Identification of Sources of Air Pollution Using Novel Analytical Techniques and Instruments

Nitish Bhardwaj
Brigham Young University

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Identification of Sources of Air pollution Using Novel Analytical Techniques and Instruments

Nitish Bhardwaj

A dissertation submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Jaron C. Hansen, Chair
Steven R. Goates
Matthew R. Linford
Daniel E. Austin

Department of Chemistry and Biochemistry
Brigham Young University

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Identification of Sources of Air Pollution Using Novel Analytical Techniques and Instruments

Nitish Bhardwaj
Department of Chemistry and Biochemistry, BYU
Doctor of Philosophy

This dissertation is a collection of studies that investigates the issue of air pollution in the field of environmental chemistry. My thesis consists of research works done to measure the concentration of particulate matter (PM) and gas-phase species in ambient air. High concentrations of PM is a significant problem in Utah and in other regions of the world. Particles having an aerodynamic diameter of 2.5 micrometers and smaller play a crucial role in air pollution and pose serious health risks when inhaled. The organic fraction in PM ranges from 10-90% of the total particle mass. Several methods have been employed to measure the organic fraction of PM, but these techniques require extensive laboratory analysis, and expensive bench top equipment. The Hansen Lab has developed a new instrument called the Organic Aerosol Monitor (OAM) which is based on gas chromatography followed by mass spectrometry detection platform for measuring the carbonaceous component of PM$_{2.5}$ on an hourly averaged basis. Organic marker data collected in 2016 using the OAM was used in a Positive Matrix Factorization (PMF) analysis to identify the sources of PM in West Valley City, Utah. Additionally, data was collected in Richfield and Vernal, UT in 2017 – 2018 to quantitatively monitor the composition of organic markers of PM$_{2.5}$. Some previously unidentified organic compounds in PM were successfully identified during this study.

Gas-phase species play a significant role in driving the formation of air pollutants in Earth's atmosphere. Traditional gas detection methods do not provide high temporally and spatially resolved data; therefore, it becomes important to detect and measure gas-phase species both qualitatively and quantitatively to better understand the sources of air pollution. An incoherent broadband cavity enhanced absorption spectrometer (IBBCEAS) combines a broadband incoherent light source, a stable optical cavity formed by two highly reflective mirrors and a charged-coupled device (CCD) detector to quantitatively measure the gas-phase compounds present in the atmosphere. The concentrations of formaldehyde (HCHO) were measured using IBBCEAS to investigate the sources of this hydrocarbon in Bountiful, Utah during 2019.

Another important species is OH radical. It is one of the most predominant oxidizing species present in the atmosphere. It is found in low concentrations, 0.1 ppt. Detecting concentrations this low is challenging. A new IBBCEAS instrument has been designed and elements of this instrument were tested by measuring the OH overtones in a variety of short chained alcohols. Because OH radical’s lowest energy electronic state occurs in the same wavelength region (i.e., 308 nm) that SO$_2$ absorbs (300-310 nm), a study was conducted in which the concentrations of SO$_2$ were measured using an IBBCEAS and compared with a commercially available SO$_2$ monitor.

Keywords: particulate matter, gas-phase species, gas chromatography-mass spectrometry, organic aerosol monitor, incoherent broadband cavity enhanced absorption spectroscopy, radicals, volatile organic compounds, source apportionment, secondary organic aerosol, positive matrix factorization.
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<td>AIM</td>
<td>Ambient Ion Monitor</td>
</tr>
<tr>
<td>AMS</td>
<td>Aerosol Mass Spectrometer</td>
</tr>
<tr>
<td>BC</td>
<td>Black Carbon</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Couple Devise</td>
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<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
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<tr>
<td>FDMS</td>
<td>Filter Dynamics Measurement System</td>
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<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
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<tr>
<td>GC</td>
<td>Gas Chromatography</td>
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<tr>
<td>LOD</td>
<td>Limit of Detection</td>
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<tr>
<td>NAAQS</td>
<td>National Ambient Air Quality Standards</td>
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<tr>
<td>NVOC</td>
<td>Non-Volatile Organic Carbon</td>
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<td>NVOM</td>
<td>Non-Volatile Organic Material</td>
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<tr>
<td>OAM</td>
<td>Organic Aerosol Monitor</td>
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<tr>
<td>PAHs</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
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<td>PCC</td>
<td>Pre-Column Concentrator</td>
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<tr>
<td>PM</td>
<td>Particulate Matter</td>
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<tr>
<td>PMF</td>
<td>Positive Matrix Factorization</td>
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<tr>
<td>RIC</td>
<td>Reconstructed Ion Chromatogram</td>
</tr>
<tr>
<td>RT</td>
<td>Retention Time</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary Organic Aerosol</td>
</tr>
<tr>
<td>SVOC</td>
<td>Semi-Volatile Organic Compounds</td>
</tr>
<tr>
<td>SVOM</td>
<td>Semi-Volatile Organic Material</td>
</tr>
<tr>
<td>TEOM</td>
<td>Tapered Element Oscillating Microbalance</td>
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<td>TIC</td>
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Chapter 1: Introduction

Over the last 100 years or so, atmospheric chemistry has gained much interest and attention worldwide. Atmospheric chemistry is an exciting field that envelops the whole world, ranging from the region closest to earth’s atmosphere, troposphere (~10 – 15 km) all the way through the stratosphere (~10 – 50 km). In the tropospheric region of earth’s atmosphere, several physical and chemical processes take place in a balanced way. However, the stability and dynamic balance of the troposphere can be disturbed due to anthropogenically and biogenically emitted molecules.

This disturbance or instability in earth’s atmosphere can be introduced by air pollution. Air pollution can be defined as the release of harmful pollutants or materials in earth’s atmosphere (mainly troposphere), which are harmful to the health of living beings. This air pollution can take the form of both primary and secondary emission. Primary, meaning that the pollutant is directly released into the atmosphere and secondary meaning that a compound undergoes some chemical reaction to convert it from a benign substance to an air pollutant.

In the state of Utah and in other parts of the country, there is a significant problem with high concentrations of particulate matter (PM). Particulate matter, especially particles that are 2.5 micrometers in diameter and smaller, play a significant role in air pollution and when inhaled can cause serious health problems. Additionally, gas-phase species can play a significant role in driving the formation of air pollutants. Therefore, it is important to detect and measure both PM and gas-phase species both qualitatively and quantitatively to better understand the sources of pollution associated with them.
1.1 Particulate Matter & Measurement Techniques

Particulate matter (PM) is a complex mixture of particles and liquid droplets suspended in air. PM is referred to as particle phase air pollution and is a type of aerosol. Primary emitted particles are directly emitted from the single-point sources such as wood stoves, forest fires and volcanic eruptions. Secondary emitted particles are formed from gaseous precursors emitted from primary sources that typically undergo photooxidation in the atmosphere to form less volatile compounds that can condense to form particles. Exposure to fine particulate matter (PM) poses serious health problems and has a substantial effect on overall climate.\textsuperscript{1-3} PM can be further classified based on particle size and can be broadly divided into two categories. Particles larger than 2.5 micrometers and smaller than 10 micrometers in diameter are known as “inhalable coarse particles”. These coarse particles originate and are often found near roadways and dusty industries. Particles which are 2.5 micrometers and smaller in diameter are referred to as “fine particles” and are often found in smoke and haze. These fine particles are directly emitted from both anthropogenic and natural sources including forest fires, power plants, industries, and automobiles. As the name suggests, these inhalable fine particles are so small that they can easily enter through our nose and reach our lungs where they can initiate an inflammatory response or even become dissolved in our bloodstream causing serious health problems.

PM is composed of both organic and inorganic components. The organic fraction in PM ranges between 10 – 90% of the total particle mass.\textsuperscript{4-6} Quantifying the organic fraction in PM is a significant challenge due to the possible presence of chemical reactivities and properties of these compounds. Previous research has demonstrated the advantages of routine monitoring of the organic component of PM in source apportionment studies.\textsuperscript{7, 8}
A variety of methods have been used to measure the organic fraction of PM. These methods typically involve collection of PM samples on a filter followed by an extraction step and then analysis by GC-MS or HPLC. These techniques have been used to identify many organic compounds that are linked to various sources of pollution. However, these techniques require extensive laboratory analysis and expensive bench top equipment. These techniques make the sample analysis process costly and poor in terms of time resolution. Recently, rapid methods have been developed to analyze samples without liquid extraction. But these methods do a poor job of capturing important diurnal or daily variations of the concentrations of ambient organic compounds and are unable to give time-dependent correlation among different pollutants.

Instruments, such as the Aerodyne aerosol mass spectrometer (AMS) and the TSI aerosol time-of-flight mass spectrometer, provide size and time resolved chemical composition data, which also include total carbon and inorganic species. However, these instruments are not capable of identifying or quantifying organic compounds due to the strong ionization techniques used and sample matrix effects. Additionally, these instruments can be limited by size and portability. Williams et al. have reported an instrument capable of continuously monitoring particulate phase organic carbon compounds. In their instrument, particles were collected using inertial impact. These particles were then separated and detected by thermal desorption and GC-MS. During its deployment in the field for two-months, different species of primary and secondary aerosols were identified. Williams et al. further demonstrated the importance of information obtained by these organic marker compounds and the primary need to develop more in-field techniques to monitor many more of these organic compounds. Because PM$_{2.5}$ are typically mainly composed of organic species, it is advantageous to measure the organic component of PM to better characterize the sources of pollution.
A gas chromatography-mass spectrometry organic aerosol monitor (GC-MS OAM) instrument has been developed in our laboratory. It is an autonomous instrument, which has the capability to measure the carbonaceous components of PM on an hourly averaged basis. This instrument is based on collection of particles on an inert filter, desorption of the organic material in an inert atmosphere with subsequent GC separation and MS detection of the desorbed compounds. The schematics and working of this instrument are explained in Chapter 2 and 3 of this dissertation.

