2.537	0.218	2.751	0.512	0.000	0.010

site	hop24	hop24u	hop25	hop25u	hop26	hop26u	hop27	hop27u	ster42
510	0.000	0.010	3.521	0.176	1.659	0.286	2.273	0.116	3.458
773	3.678	0.482	6.788	0.339	3.875	0.669	4.516	0.231	5.717
772	3.909	0.512	5.235	0.262	3.317	0.573	5.360	0.274	16.000
215	3.652	0.479	7.421	0.371	4.600	0.794	4.926	0.252	12.845
721	6.970	0.914	9.222	0.461	4.896	0.846	4.976	0.255	6.879
615	3.116	0.408	3.239	0.162	3.392	0.586	4.155	0.213	7.400
753	5.271	0.691	2.208	0.110	3.025	0.522	4.846	0.248	4.416
735	0.834	0.109	1.237	0.062	1.578	0.272	3.527	0.181	3.921

site	ster42u	ster43	ster43u	ster44	ster44u	ster45_40	ster45_40u	ster46	ster46u
510	0.291	6.851	0.427	0.239	0.014	4.944	0.315	0.756	0.038
773	0.481	7.926	0.494	0.499	0.029	5.107	0.326	0.000	0.010
772	1.347	23.908	1.490	1.226	0.072	17.551	1.120	0.000	0.010
215	1.082	19.007	1.184	0.651	0.038	15.991	1.020	0.000	0.010
721	0.579	9.160	0.571	0.944	0.055	4.988	0.318	0.000	0.010
615	0.623	12.724	0.793	0.940	0.055	10.252	0.654	0.000	0.010
753	0.372	5.425	0.338	0.073	0.010	3.513	0.224	0.000	0.010
735	0.330	5.927	0.369	0.302	0.018	5.218	0.333	0.832	0.042

site	ster47	ster47u	ster48	ster48u	ster49	ster49u	ster50	ster50u	ster51
510	1.456	0.073	0.238	0.047	2.965	0.148	0.000	0.010	0.844
773	1.774	0.089	0.926	0.182	3.358	0.168	1.157	0.089	0.769
772	0.846	0.042	1.532	0.301	9.449	0.473	1.471	0.113	2.330
215	0.255	0.013	0.907	0.178	6.326	0.316	0.147	0.011	2.359
721	0.000	0.010	0.465	0.091	3.365	0.168	2.466	0.189	1.066
615	1.465	0.073	0.689	0.135	7.162	0.358	1.464	0.112	1.254
753	0.000	0.010	0.042	0.010	2.487	0.124	0.128	0.010	0.796
735	1.823	0.091	0.000	0.010	3.123	0.156	0.030	0.010	1.360

site	ster51u	ster52	ster52u	ster53	ster53u		analdate	filename	blanksubtr
510	0.093	1.783	0.194	3.449	0.547		1/28/2011	P112M001I001-MS.TXT	Y
773	0.084	1.981	0.216	3.896	0.617		1/28/2011	P112M001I002-MS.TXT	Y
772	0.255	3.211	0.350	6.310	1.000		1/28/2011	P112M001I003-MS.TXT	Y
215	0.259	2.004	0.218	8.955	1.419		1/28/2011	P112M001I004-MS.TXT	Y
721	0.117	1.639	0.178	10.954	1.736		1/28/2011	P112M001I005-MS.TXT	Y
615	0.137	1.919	0.209	2.600	0.412		1/28/2011	P112M001I006-MS.TXT	Y
753	0.087	0.906	0.099	3.935	0.624		1/28/2011	P112M001I007-MS.TXT	Y
735	0.149	1.557	0.170	2.737	0.434		1/28/2011	P112M001I008-MS.TXT	Y

A.2 Coal Elemental Analysis Results

The University of Montana - Geosciences Department
Environmental Biogeochemistry Laboratory

ICP Sample Analysis Results

Template

Analysis Date:	7/11/2011
Units:	mg/kg
Sample Dilution (mL):	40

PQL	Practical Quantitation Limit (lower reporting limit)
b.d.	Concentration < PQL