1.2 Gas-phase Pollutants & Measurement Techniques

Gas-phase species play a significant role in driving the formation of air pollutants in earth’s atmosphere. These air pollutants include gas-phase species such as ozone (O₃), CO, SO₂, NOₓ (NO, NO₂), NH₃, and volatile organic compounds (VOCs). The sources of gaseous air pollutants’ emissions can be broadly classified into two categories: (i) natural (biogenic) (ii) anthropogenic. Natural sources refer to the emission of pollutants from natural activities including volcanic eruptions, forest/wildfires, desert dust, biogenic emissions from trees, and anaerobic wetlands. Anthropogenic sources include combustion of fossil fuels, industrial or manufacturing processes, automobiles, and vehicle emissions; these are responsible for the increase of gaseous pollutants causing air pollution in the atmosphere.

Air pollution in many major urban areas around the world is mainly due to anthropogenic emissions and is characterized more by the formation of ozone than by particle or any other gas formation. This is due to the fact that the primary pollutants in these regions, which are NOₓ and VOCs, undergo photochemical reactions in the presence of sunlight to predominately form ozone, and other secondary pollutants, including gaseous peroxyacetyl nitrate (PAN) and formaldehyde (HCHO), as shown in Figure 1.1.
Figure 1.1. Diagram of atmospheric oxidation, including the major initiator or atmospheric oxidant OH

$\text{VOC} \ (\pm \text{OH/NO}_2/\text{O}_3/\text{hv}) \rightarrow R'$

$\text{ROOH} \xrightarrow{\text{Isomerization}} \text{RO}_2$

$\text{RO}_2 \xrightarrow{\text{HO}_2} \text{NO}_2 \xrightarrow{\text{ROONO}_2}$

$\text{carbonyl} \ + \ \text{alcohol}$

$\text{RO'} \ + \ \text{NO}_2 \rightarrow \text{products}$

$\text{O}_2$

$\text{NO}$

$\text{RONO}_2$

$\text{NO}_x$ and VOCs emissions are attributed to major mobile and stationary sources, including vehicles, industries, and refineries. In remote areas, the concentration of gaseous pollutants is relatively low due to low NOx emissions. It is unlikely to find any regions at the earth’s surface that have not been impacted anthropogenically. Moreover, significant contributions from anthropogenic emissions have been observed over both the Pacific and central Atlantic oceans.\textsuperscript{19, 20}

A wide range of analytical techniques have been applied to the measurements of these gas-phase species.\textsuperscript{21} Traditionally, gases are detected by chemical sensing method. These methods involve the collection of gas samples at a site, followed by the analysis in a laboratory.\textsuperscript{22} Using this method, several trace species have been collected and analyzed to aid in understanding pollution formation. However, this method does not provide highly temporally and spatially resolved measurements due to the limitation of on-site processing. Additionally, the whole process of collecting a sample, transferring, and analyzing it in the laboratory changes the sample quality, which can lead to erroneous results. Therefore, it becomes important to detect and measure these gases both
qualitatively and quantitatively to better understand the sources of pollution associated with these gas-phase species.

Absorption spectroscopy is a widely used approach for the in-situ detection of gas phase species concentration. Quantification of concentrations of molecules by absorption spectroscopy requires that their absorption cross-sections are known\(^2^3\). The advantages of absorption spectroscopy including in-situ real-time measurements and high spatial and temporal resolution makes it an important technique for the detection of gas-phase species. Different absorption spectroscopy techniques, such as cavity ring-down spectroscopy (CRDS),\(^2^4,\)\(^2^5\) cavity-enhanced absorption spectroscopy (CEAS),\(^2^6\) and broadband cavity-enhanced absorption spectroscopy (BBCEAS),\(^2^7\) have been employed to measure trace gas concentrations. Based on the sensitivity, selectivity and cost of such absorption techniques, these approaches have pros and cons.

1.2.1 Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS)

Broadband cavity-enhanced absorption spectroscopy, first reported in 2003 by Fiedler et al.,\(^2^7\) has emerged as one of the highly sensitive methods of detection of gaseous samples measurements. In BBCEAS, usually a broadband incoherent light source is used for the transmission of light through a stable optical cavity, formed by two highly reflective mirrors. A small fraction of light that leaks from the back end of the optical cavity is then dispersed by a grating, and finally detected with the help of a charged-coupled device (CCD) or a photo-diode array detector.

BBCEAS offers a lot of advantages in terms of selectivity, sensitivity, compactness, mechanical stability, and short integrated time measurements compared to other absorption techniques. Additionally, BBCEAS has a wide range of practical applications including: (i) simple experimental setup; (ii) does not require any sophisticated and complicated electronic accessories such as fast optical switches, feed-back gates or loops; (iii) unlike in CEAS, no mode-hop-free
scanning is required: (iv) unlike diode-lasers which are unable to access short wavelength region, BBCEAS has the ability to cover a wide range of the electromagnetic spectrum ranging from the short wavelength region of UV (190 nm) to the infrared region (10 \( \mu \)m); (v) due to the broad-band nature of the BBCEAS technique, many gas-phase species can be detected at a one time.

A custom built BBCEAS instrument has been developed with the help of Dr. Ryan Thalman from Snow College, UT. This instrument has been used to successfully measure SO\(_2\) and vibrational OH overtones of several short-chain alcohols, as discussed in Chapter 5 and 6 in detail.

1.2.2 Principle of BBCEAS for gas-phase species measurements

In BBCEAS, the time-integrated steady-state transmitted light intensity from a cavity, which is formed by two reflective mirrors, is inversely proportional to the absorption coefficient (\( \alpha \)) of target gas molecules. Consider a cavity of length \( d \) formed by two mirrors with reflectivities of \( R_1 \) and \( R_2 \) respectively, shown in figure 3. The input light intensity from an incoherent light source is denoted as \( I_{in} \), and \( I \) represents the total intensity of light transmitted through the cavity. The main loss of light in this spectroscopy technique is due to gas absorption, represented as \( (1-L) \), per pass of light within the cavity. \( (1-R_i) \) represents the transmission loss caused by the imperfect reflectivity of the mirrors. Now, the total intensity of light transmitted through the cavity can be calculated as the sum of each individual light intensity leaked through the cavity\(^{27,28}\). The total intensity of transmitted light through the cavity can be written as an infinite sum:

\[
I = I_{in}(1 - R_1)(1 - L)(1 - R_2) \quad (\text{zeroth pass})
\]

\[
I_{in}(1 - R_1)(1 - L)R_2(1 - L)R_1(1 - L)(1 - R_2) + \cdots \quad (\text{first pass})
\]

\[
I_{in}(1 - R_1)(1 - R_2)R_1^n R_2^n(1 - L)^{2n+1} + \cdots \quad (\text{nth pass})
\]

7
\[ I_{in} (1 - R_1)(1 - R_2)(1 - L) \sum_{n=0}^{\infty} R_1^n R_2^n (1 - L)^{2n} \]  

(1)

Because the reflectivity of both the mirrors R_1 and R_2 and losses L are less than 1, we can write equation (1) as:

\[ I = I_{in} \frac{(1 - R_1)(1 - R_2)(1 - L)}{1 - R_1 R_2(1 - L)^2} \]  

(2)

For an empty cavity without an absorber, L = 0, time integrated transmitted intensity of light is given by:

\[ I = I_{in} \frac{(1 - R_1)(1 - R_2)}{1 - R_1 R_2} \]  

(3)

Assuming, Beer-Lambert’s law is related to the single-pass loss as \( 1 - L = e^{-\alpha d} \) and the same reflectivities for both mirrors \( R_1 = R_2 = R \), where d is cavity length, the absorption coefficient \( \alpha \) can be written as:

\[ \alpha = \frac{1}{d} \ln \left( \frac{1}{2R^2} \left( \sqrt{4R^2 + \left( \frac{I_0}{I} (R^2 - 1)^2 \right) + \frac{I_0}{I} (R^2 - 1)} \right) \right) \]  

(4)

An approximation can be made in case of small loss per pass \( L \to 0 \) and high reflectivity of mirrors \( R \to 1 \), \( \alpha \) can be approximated as:

\[ \alpha \approx \frac{1}{d} \left( \frac{I_0}{I} - 1 \right) (1 - R) \]  

(5)

Fiedler et al.\textsuperscript{29} demonstrated the relationship between cavity length (d), mirror reflectivity (R_1, R_2) and absorption coefficient (\( \alpha \)) on cavity output. The specific gas concentration can be calculated
by using a least-square polynomial fit.\textsuperscript{30} This is done by fitting the absorption cross section ($\sigma$) of desired gas to the experimentally calculated absorption coefficient ($\alpha$) as:

$$\alpha = \sum_i n_i \sigma_i + a\lambda^2 + b\lambda + c$$  \hspace{1cm} (6)

Where $\sigma_i$ represents the absorption cross-section of $i$th gas-phase species. The second order polynomial in the equation represents several parameters, such as scattering due to Rayleigh and Mie phenomena, baseline shift due to coupling and intensity variations, and other mechanical disturbances.

\textbf{1.3 Source Apportionment of Air Pollution}

One of the major goals of developing the GC-MS OAM was to quantitatively determine the organic markers of PM on an hourly-averaged basis, which helps in improving the source apportionment models for air pollution. Source apportionment studies rely on receptor modelling techniques which enables the measurement and understanding of the origin of air pollution in a given geographical location. The source apportionment of air pollution helps in identifying the sources and the extent of their contribution to overall pollution levels. Air pollution can be reduced to a great extent by relating its composition to specific sources with the help of source apportionment studies.

Several statistical analysis tools such as positive matrix factorization (PMF), chemical mass balance (CMB) and principal component analysis (PCA) have been used to analyze time resolved data sets containing concentrations of various pollutants. For example, Thurston et al.\textsuperscript{31} applied mass regression analysis and PCA approaches to identify and quantify the major sources of fine
particulate matter (PM$_{2.5}$) components in the U.S. They used PM$_{2.5}$ composition data from the U.S. EPA 2000-2005 chemical speciation network (CSN) from over 200 sites. They were able to find the major sources of PM$_{2.5}$ in this nationwide analysis, but the results from both the approaches did not coincide well with each other. They noted the issue of co-linearity between the two models used which made the results less robust. In another study conducted by Pindado et al.$^{32}$ in 2004 – 2005, PMF receptor model was used to identify possible sources and their contribution to PM in a rural area of Madrid (Spain). Hopke et al.$^{33}$ reviewed the application of source apportionment to air pollution recently. Techniques such as PMF, CMB, least square approaches were suggested by the authors to use for source apportionment analysis. Additionally, it was recommended to include some information including coordinates of the sampling site, start/stop time of sampling, detailed apportionment calculations, and processes used for error estimations in PMF to improve the quality of data used in source apportionment analysis.$^{33}$

PMF is one of the most frequently used receptor models used to identify and quantify the contribution of probable sources to particulate matter. It is a mathematical approach which is used to quantify the contribution of sources to samples based on the composition of the sources. The PMF model was first introduced by Paatero in mid 1990s at the University of Helsinki.$^{34, 35}$ It solves the chemical mass balance between the measured species concentrations and source profiles. PMF assumes that a linear combinations of source emissions impact the concentrations at receptor sites. Therefore, this receptor model assumes a receptor is impacted by $p$ sources, and the linear combinations of these impacts from $p$ sources sum to give the observed concentrations of various species, shown in equation (7) below:

$$X_{ij} = \sum_{k=1}^{p} G_{ik} F_{kj} + E_{ij} \quad (7)$$
where \( X_{ij} \) is the speciated data matrix of \( i \) by \( j \) dimensions, in which \( i \) is number of samples and \( j \) chemical species measured; \( p \) is number of factors, \( G_{ik} \) is the amount of mass contributed by each factor to each individual sample, \( F_{ij} \) is the species profile of each source, and \( E_{ij} \) is the residual for each sample/species.

The factor profiles interpretation is dependent on the user who is responsible to identify the source types that may be contributing to sample. The task of the PMF model is to minimize the function \( Q \), which is a critical parameter for PMF, by use of the constrained, weight least squares method.\(^{32} \) Mathematically, this function \( Q \) is defined as:

\[
Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{X_{ij} - \sum_{k=1}^{p} G_{ik} F_{kj}}{S_{ij}} \right]^2
\]

(8)

Where \( S_{ij} \) is an uncertainty estimate in each sample/species measured.

A qualitative knowledge of the sources is required to perform the PMF model. However, this model has some limitations such as its inability to convincingly separate covariant sources. It is exceptional that this model groups only the temporally covary species revealed by it. However, changes in emissions do not solely determine the temporal variability of a pollutant, as assumed by the PMF method. Therefore, no direct link should be made between the factors and source profiles.\(^{32} \) PMF requires two input files, one with the sample species concentration values, and other with the sample species uncertainty values or parameters for calculating uncertainty. The selection of modelling parameters is quite complex and is usually dependent on the experience of the authors.\(^{37} \) The results from the PMF model provide information about the regression diagnostics, which help to optimize the solution obtained from the model. A good fit should give r-squared values greater than 0.6, intercept values near 0, and slope values near 1.
There are several advantages of using the PMF model for factor analysis. The inclusion of uncertainties in the analysis is one of the most important advantages of using PMF model because it allows the user to assign different weights to different variables, which is remarkable, considering the lack of precision of analytical methods. Additionally, PMF can identify and provide the contribution of particulate matter sources individually, without any prior information of sources. Moreover, unlike CMB and PCA models, PMF is capable of identifying and quantifying sources faster.

It has been previously observed that the inclusion of organic markers into source apportionment data sets greatly enhances source apportionment analysis. For instance, Li et al. demonstrated that the development of new analytical instruments for the quantitative determination of organic marker compounds could immensely help in the apportionment of the contribution of wood smoke emitted particles to PM$_{2.5}$. However, these markers have generally been measured in 24-hour averaged samples. As a result, organic marker compounds in PM$_{2.5}$ have generally not been included in field studies where the source apportionment analysis has been conducted on an hourly averaged basis due to limitations in available sampling techniques.

The Hansen lab has developed an autonomous instrument, the GC-MS OAM, which has the capability to measure the carbonaceous components of PM$_{2.5}$ on an hourly-averaged basis. This instrument has now been used in several source apportionment studies, as discussed in Chapters 2 and 3 in detail, and has provided valuable information required for source apportionment by PMF. An interested and unexpected finding from these studies was the quantification of the contribution of secondary organic aerosols (SOA) from gases present in wood smoke in addition to primary wood smoke emitted particles, which is explained in detail in Appendix 3 of this dissertation. Since SOA is very complex in nature and is among the most harmful pollutants to
human health, it is necessary to understand the composition of SOA’s to further understand the sources and health effects of fine particulate matter.

1.4 Layout of Dissertation

This dissertation contains research that describes the studies conducted by two analytical instruments, the GC-MS OAM and BBCEAS, developed in our laboratory to measure pollutants in ambient air. Several research studies have been conducted using both instruments. Chapter 2 and 4 are published works, whereas chapter 3 is submitted as a part of research report submitted to Utah Science Technology and Research (USTAR) agency funded by the state of Utah. Chapter 5 is being prepared for publication and chapter 6 has been accepted for publication. Chapter 2 details an extensive source apportionment study conducted in 2016 to identify winter-time sources of fine particulate material in West Valley City, Utah. Chapter 3 details a study conducted to detect and quantitatively measure the organic components of PM$_{2.5}$ using GC-MS OAM in Sevier Valley and Uintah basin, Utah. Chapter 4 details the collaborative study conducted to examine the sources of formaldehyde in Bountiful, Utah. Chapter 5 details the measurement of absorption cross-sections for the 5$^{th}$ and 6$^{th}$ vibrational overtones in a series of short chained alcohols using BBCEAS. Chapter 6 details the detection of sulfur dioxide by BBCEAS. Chapter 7 details conclusions and future work. The appendix contains supplemental information for chapters 4 and 6 and a paper which describes the formation of secondary organic material from gaseous precursors in wood smoke from three source apportionment studies described in chapter 2 and 4.
Chapter 2: Source Apportionment analysis of winter 2016 Neil Armstrong Academy data (West Valley City, Utah)

2.1 Contributions

The following chapter is presented in its entirety (with minor changes) from the published version of the paper in Atmospheric Environment. Paul M. Cropper, Nitish Bhardwaj, Devon K. Overson, Jaron C. Hansen, Delbert J. Eatough, Robert A. Cary, Roman Kuprov and Munkhbayar Baasandorj. Source apportionment analysis of winter 2016 Neil Armstrong academy data (West Valley City, Utah). Atmospheric environment, Volume 219, 116971, ISSN 1352-2310. Devon K. Overson and I analyzed the GC-MS OAM data and calculated the concentrations of different organic compounds detected by the instrument. Dr. Paul M. Cropper wrote the paper and Dr. Delbert J. Eatough helped analyze the data by PMF analysis. Dr. Jaron C. Hansen reviewed and edited the work.

2.2 Abstract

A significant need exists to better characterize air pollution and its sources. This especially pertains to fine particulate matter (PM$_{2.5}$). PM$_{2.5}$ is chemically complex, and its sources of emission and secondary production are highly variable. PM$_{2.5}$ complexity is largely due to the organic fraction, which ranges from 10-90% of its total mass. However, the organic compounds in PM$_{2.5}$ have generally not been monitored in the field due to limitations in available sampling techniques. A source apportionment study was conducted at the Neil Armstrong Academy campus, 5194 Highbury Pkwy, West Valley City, UT 84120, during January and February 2016. Among the
objectives of the study was to identify winter-time sources of fine particulate material in West Valley City, Utah. Fine particulate mass and components, particulate organic marker and related gas phase species were all measured on an hourly average basis. The following hourly averaged data were used in the Positive Matrix Factorization (PMF) analysis, fine particulate mass, cations and anions, carbonaceous material, organic marker compounds, gas phase species including NO\textsubscript{X}, NO\textsubscript{2} and CO and mass spectrometric measurements of gas phase methanol and C\textsubscript{8} aromatics. A total of 557 hourly averaged data sets with 23 components were available for an EPA Positive Matrix Factorization (v5.0) analysis of the data set. The data were best described by a solution with 7 factors. Two of the factors were associated with emissions from mobile sources, diesel and automotive. One factor was associated with wood smoke emissions. Three factors were associated with the formation of secondary fine particulate material. The larger of the three was associated with the production of secondary nitrate and accounted for 70\% of the PM\textsubscript{2.5}, while the other two were associated with secondary formation of particulate organic material from wood smoke associated gas phase organic compounds but accounted for only 3\% of the total PM\textsubscript{2.5} mass. The final factor was associated with fine particulate sulfate and SO\textsubscript{2}. Meteorological backtrajectory data clearly indicted the source was associated with emissions from a copper smelter to the west of the sampling site.

2.3 Introduction

Utah has been one of the fastest growing states in the nation for the past eight years. 80\% of Utahns live in urban areas along the Wasatch Front and the population growth is expected to continue in existing urban areas. The densely populated Salt Lake Valley is surrounded by the Wasatch Mountains to the east and the Oquirrh mountains to the west.
and is open to the Great Salt Lake to the northwest. The unique topographical and meteorological conditions of the Salt Lake Valley favor air stagnation that traps air pollutants for several consecutive days in winter, leading to high pollutant levels. During these events, atmospheric pollutants such as NO$_x$, CO and particulate matter with aerodynamic diameter less than 2.5 microns (PM$_{2.5}$) are found to accumulate in the valley, with PM$_{2.5}$ levels exceeding the National Ambient Air Quality Standard (NAAQS) for PM$_{2.5}$ about 18 times per year.\textsuperscript{51}

As part of an intensive study to better understand hazardous air pollutants in the Salt Lake Valley both winter and summer intensive studies were conducted in 2016 to better characterize the origins, formation, and stability of a variety of pollutants, including PM$_{2.5}$.\textsuperscript{52} Positive Matrix Factorization (PMF) analysis and 24-hour back trajectory analyses were conducted for better interpretation of the source apportionment of the results of the study. The results of the PM$_{2.5}$ source apportionment during the winter study are reported here.