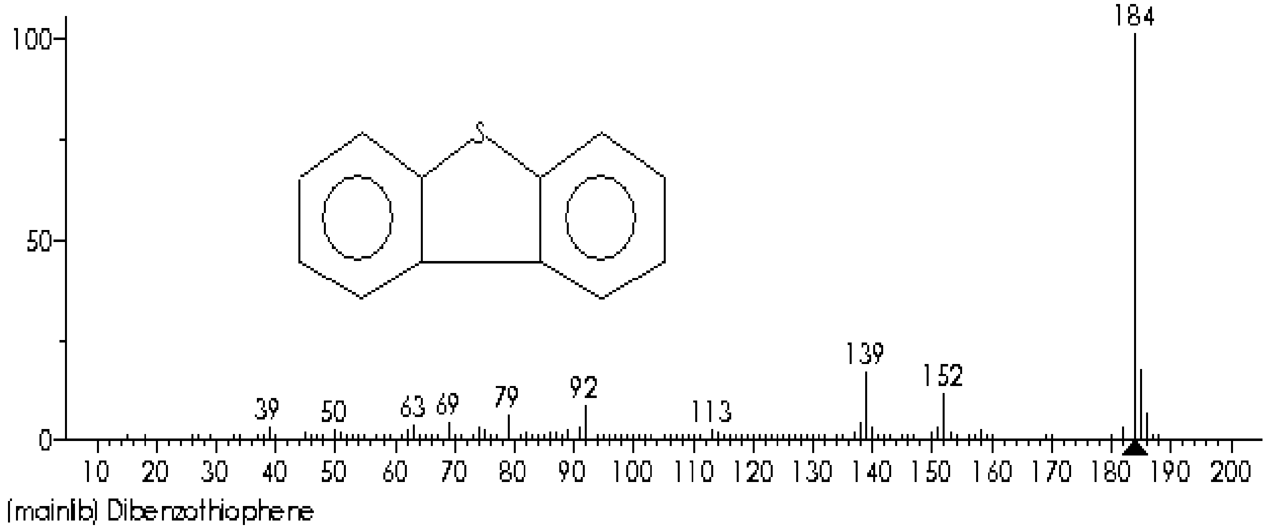
Sample Name				**Al**	**As**	**B**	**Ba**	**Be**
Client ID	**EBL ID**							
		PQL (if spl m = 0.4 g)	0.4	5	1.5	1	1	0.05
	J. Ormond Coal 1		0.3984	2015	1.883	7.96	297	0.12
	J. Ormond Coal 2		0.8017	1897	1.414	6.56	245	0.11

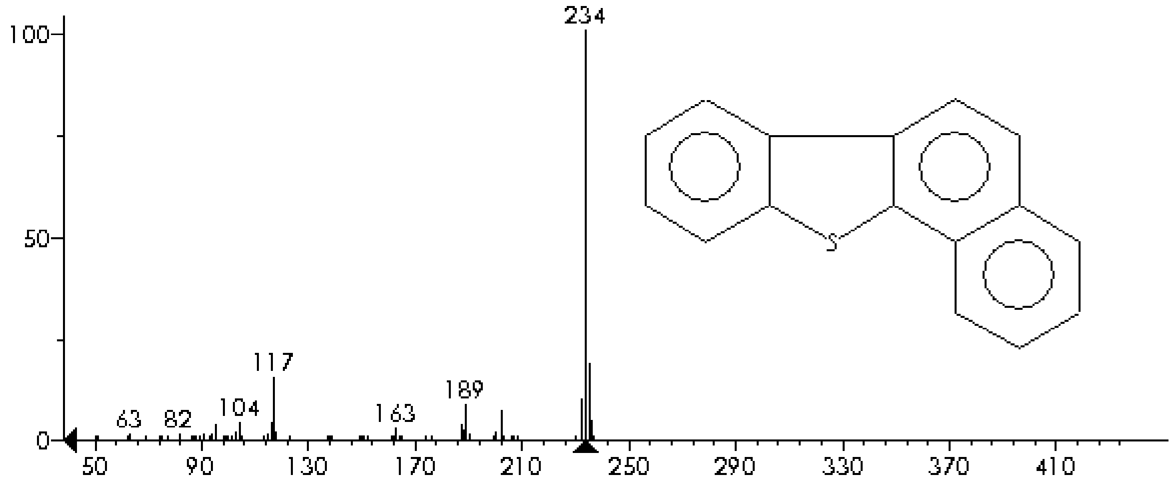
Ca	**Cd**	**Co**	**Cr**	**Cu**	**Fe_r**	**K**	**Li**	**Mg**
10	0.4	0.5	0.5	0.5	10	50	5	10
10482	b.d.	1.65	3.51	14.71	5040	608	14.4	1589
9001	b.d.	1.43	3.11	9.625	4328	452	6.79	1376

Mn	Mo	Na	Ni	P	Pb	S	Sb	Se
0.1	0.5	50	1	6	5	10	5	5
104	1.14	58.8	7.82	82.4	b.d.	1188	b.d.	b.d.
90.9	0.82	45.9	6.66	53.8	3.57	1003	b.d.	b.d.