There have been a limited number of past studies which have addressed the source apportionment of fine particulate material in the Salt Lake Valley. Two important concepts resulted from the current study. One is the identification of two types of factors related to wood combustion; one source is the primary material from the combustion of wood, and the other, the formation of secondary organic particulate matter from the co-emitted gas phase VOC compounds. The second is the identification of fugitive emission from smelter operation to the west of the sampling site. Previous source apportionment studies have addressed the importance of primary wood smoke emissions in the Salt Lake Valley. These studies were all conducted at the State of Utah Hawthorne site located in the Salt Lake urban area 18 km east of the Neil Armstrong study site reported here. The most recent study is by
Kelly et al., who reported on the PMF and UNMIX analysis of daily averaged data from the Speciation Trends Network station at the State of Utah Hawthorne site in Salt Lake. They focused on the two-year period from 2007 to 2011 and had available gravimetric PM$_{2.5}$ mass, elemental, IMPROVE protocol carbon data and sulfate data. Their PMF analysis ($n = 429$) indicated that wood smoke was about 30% of the primary PM$_{2.5}$, gasoline about 25%, and diesel about 8% at Hawthorne. An UNMIX analysis of a six-day period ($n=144$) of hourly averaged data by Long et al. (2005) at the Hawthorne site that included total PM$_{2.5}$ (including the volatile species), the semi-volatile PM$_{2.5}$, BC, UV, NO$_X$ and CO indicated that the average wood smoke contribution to PM$_{2.5}$ was 50% higher than the average mobile contribution. A 2009 study at the Hawthorne site during January 14-24 and January 19-February 6 cold pool periods measured PM$_{2.5}$, nitrate, nitrite, sulfate, CO, NO$_X$, NO$_2$, O$_3$ and SO$_2$ and gas phase HONO, HNO$_2$, HNO$_3$ and NH$_3$ all on an hourly average basis. The manuscript focused on the formation of ammonium nitrate, but an extended abstract reported PMF analysis of the data set ($n = 300$) which indicated that the wood smoke factor was about 10 times the average mobile factor.
2.4 Experimental

2.4.1 Site Location

The study was conducted at the Neil Armstrong Academy elementary school campus, 5194 Highbury Pkwy, West Valley City, UT 84120, during January and February 2016, Figure 2.1. This site was chosen because of its central location and low elevation, which makes it susceptible to a buildup of high levels of PM$_{2.5}$ and other pollutants during winter months. Several major highways run on its eastern and northern borders. The eastern part of the town is below the landing approach paths from the south for the Salt Lake City International Airport. Local industries and refineries are located at the northern edge of the city, northeast from the site. A copper refinery and associated power plant is located west of the site.

The predominant winds are northwesterly during the day and southeasterly at night. Hence, the site is often impacted by lake-breeze during the day and southerly flows at night. Influence from the northeast appears to be minor indicating the site is expected to be impacted by the emissions from refineries to lesser extent. However, the site is frequently influenced by the easterly and southeasterly flows, which transport pollutants from the urban corridor of Salt Lake Valley.

Among the objectives of the study was to identify winter-time sources of fine particulate material in West Valley, Utah. Fine particulate mass and components, particulate organic markers and

Fig. 2.1. Location of the Neil Armstrong Academy sampling site in West Valley City and major SO$_2$ sources in the valley. The emission rates for the SO$_2$ are annual averages (ton year$^{-1}$) based on 2014 inventory and represent the entire facility (courtesy of Chris Pennell, UDAQ)
related gas phase species were measured all on an hourly-average basis. The following hourly averaged data were used in the PMF analysis:

2.4.2 Fine Particulate Mass

PM$_{2.5}$ mass was measured using an R&P Model 8599 FDMS (Filter Dynamics Measurement System) Tapered Element Oscillating Microbalance (TEOM) sampler. The FDMS TEOM measures all fine particulate mass including ammoniums nitrate and semi-volatile organic material but does not measure fine particulate water.$^{44,57}$

2.4.3 Fine Particulate Cations and Anions

A URG model 9000D Ambient Ion Monitor (AIM) was used to measure particulate phase anions and cations. The instrument draws in air at a rate of 3 LPM (liter per minute) through a PM$_{2.5}$ sharp-cut cyclone filter. The air is passed through a liquid diffusion denuder where gases are removed by reaction with dilute H$_2$O$_2$ (0.003% in water). The gas phase ions are collected for 55 min., and then analyzed with ion chromatography (Dionex ICS-1000). After removal of the gas phase compounds, the air stream containing particles enters a steam chamber, condensed and collected in a sampling gathering syringe for injection into the ion chromatograph for analysis. The lower limit of detection for both particle and gas phase ions is species dependent but is approximately 0.05 µg/m$^3$. The instrument was calibrated every two weeks with a seven ion standard purchased from Dionex (part number 56933). The only ions present in significant concentrations were nitrate, sulfate, and ammonium ion, with reasonable equivalent balance between the anions and the cations. Ammonium nitrate and ammonium sulfate were used in the PMF analysis. In addition, chloride anion and sodium cation were included in the PMF data set.
2.4.4 Carbonaceous Material

Black carbon and UV absorbing carbon were determined with a dual wavelength aethalometer (Magee Scientific). The aethalometer sampled ambient air at a rate of 2.5 LPM, through 4m of anti-static tubing, with a diameter of 1/4". Aerosol carbon was also measured with a Sunset Laboratories Semi-Continuous OC/EC Field Analyzer. The Sunset OC/EC Field Analyzer sampled ambient air with a flow of 8.0 LPM, through PM$_{2.5}$ cyclone cut off filter and 4m of 3/8" stainless steel tubing. The Sunset OC/EC Field Analyzer provided elemental carbon and nonvolatile organic carbon (NVOC) data. The NVOC values were converted to nonvolatile organic mass, NVOM, using a factor of 1.6 (Turpin and Lim, 2001). Semi-volatile organic mass (SVOM) was estimated as the FDMS TEOM measured PM$_{2.5}$ minus all other measured fine particulate species.

2.4.5 Gas Phase Species

CO, O$_3$, and NO$_x$ (NO, NO$_2$) were monitored with analyzers from the Utah Department of Air Quality (UDAQ), which included a Teledyne Advanced Pollution Instrumentation (API) gas filter correlation CO analyzer (Model 300 E), photometric ozone analyzer (Model 400 E), and T series NO$_x$ analyzer (Model T200U) equipped with a NO$_2$ photolytic converter. The trace gas analyzers were calibrated bi-weekly and daily and automated precision, zero and span (PZS) checks were performed automatically monitor any drifts. The ambient air was drawn into the room at ~ 10 LPM through ~ 10 m long 1/2” O.D. PFA tubing to a 6-port glass manifold. The trace gas analyzers sub-sampled from this manifold at 600 – 700 sccm. Mass spectrometric measurements of methanol and C8 aromatics were also available and used in the PMF analysis.$^{52}$ A Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Ionicon Analytik, Innsbruck, Austria) was used to make hourly averaged measurements. A wide suite
of volatile organic compounds (VOCs) was measured using a high sensitivity standard PTR-MS that was brought from the University of Minnesota. Details about the instrumentation including the gas sampling inlet system for the PTR-MS have been discussed previously.\textsuperscript{58-60} The ambient air was drawn in through ~ 8 m long 1/2" O.D. heated inlet at ~ 10 LPM and the inlet system sub-sampled 700 sccm of the total flow and the PTR-MS sampled at ~ 35 sccm. The PTR-MS drift tube pressure and voltage were maintained at 2.3 mbar and 600 V (E/N = 126 Td), with the water flow at 6.5 sccm. Automated background measurements were performed every two hours and calibrations were made every ~ 6 hours. The backgrounds and calibration factors were extrapolated for the ambient measurements and used to obtain the concentration in ppb.\textsuperscript{61} The PTR-MS sensitivities for some VOCs showed a humidity dependence and were corrected using reported correction factors when available.\textsuperscript{61-63}

The PTR-MS measures all C8 and C9 aromatic compounds at m/z 107 and 121, respectively; here we use the approach of de Gouw et al. to calculate a weighted calibration factor for the sum of C8 aromatics based on the measured p-xylene sensitivity and its typical abundance relative to its isomers.\textsuperscript{62} Similarly, a weighted calibration factor for the sum of C9 aromatic compounds based on the measured 1,2,3-trimethylbenzene sensitivity was derived and used to calculate the concentration of the sum of C9 aromatic compounds.

2.4.6 Organic Marker Compound Data

The Gas Chromatography–Mass Spectrometry Organic Aerosol Monitor (GC-MS OAM) used in this study has been described previously.\textsuperscript{14} The GC-MS OAM combines fully automated filter collection of fine particles with thermal desorption, GC and MS to quantitatively measure carbonaceous components of PM on an hourly averaged basis. Ambient air was pulled at 16.7 LPM through a PM\textsubscript{2.5} cyclone cutoff filter, with a sample
collection flow rate of 8 LPM and bypass flow of 8.7 LPM. A chemically deactivated quartz filter was utilized for collection followed by thermal desorption at 280°C into the GC-MS, and subsequent GC-MS analysis. Compounds measured by the GC-MS OAM and used in the PMF analysis included fluorene, levoglucosan (and its isomers), stearic acid, dehydroabietic acid, syringe aldehyde, o-phthalic acid, adipic acid and 4-oxoheptanedioic acid.

Complete data were available for the time period from 16:00 January 13 through 19:00 January 19, 12:00 January 21 through 16:00 January 26, 17:00 January 28 through 14:00 February 2 and 14:00 February 9 through 23:00 February 15, 2016, providing 689 data sets for the EPA PMF v5.0 analysis reported here. The data are given in Figures 2.2-2.4.
Fig. 2.2. PM$_{2.5}$ and PM component hourly averaged data used in the EPA PMF v5.0 analysis. Weekends are noted with a crosshatch bar below the X axis.
Fig. 2.3. PM$_{2.5}$ and gas phase hourly averaged data used in the PMF analysis. SO$_2$ data is given in red because it was used to interpret the PMF analysis but was not used directly in the analysis. Weekends are noted with a crosshatch bar below the X axis.
Figure 2.4. PM$_{2.5}$ and particulate organic marker data used in the final PMF analysis. Weekends are noted with a crosshatch bar below the X axis.
2.5 EPA PMF v5.0 analysis

The concept of Positive Matrix Factorization (PMF) and the algorithm used in the analysis has been previously described.\textsuperscript{34} With PMF, the results are constrained so that factor contributions cannot be negative for any species. The PMF program used in this analysis was EPA PMF v5.0.(EPA, 2014). One of the advantages of PMF is the ability to account for missing and below detection limit data as well as perform Bootstrap and Displacement analysis. The uncertainty in each measurement can be adjusted to account for aberrations in the data set. In this study, uncertainty estimates were chosen similar to those previously outlined.\textsuperscript{8, 44} For what were determined to be “reliable” data, the concentration values were directly used, and the uncertainty estimates were assigned as the measurement uncertainty plus one third the limit of detection (LOD). In the few instances when the measurement was below the LOD, the uncertainty was estimated as 5/6 the LOD. Missing values in the data set were accounted for by taking the geometric mean of the hour preceding and following the missing data point. In this study, SVOM concentrations were obtained as the difference between the FDMS TEOM and the sum of the other measured components of PM\textsubscript{2.5}. Therefore, the uncertainty estimate was performed as described above using the highest LOD of the various measurement techniques. The uncertainty of the fitted parameter, FDMS mass, was taken to be four times the measured value.\textsuperscript{64}
2.6 Results

EPA PMF v5.0 analysis was conducted by 222 incrementally assuming 4 to 9 factors as solutions. After examining the results from the various analyses, it was observed that three factors in each solution consistently gave results which reflected little predicted mass, and contribution from essentially only the component. These components, ozone, pyrene and anthracene were dropped from consideration in the final analyses and the data are not included in Figure 2.4. The resulting data were best described with 7 factors. The final EPA PMF v5.0 solution was further analyzed using the “constrained analysis” option of PMF to optimize the description of the major PM components (but not the assignment of the various minor aerosol marker species). The comparison of measured and PMF predicted mass is shown in Figure 2.5 with the time series for each factor shown in Figure 2.6 and the associated profiles given in Table 2.1.

As indicated in Figure 2.5, the regression slope of experimental compared to PMF calculated mass (n=557, $R^2 = 0.968$) gave a regression slope of $1.01 \pm 0.01$. Average error in the fit of PM$_{2.5}$ (average of 25.2 µg/m$^3$) is 2.4 µg/m$^3$. 

![Fig. 2.5. Comparison of the measured and PMF experimental (exp.) PM$_{2.5}$ mass.](image)
Figure 2.6. Diurnal variations in the concentrations of the identified 7 factors in the PMF analysis. Weekends are noted with a crosshatch bar below the X axis. Note that the Y axis scales are different for each plot.
### 2.7 Discussion

#### 2.7.1 Discussion of Each Factor Identified in the PMF Analysis

Factor 1 is present at an average of 2.56 µg/m³. It contains 10% of the CO and 21% of the NOₓ, Table 2.1. The mass is reasonably well predicted (a ratio of components to mass of 1.09) and consists of NVOM, SVOM and BC present as 78, 25 and 3% of the factor mass, respectively, Table 2.1. The factor is present primarily in the day. These characteristics are all typical of a factor dominated by emissions from gasoline powered vehicles. In addition, the strong presence of C8 aromatics (40% of the total) and methanol (60% of the total) in the profile are also consistent with this assumption. Factor 1 is assumed to be an auto emissions related factor.

<table>
<thead>
<tr>
<th>Species</th>
<th>Average Concentration</th>
<th>Auto</th>
<th>Diesel</th>
<th>Wood Smoke</th>
<th>Sec OM1</th>
<th>Sec OM2</th>
<th>Sec Nitrate</th>
<th>Smelter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM₂.₅ fit</td>
<td>21.49 µg/m³</td>
<td>2.56 µg/m³</td>
<td>2.59 µg/m³</td>
<td>0.39 µg/m³</td>
<td>0.02 µg/m³</td>
<td>1.09 µg/m³</td>
<td>12.12 µg/m³</td>
<td>2.72 µg/m³</td>
</tr>
<tr>
<td>PM₂.₅ exp.</td>
<td>22.16 µg/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>21.49 µg/m³</td>
<td>11.9%</td>
<td>12.0%</td>
<td>1.8%</td>
<td>0.09%</td>
<td>5.1%</td>
<td>41.3%</td>
<td>20.2%</td>
</tr>
<tr>
<td>NVOM</td>
<td>4.25 µg/m³</td>
<td>(78%)</td>
<td>15.2%</td>
<td>1.8%</td>
<td>0.2%</td>
<td>3.3%</td>
<td>20.4%</td>
<td>11.8%</td>
</tr>
<tr>
<td>SVOM</td>
<td>2.42 µg/m³</td>
<td>(25%)</td>
<td>2.2%</td>
<td>6.9%</td>
<td>2.1%</td>
<td>0</td>
<td>27.2%</td>
<td>20.2%</td>
</tr>
<tr>
<td>EC</td>
<td>0.34 µg/m³</td>
<td>0</td>
<td>88.9%</td>
<td>0</td>
<td>1.5%</td>
<td>0</td>
<td>0</td>
<td>9.0%</td>
</tr>
<tr>
<td>BC</td>
<td>0.63 µg/m³</td>
<td>10.9%</td>
<td>74.7%</td>
<td>0</td>
<td>1.1%</td>
<td>0.4%</td>
<td>0</td>
<td>12.8%</td>
</tr>
<tr>
<td></td>
<td>Value 1</td>
<td>Value 2</td>
<td>Value 3</td>
<td>Value 4</td>
<td>Value 5</td>
<td>Value 6</td>
<td>Value 7</td>
<td>Value 8</td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>UV</td>
<td>0.69 µg/m³</td>
<td>17.6%</td>
<td>70.4%</td>
<td>0.3%</td>
<td>0.7%</td>
<td>1.0%</td>
<td>0%</td>
<td>10.1%</td>
</tr>
<tr>
<td>NH4NO3</td>
<td>12.69 µg/m³</td>
<td>0 (4%)</td>
<td>11.7%</td>
<td>0.1%</td>
<td>2.9%</td>
<td>5.4%</td>
<td>68.9%</td>
<td>11.1%</td>
</tr>
<tr>
<td>(NH4)2SO4</td>
<td>0.98 µg/m³</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.3%</td>
<td>41.6%</td>
<td>56.1%</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>0.34 µg/m³</td>
<td>21.7%</td>
<td>0</td>
<td>2.1%</td>
<td>0</td>
<td>2.3%</td>
<td>54.7%</td>
<td>19.1%</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.02 µg/m³</td>
<td>0</td>
<td>85.9%</td>
<td>0.9%</td>
<td>2.3%</td>
<td>11.8%</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>194 ppb</td>
<td>9.9%</td>
<td>79.0%</td>
<td>1.1%</td>
<td>0.9%</td>
<td>9.1%</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NOX</td>
<td>33.8 ppb</td>
<td>21.2%</td>
<td>70.7%</td>
<td>0</td>
<td>0</td>
<td>4.3%</td>
<td>0</td>
<td>3.8%</td>
</tr>
<tr>
<td>NO2</td>
<td>23.3 ppb</td>
<td>29.9%</td>
<td>50.0%</td>
<td>0</td>
<td>0</td>
<td>4.3%</td>
<td>7.7%</td>
<td>7.3%</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.38 ng/m³</td>
<td>6.1%</td>
<td>0.3%</td>
<td>0.6%</td>
<td>47.0%</td>
<td>25.8%</td>
<td>2.7%</td>
<td>17.5%</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>13.3 ng/m³</td>
<td>0</td>
<td>9.2%</td>
<td>66.9%</td>
<td>23.9%</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>11.1 ng/m³</td>
<td>0</td>
<td>0</td>
<td>90.2%</td>
<td>4.8%</td>
<td>0.8%</td>
<td>3.3%</td>
<td>1.0%</td>
</tr>
<tr>
<td>DHA Acid</td>
<td>1.9 ng/m³</td>
<td>2.9%</td>
<td>4.4%</td>
<td>92.7%</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Syringe Ald.</td>
<td>0.19 ng/m³</td>
<td>0</td>
<td>0</td>
<td>85.1%</td>
<td>9.9%</td>
<td>3.6%</td>
<td>1.3%</td>
<td></td>
</tr>
<tr>
<td>o-Phathalic Acid</td>
<td>1.53 ng/m³</td>
<td>0</td>
<td>4.3%</td>
<td>1.4%</td>
<td>1.8%</td>
<td>10.6%</td>
<td>0</td>
<td>81.9%</td>
</tr>
<tr>
<td>Adipic Acid</td>
<td>0.12 ng/m³</td>
<td>4.0%</td>
<td>0</td>
<td>0</td>
<td>2.6%</td>
<td>89.7%</td>
<td>3.6%</td>
<td>0</td>
</tr>
<tr>
<td>4-oxyHD</td>
<td>0.026ng/m³</td>
<td>51.6%</td>
<td>0</td>
<td>19.2%</td>
<td>0</td>
<td>1.1%</td>
<td>28.0%</td>
<td>0</td>
</tr>
<tr>
<td>Methanol</td>
<td>24.1</td>
<td>59.8%</td>
<td>32.0%</td>
<td>4.3%</td>
<td>3.8%</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C8Aromatics</td>
<td>0.86</td>
<td>39.8%</td>
<td>53.3%</td>
<td>1.3%</td>
<td>1.0%</td>
<td>5.0%</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% Mass of Source Accounted For By Species</td>
<td>94</td>
<td>109%</td>
<td>103%</td>
<td>69%</td>
<td>----</td>
<td>78%</td>
<td>92%</td>
<td>113%</td>
</tr>
</tbody>
</table>

**Table 2.1.** Factor profiles of the 7 factors identified in the PMF analysis giving the average mass in each factor. The percent mass accounted for by the source is shown across the row. For example, 47% of NVOM is accounted for by the Auto source, and 15.2% of NVOM is accounted by the Diesel source. The species % mass for each source, is given for each column, and is shown in parenthesis. For example, 78% of Auto total mass is NVOM and 25% of the Auto total mass is SVOM. Both the experimental (exp) average PM2.5 mass and the PMF fit average PM2.5 mass are given. Species with negligible contributions or very low mass are shown as zero. The last row gives the percent of each factor mass explained by the particulate species. See OM total % Mass accounted for is denoted as “---” due to the very low mass associated with this factor.