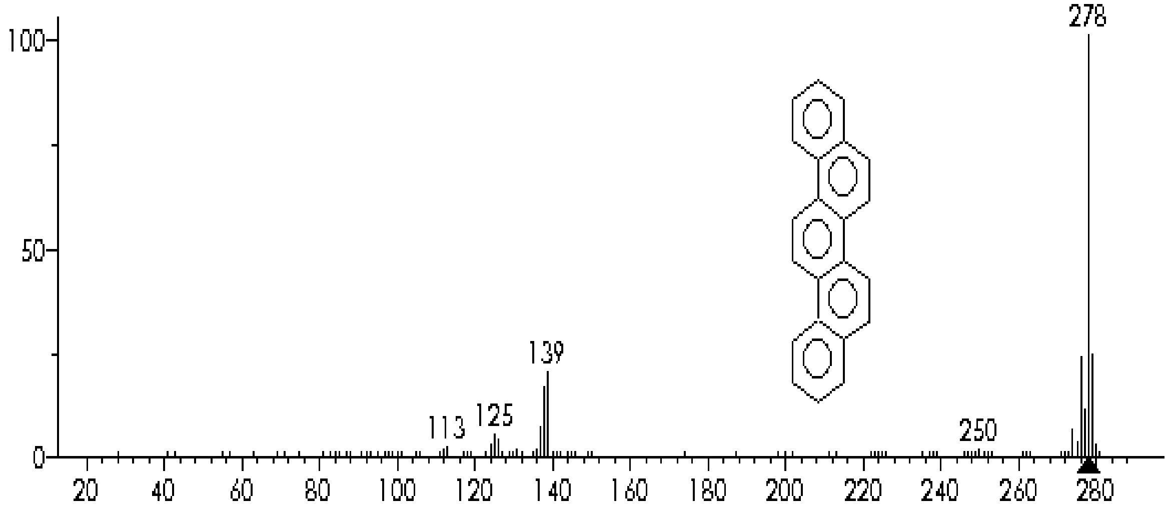
Si	Sn	Sr	Ti	Tl	V	Zn
10	1	0.5	1	10	1	0.1
603	b.d.	88.09	62.5	b.d.	7.81	21.16
348	b.d.	78.43	55.3	b.d.	6.90	15.73

A.3 Mass Spectra of Select Compounds (NIST Library)

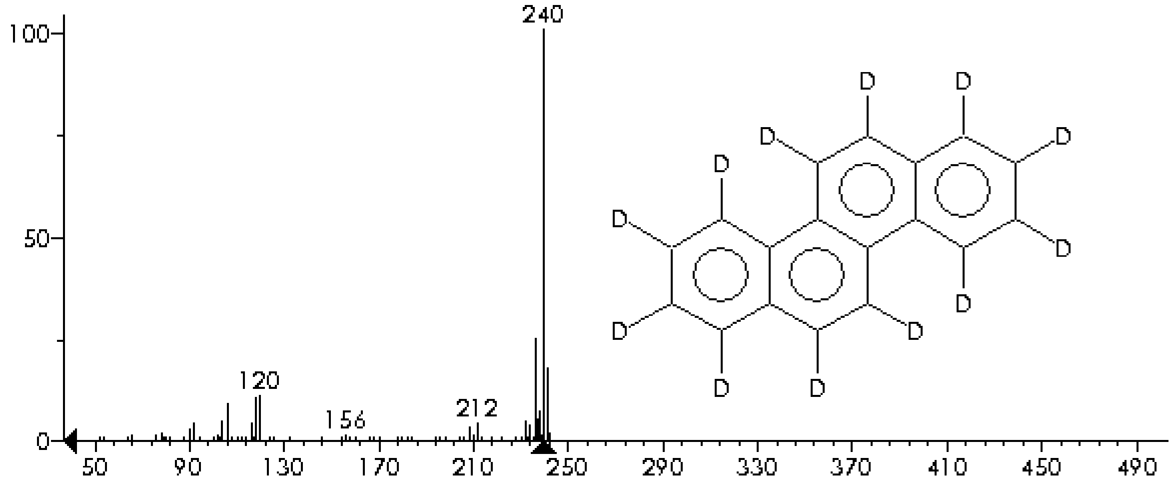




(replib) Benzo[b]naphtho[2,1-d]thiophene



(mainlib) 1,2:7,8-Dibenzophenanthrene



(mainlib) Chrysene-D12

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