Factor 2 is present at an average of 2.59 µg/m³. It contains 79% of the CO, 71% of the NOₓ and 75% of the BC (Table 2.1). The mass is well predicted by the PMF results by a factor of 1.03 and consists of NVOM, SVOM and BC in the ratio of 26, 2 and 18% of the factor mass, Table 2.1. It also consists of 57% ammonium nitrate. However, the ratio of NVOM to BC is typical of that expected for diesel emissions. These characteristics are all typical of a factor dominated by emissions from the diesel-powered vehicle fleet. In addition, the presence of much of the remaining C8 aromatics (53% of the total) and methanol (32% of the total) in the profile are also consistent with this assumption. However, the diurnal pattern of PM₂.₅ does not always show the
expected morning peak and weekend reduction normally seen for a diesel related factor. This probably reflects that the Neil Armstrong Academy is not near any major traffic ways expected to carry diesel vehicles (Figure 2.1). Factor 2 is assumed to be a diesel traffic emissions related factor.

Factor 3 is present at an average of 0.39 μg/m³, although it is only sporadically present. It is present only in the evening and tends to be present on weekends or Monday night. The mass of this factor is not well explained by the PMF results (ratio of components to mass of 0.69). It consists of 20% NVOM, 17% SVOM and 3% ammonium nitrate. These characteristics are all typical of a factor dominated by wood smoke emissions. In addition, the presence of levoglucosan (67% of the total) and dehydroabietic acid (93% of the total) in this profile are also consistent with this assumption. The factor also contains 90% of the adipic acid. Furthermore, the occurrence of this factor on Monday night peaks are consistent with the tradition of members of the Church of Jesus Christ of Latter-day Saints which constitutes a significant fraction of the population in West Valley City, to hold a “Family Home Evening” on Mondays. Factor 3 is assumed to be a wood smoke related factor.

Factors 4, 5 and 6 appear to be related to the formation of secondary particulate material. Factors 4 and 5 are not related to one another, but both are present during a portion of the time that the Wood Smoke related factor 3 is present, Factor 4 only averages 0.02 μg/m³, and is present with Factor 3 with peaks of 0.2 μg/m³ the evening of Jan 28 also with peaks of 0.2 μg/m³ the evening of Feb 13. Because of the very low mass associated with this factor, the composition is not well described by the PMF result but is similar to the composition of Factor 3. Factor 4 contains 24% of the levoglucosan. It also contains 85% of the syringe aldehyde and its diurnal pattern follows this organic marker. Factor 5 is present at an average of 1.09 μg/m³ and is present with Factor 3
(with a peak of 2 µg/m³) the evenings of Jan 24, Jan 5 (with peaks of 3 µg/m³, and as a double peak similar to Factor 3), and the evening of Feb 13, with peaks of 10 to 15 µg/m³.

The mass of the factor is reasonably well explained by the PMF results (ratio of components to mass of 0.78). It consists of 13% NVOM, and 56% ammonium nitrate, typical of a factor dominated by secondary material. Levoglucosan is not present in the factor profile but the factor contains 90% of the adipic acid. We conclude that the both factors are secondary material, not emitted with wood smoke, but formed from the gases associated with wood smoke emissions. A similar factor has been identified in a study in Provo, Utah using a smaller set of organic marker 1-hour data. This assumption is further discussed after the discussion which follows on Factor 6 and 7. Factor 6 is present at an average of 12.12 µg/m³ and represents 41% of the total PM$_{2.5}$. The mass of the factor is well explained by the PMF results (ratio of components to mass of 0.92). It contains 7% NVOM, 8% SVOM, 72% ammonium nitrate and 3% ammonium sulfate (42% of the total ammonium sulfate). It is not significantly associated with any of the marker compounds. Factor 6 is assumed to be associated with the secondary production of ammonium nitrate from NOX emissions.

Factor 7 is present at an average of 2.72 µg/m³, although it is only present in significant amounts during the time period of February 11-14. The mass of the factor is reasonably well explained by the PMF results (ratio of components to mass of 1.13). It consists of 12% NVOM, 20% SVOM, 3% BC, 52% ammonium nitrate and 19% ammonium sulfate (56% of the total ammonium sulfate). It is also associated with the highest concentrations of SO$_2$ (g) measured during the study, Figure 2.8. It is interesting to note that this factor also contains 82% of the o-phthalic acid. As shown in Figure 2.1, there are two possible sources for SO$_2$, and correspondingly for the source responsible for Factor 7. Several oil refineries are located to the NNE of the Neil Armstrong Academy site,
with the largest being the Teroso complex 14 km NE of the sampling site. The other major source is the Kennecott Smelter and Power Plant, about the same distance west of the sampling site. During the times periods of high SO₂, air flow to the sampling site is from the NW, and thus potentially from either site. However, meteorological back trajectories indicate that the air flow at the sampling site is from the NW, but as the trajectory reaches the Great Salt Lake, the trajectory shifts to the S, SW and passes over the Kennecott Facilities. We conclude that Factor 7 is associated with smelter fugitive emissions.

Further justification of sources 4 and 5 being associated with formation of secondary particulate matter from gaseous emission from the combustion of wood can be seen by comparison of the time patterns of Factors 5, 6, and 7 (see Figure 2.9). As shown in Figures 2.6 and 2.7, the Wood Smoke Factor 3 is associated with either Factor 4 or 5 and sometimes both. The major peak for Factor 5 occurs on February 13 and 14. While both Factor 6 (Secondary Nitrate) and Factor 7 (Smelter Related) are also both present during this time period, Figure 2.8, they are also present with prominent peaks at other time periods when Factor 5 is not present. In contrast, when Factor 5 is present, The Wood Smoke Factor is also always present, Figures 2.6 and 2.7 and preceding discussion.
Figure 2.7. Comparison of diurnal variation in the concentrations of Factors 3, 4 and 5. As discussed in the text, Factor three is associated with emissions from the burning of wood smoke and Factors 4 and 5 are associated with the formation of secondary material from wood smoke gaseous emissions.

Figure 2.8. Comparison of the diurnal variation in the concentration of the Factor 7 PMF identified material (black) and the concentration of SO₂ (heavy gray).
2.7.2 Formation of secondary organic particulate matter from wood smoke gases

It is informative to compare the results of this study with a previously published study where sampling was done on the Brigham Young University (BYU) campus in Provo, UT. In that study, hourly averaged measurements of organic markers with the GC-MS OAM were also included in a PMF analysis. However, the data were not as extensive as those reported here; organic markers used included only levoglucosan, dehydroabietic acid, stearic acid, pyrene and anthracene. A total of 248 hourly averaged data sets were available for the PMF analysis. A total of six factors were reported which accounted for the essence of the observations. Two factors were associated with emissions from automobiles or diesel, one was related to primary wood smoke emissions, one related to the secondary formation of nitrate, one to ozone related secondary formation and one to the formation of secondary fine particulate material from wood smoke emitted gases. The results of this study and the previous BYU study are compared in Figure 2.10.
In both studies the major factor was Secondary Nitrate, with this factor being a larger fraction of the total at Neil Armstrong Academy than at BYU. The composition of this factor was comparable at the two sites. In addition, the fraction of the aerosol presents as Automotive or Diesel related factors were about five times larger at Neil Armstrong Academy, but with comparable compositions at the two sites. The Wood Smoke Factor was 31% of the PM composition at BYU, but only 2% at Neil Armstrong Academy. At both locations a factor associated with the formation of particulate material from wood smoke emitted gases was seen. At BYU this factor was essentially all organic material and was associated with a fraction of both levoglucosan and dehydroabietic acid. At the Neil Armstrong Academy, two factors due to formation of particulate matter from wood smoke emitted gases were identified. The two were dominated by mass of the OM2 Factor. The OM1 Factor was identified based mainly on the diurnal pattern of the syringe aldehyde marker (plus levoglucosan) and the OM2 Factor was identified based mainly on the
diurnal pattern of the adipic acid marker. Neither the aldehyde nor acid markers were present in the BYU data set.

In the manuscript describing the BYU study it was observed that the Wood Smoke and OM related factors both tended to appear during the evenings. However, in spite of the presence of levoglucosan in the OM Factor, OM was not associated with secondary chemistry of gases emitted with wood smoke in that manuscript. The diurnal pattern of both the Wood Smoke and OM Factors from the BYU study are shown in Figure 2.11. As was the case in West Valley, wood is expected to be used more extensively on Saturday and Monday nights (evenings of Jan.19, 24 and 26 in Figure 2.11).

![Figure 2.11. Diurnal patterns of the Wood Smoke and OM Factors identified in a source apportionment study at BYU in Provo, Utah.](image)

The peaks in primary wood smoke during these time periods are evident. In addition, there is clear association of the concurrent formation of the OM factor material during these same time periods. It should be noted that the wood smoke signatures never quite drop to zero in the BYU study, presumably because of the greater concentrations of wood smoke identified in the BYU study as compared to the West Valley study (a factor of 13 times more). We conclude that the OM Factor described in the BYU study is also associated with the formation of secondary OM particles from
gas phase compounds emitted with wood smoke. As mentioned above, the OM Factor identified in the BYU study was essentially all organic material. In contrast, the OM2 Factor identified in the Neal Armstrong Academy study was dominated by ammonium nitrate and not by NVOM, Table 2.1. This may be an artifact of the presence of the OM2 Factor being present during a period of significant concentrations of ammonium nitrate, Figure 2.9, limiting the ability of PMF to cleanly identify the composition of OM2. If we assume that the NVOM of the OM2 Factor and the total OM1 Factor is a result of wood smoke (Table 2.1), then total secondary OM formed from wood smoke related gases would be 0.16 µg/m³. This total secondary OM mass is 41% the size of the primary Wood Smoke Factor mass, comparable to the value of 60% seen in the BYU study. It is interesting to note that even though the fraction of PM₂.₅ present as wood smoke at the Neil Armstrong site was quite low (presumably because of the site location as discussed above) the fraction of the PM₂.₅ in the BYU study present as primary Wood Smoke, 31%, was much higher and the ratio of primary Wood Smoke to the Auto factor was 12, comparable to the PMF analysis of the 2009 Hawthorne data as summarized in the Introduction. This was the previous PMF analysis based on hourly averaged data and conducted in at urban center similar to that for the BYU study.

2.7.3 Correlations Among the Factors

Possible independence or dependence of the various factors was conducted by examination of G-Space edges. G-space plotting for PMF models such as this helps identify unrealistic factors by plotting the factors against each other. As explained by Paatero, et al., if the PMF is model is realistic, the limiting edges usually coincide with the axes or lay parallel with them. The G-Space comparison of the concentration data for Factor 3, Wood Smoke and Factor 4, OM1 and Factor 3, Wood Smoke and Factor 5 are shown in Figures 2.12A and 2.12B, respectively. The comparison
between factors OM1 and OM2 is shown in Figure 2.12C. As indicated edges are present for both the Y and the X axis for each figure. It should be noted that the average concentration for Factor OM1 is only 0.02 µg/m³, compared to 0.38 and 1.09 µg/m³ for Factors 3 and 5, respectively. Thus, more uncertainty is expected in the OM1 comparisons. With this in mind, the results in Figures 2.12A, 2.12B, and 2.12 C indicate that the factors are not independent but are highly correlated. These results are consistent with the assumption made above that all three factors are related to the presence of wood smoke emissions, Factor 3 being the primary fine particulate emissions from the combustion of wood and Factors 4 and 5 being the fine particulate material which forms from the wood smoke emitted gas phase VOCs. These observations are in contrast to what is seen in Figures 2.12D and 2.12E where the G-Space comparisons are given for Factor 6, Secondary Nitrate vs Factor 7, Smelter and for Factor 1, Auto vs Factor 2, respectively. The lack of well-defined edges along the X or Y axes for the two comparisons and poor correlation between either of the two comparisons indicates the compared factors are independent of each other.
Figure 2.12. G-Space comparisons of the indicated pairs of Factors.

2.8 Conclusions

An extensive set of data consisting of PM$_{2.5}$ mass and chemical composition, gas phase compounds indicative of both primary emissions and secondary aerosol formation pathways and particulate organic marker compounds all measured on an hourly averaged basis have been used in an EPA PMF v5.0 analysis of measured PM$_{2.5}$ at the Neil Armstrong Academy in West Valley City (Salt Lake urban area) during the winter of 2017. A total of seven factors were identified in this analysis.
Two of the factors are related to emissions from automotive and diesel traffic. One of the factors is associated with fugitive emissions from the copper smelter west of the sampling site. One of the factors, which is associated with 41% of the PM$_{2.5}$ mass is associated with the secondary formation of ammonium nitrate. Three factors are related to wood smoke emissions, with one of these three factors representing primary wood smoke particulate emissions and the other two representing the formation of secondary aerosol from wood smoke combustion emitted gases. This formation of secondary organic aerosol from wood smoke emitted gases has also been observed in a previous study at BYU. These data suggest that in addition to the primary emissions of wood smoke often identified in a source apportionment analysis, wood smoke is also responsible for the precursors to secondary organic material at a level of about 60% of the attributed primary wood smoke emissions. A point not emphasized in the discussion, but true, is that the PMF analysis is greatly aided using hourly averaged data, as opposed to daily averaged data. This is because the diurnal variations in the data which drive the PMF results reflect the changes in what factors are present with time as the diurnal variations in the atmosphere occurs. This information is not present in daily averaged data, even as the number of data sets are increased.
Chapter 3: Measurement of air pollutants using GC-MS Organic Aerosol Monitor in Sevier Valley and Uintah basin, UT

3.1 Contributions

The following chapter is presented in its entirety (with minor changes) as a part of interim research report submitted to Utah Science Technology and Research (USTAR) agency funded by the state of Utah. I collected, analyzed, and wrote the research part of the interim report. Devon Overson helped with the collection and analysis of OAM data. Dr. Jaron C. Hansen reviewed and edited the work.

3.1 Introduction

Among all the components of air pollution, particulate matter 2.5 (PM$_{2.5}$, particulate matter composed of particles with a diameter ≤2.5µm) is the most complex and the least understood. Since PM$_{2.5}$ is a primary contributor to health problems and environmental problems such as poor visibility, understanding and monitoring its composition is of upmost importance. 20-80% of PM$_{2.5}$ is composed of semi-volatile organic compounds (SVOC) and while the total mass of PM$_{2.5}$ is routinely measured on an hourly basis, individual SVOC concentrations are not. These concentrations provide a wealth of knowledge concerning PM$_{2.5}$ particles and their origin than cannot be obtained in any other way. This is because many SVOCs are specific to a particular emission source, thus they act as organic markers for their source.

Currently, measurements of organic markers are limited to 4-24 hour averaged samples. Though some methods that have been developed are fast, most methods are limited to timely solvent extraction followed by GC/MS analysis, and all require individual laboratory analysis and bench
top equipment. These and other restrictions have prevented the monitoring of organic markers continuously, on a short time scale. There are many advantages to automated, in-field, monitoring of these organic markers. A primary advantage is that by measuring hourly averaged values, their concentrations can be linked to wind speed, wind direction and other pollutant concentrations, and thus provide invaluable information concerning PM\(_{2.5}\) origins and sources thus providing robust source apportionment analysis and conclusions.

Instruments have been deployed in the field to monitor PM\(_{2.5}\) composition, such as the Aerosol Mass Spectrometer, however this and other instruments do not quantitatively measure organic markers. Their speciation data is often limited to the inorganic material, particle size, and total carbonaceous material. There is a great need for an autonomously operating monitoring device that can be deployed in the field for analysis of PM\(_{2.5}\) organic markers. Ideally, the lower limit of detection should extend to concentrations that will allow for detection of organic markers on at least a 1-hr time scale.

Due to the over-arching need to quantitatively monitor the composition of PM\(_{2.5}\), specifically organic markers, an instrument has been developed for this purpose based on a GC/MS detection platform. This instrument has been deployed in the field and has been shown to provide invaluable information needed for source apportionment. This report describes the instrument and the data obtained from deployment of the GC-MS OAM in Richfield, Vernal and Provo UT. These three locations were chosen because they represent air sheds that are primarily urban, rural, and influenced by gas and oil mining operations. As part of this project the software used for data analysis was upgraded to make it more user friendly.
3.2 Instrument Design

The GC-MS Organic Aerosol Monitor (GC-MS OAM) is composed of an auto-sampler connected to a gas chromatography-mass spectrometer. Auto-sampling is performed using a quartz oven composed of a quartz chamber, a collection filter at the center of the chamber, and nichrome wire wrapped around the outside of the quartz chamber. Sampling is performed by pulling ambient air across the collection filter and through a side-arm (see figure 3.1). After sample collection, the side-arm valve is closed and He flow is directed through the oven, through a 6-port valve, and into the GC column. The sample is then desorbed off the filter and into the column. Desorption temperatures vary based upon the desired semi-volatile window. The semi-volatile material is concentrated on the column, which is kept at room temperature. Desorption and column concentration is then followed by GC-MS separation and analysis.

The GC-MS is a modified model Guardian 7, manufactured by Torion Technologies. Modifications include a larger turbo-pump, and a 250µm I.D. column, including a miniaturized GC produced at BYU. The GC column is a Restek Rxi-5 fused silica column, optimized for semi volatile separation. The GC ramp rate varies from 1.5 °C to 2.5 °C.
3.3 Chemicals and system testing

Standards used to test the system performance include levoglucosan, dehydroabietic acid, and stearic acid, each purchased from Sigma-Aldrich. A mixture of these three compounds was made and diluted to varying concentrations to test for chemical degradation and separation and detection. A standard mixture of polycyclic aromatic hydrocarbons (EPA 525 PAH Mix-B standard) was purchased from Sigma-Aldrich. All mixtures were made in acetone.

All standard mixtures were loaded directly onto the collection filter using 1-5 µL injections, followed by thermal desorption and GC-MS analysis. To test the retention of sample by the filter during periods of high air flow, ambient air was pulled across the sample loaded filters for 1-2 hours. Since liquid introduction of the standard is inherently different than sample collected solely on the front end of the filter, a small piece of sample loaded filter was placed in front of the collection filter, followed by 2-hours of high air flow. The quartz ovens and the quartz filters were deactivated using silazanes.

3.4 In-field testing

The instrument was operated in the field in Richfield, UT on the campus of Snow College, Uintah Basin (Horsepool sampling site) and at the Lindon Elementary School (Lindon, UT). These sites were chosen because they represent air sheds that are primarily urban, rural, and influenced by gas and oil mining operations. Samples were collected on a 1-hour basis. PM$_{2.5}$ was targeted by using a PM$_{2.5}$ cyclone cut-off filter on the front end of the sampling inlet.
3.5 Sampling Results

Figure 3.2 compares two chromatograms; one collected in Richfield (May 2017) and the other in the Uintah Basin (Horsepool, June 2017). Evidence in the form of detection of levoglucosan from the combustion of wood is observed to be contributing to the PM load in the Uintah Basin but not in the sample collected in Richfield. Clovene and flurtamone are markers for pesticide and herbicide use and were observed in samples collected from Richfield but not in the sample from the Uintah Basin. Diethyl phthalate was also observed in this sample collected in Richfield. Diethyl phthalate is commonly used as a plasticizer. Samples from Richfield were the only locations that clovene, flurtamone and diethyl phthalate were measured.

![Figure 3.2: Comparison of gas chromatograms of PM collected in Richfield and Uintah Basin (UT).](image)

Long term operation of the GC-MS OAM in Richfield and the Uintah Basin allowed for observation of the diurnal pattern for a range of marker compounds. For example, pyrene, a marker
for mobile emissions (i.e., diesel/gasoline combustion) shows a high concentration beginning on June 3 and continuing until June 7 in Richfield (Figure 3.3).

Figure 3.3: Diurnal pattern for pyrene (m/z = 202, collected May 31- June 11, 2017, Richfield)

Figure 3.4 shows the diurnal pattern for diethyl phthalate (m/z = 222) collected between June 3- June 7, 2017, in Richfield. It is apparent that there is a source in the area that is emitting diethyl phthalate starting at around 10 pm at night and continuing until approximately 6 am in the morning.
Figure 3.5 shows the concentrations of 31 different organic markers measured between April 27 and May 14 in Richfield that the GC-MS OAM is calibrated to detect. An unusually high concentration of 2-methyl benzyl alcohol is observed between May 2 to May 3. Though this product is not listed as a hazardous substance under Clean Air Act, but it can cause irritation to the digestive and respiratory tract in human beings. Additionally, 2-methyl benzyl alcohol can decompose to release harmful pollutant gases like carbon monoxide and carbon dioxide.

Figure 3.4: Diurnal pattern for diethyl phthalate (m/z = 222, collected May 31- June 11, 2017, Richfield)
Figure 3.5: Diurnal pattern of 31 different organic markers measured between April 27 and May 14, 2018, using GC-MS OAM
Table 3.1 shows a list of organic compounds in PM which were successfully detected or identified during our air sampling studies conducted during 2017-2018 at various locations in Utah including Richfield, Vernal and Lindon. New compounds were detected, which were not measured by the GC-MS OAM before. It included unidentified terpenes, diethyl phthalate, phthalic acid, PAHs and some potential herbicides and pesticides.

**Table 3.1.** Compounds detected in Uintah Basin, and Richfield (UT) during the study period.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Richfield (Sevier Valley)</th>
<th>Horsepool (Uintah Basin)</th>
<th>Probable Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levoglucosan</td>
<td></td>
<td>✓</td>
<td>Burning of wood</td>
</tr>
<tr>
<td>Clovene</td>
<td>✓</td>
<td></td>
<td>Terpene</td>
</tr>
<tr>
<td>Flurtamone</td>
<td>✓</td>
<td></td>
<td>Pesticide</td>
</tr>
<tr>
<td>Pyrene</td>
<td>✓</td>
<td>✓</td>
<td>Diesel/Fuel Combustion</td>
</tr>
<tr>
<td>Diethyl Phthalate</td>
<td>✓</td>
<td></td>
<td>Manufacture of plastics</td>
</tr>
<tr>
<td>Retene</td>
<td>✓</td>
<td></td>
<td>Burning of wood</td>
</tr>
<tr>
<td>3-methyl-4-nitrophenol</td>
<td>✓</td>
<td></td>
<td>Degradation product of pesticide</td>
</tr>
<tr>
<td>2-methyl benzyl alcohol</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### 3.6 Conclusions

Previously unidentified organic compounds in PM were successfully identified by GC-MS OAM during this study conducted in 2017 – 2018. These include terpenes, diethyl phthalate, some herbicides, pesticides, and PAHs. Majority of compounds identified are markers of biogenic sources and diesel/gasolines combustion. Levoglucosan, a marker for wood smoke, was detected in samples from Vernal. Pyrene, which is a marker of diesel/gasoline emissions was detected in both Sevier valley and Uintah basin samples. Additionally, diethyl phthalate was also detected in Richfield samples, which is used a plasticizer in small-scale industries. Hourly averaged data collection allows for measurement of diurnal pattern of organic components in PM which enables better source apportionment analysis.
Chapter 4: Sources of Formaldehyde in Bountiful, Utah

4.1 Contributions

The following chapter is presented in its entirety (with minor changes) from the published version of the paper in Atmosphere journal. Nitish Bhardwaj, Ariel Kelsch, Delbert J. Eatough, Ryan Thalman, Nancy Daher, Kerry Kelly, Isabel Cristina Jaramillo, and Jaron C. Hansen. Sources of Formaldehyde in Bountiful, Utah. Atmosphere, 2021, 12(3). I wrote the paper, collected, and analyzed data with the help of Ariel Kelsch. Dr. Jaron C. Hansen reviewed and edited the work.

4.2 Abstract

The U.S Environmental Protection Agency’s National Air Toxics Trends Stations Network has been measuring the concentration of hazardous air pollutants (HAPs) including formaldehyde (HCHO) since 2003. Bountiful, Utah (USA) has served as one of the urban monitoring sites since the network was established. Starting in 2013, the mean concentration of HCHO measured in Bountiful, Utah exceeded the non-cancer risk threshold and the 1 in 1 million cancer risk threshold. In addition, the measured concentrations were more than double those found at surrounding locations in Utah. A Positive Matrix Factorization (PMF) analysis using PMF-EPA v5 was performed using historical data (2004–2017) to better understand the sources of formaldehyde in the region. The historical data set included samples that were collected every sixth day on a 24 h basis. Beginning in February 2019 an eight-week air sampling campaign was initiated to measure formaldehyde on a two-hour averaged basis. In addition, the measurements of O3, NO, NO2, benzene, toluene, ethylbenzene, and xylenes (BTEX) were also collected. Corresponding back-trajectory wind calculations for selected time periods were calculated to aid in the understanding
of the effects of BTEX emission sources and formaldehyde formation. The results indicate that the principal formaldehyde sources are associated with biomass burning and the conversion of biogenic emissions into HCHO. Back-trajectory wind analysis of low (≤3 ppbv) and high (23.8–32.5 ppbv) HCHO cases show a clear dominance of high HCHO originating in trajectories that come from the southwest and pass over the area of the oil refineries and industrial sources in the north Salt Lake City area.

4.3 Introduction

The U.S. Environmental Protection Agency (EPA) National Air Toxics Trends Station (NATTS) Network has been in place since 2003 and was developed to provide long-term monitoring of hazardous air pollutants (HAPs) 73. Since 2003, the Bountiful, Utah monitoring site has served as one location in the NATTS network. The U.S. EPA has set guidelines for a range of HAPs, and most of these pollutants have been detected in low concentrations in Utah. The Utah Division of Air Quality (DAQ) has sponsored or collaborated on several studies to measure the concentrations of various HAPs in Utah, including formaldehyde. Formaldehyde is a ubiquitous trace compound in the atmosphere. Inhalation of formaldehyde can be irritating to the upper respiratory tract and eyes. Animal studies have shown that inhalation can affect the lungs and impair learning and change behavior 74. Formaldehyde has been classified as a probable human carcinogen (Group B1) by the U.S. Environmental Protection Agency (EPA) and carcinogen by the International Agency for Research on Cancer (IARC) 75, 76. Of 187 compounds that have been identified as HAPs, HCHO contributes over half the total cancer risk and 9% of noncancer risk in the United States (U.S.) 73, 77, 78. Over 12,000 people year−1 are estimated to develop cancer based on ambient formaldehyde exposure in the US 79.
Formaldehyde is a volatile organic compound (VOC) that plays a vital role in ozone formation in urban areas. Its photolysis is a source of both OH and HO$_2$ radicals, which both serve to drive tropospheric O$_3$ formation. As a result of formaldehyde’s carcinogenic nature and role in tropospheric ozone formation, a wealth of research has been done to better elucidate sources of formaldehyde $^{80-84}$. HCHO can be directly emitted into the atmosphere from both anthropogenic and biogenic sources. Secondary production of HCHO occurs during the photooxidation of almost every VOC albeit with varying efficiencies and rates. Fuel combustion has been identified as the dominate primary anthropogenic source, but biogenic emissions are the largest primary sources of formaldehyde in the U.S.$^{85}$ Quantifying the division between primary and secondary production of HCHO has been investigated by a variety of researchers using both experimental and modeling methods $^{86-88}$. The results of these studies are wide ranging and vary with the seasons and location. For example, Parrish et al., in an elaborate air sampling campaign focused on the Houston Texas region, found that 92% of HCHO production resulted from the atmospheric oxidation of highly reactive VOCs emitted from the regions’ petrochemical industry $^{87}$. Approximately 4% of the HCHO measured was attributed to primary emissions from these facilities with another ~1% of primary emissions from vehicles. Modeling studies using the Unified Regional Air-quality Modeling System (AURAMS) focused on Canada found that between 69–96% of HCHO during summer months was produced secondarily while 9–67% is produced during winter months from secondary sources. Primary mobile emissions during the summer contributed between 0.8–19% of HCHO while during the winter this ranged between 13–56% $^{88}$. Since 2003, HAPs measurements in Bountiful, Utah have been collected on every sixth day on a 24 h basis. A 2014 study showed that starting in 2013 the mean concentration of HCHO measured in Bountiful, Utah was more than double that found at surrounding locations in Utah $^{89}$. In 2017,
a 6-week-long summer and 7-week-long winter passive sampling study was conducted at 34 sites in the Bountiful area to better understand the sources of formaldehyde in this region. While this study provided useful data, it did not reveal the sources of elevated HCHO in the region\textsuperscript{90}. Starting in February 2019, an eight-week intensive campaign was started to measure HCHO at the Bountiful, Utah site on a two-hour averaged basis. The components expected to be important to understanding the sources of formaldehyde including benzene, ethylbenzene, toluene, and xylenes (BTEX) were also measured. In addition, the concentrations of NO\textsubscript{X} (NO, NO\textsubscript{2}) and O\textsubscript{3}, were also measured on a two-hour averaged basis. Figure 4.1 shows the location of the Bountiful sampling site, the five oil refineries located between 2–5 miles to the south, southwest of the sampling site as well as the I-15 interstate and the location of other DAQ permitted VOC emitting point sources. In 2017, the annual average daily traffic count for vehicles passing through the section of I-15 that runs parallel to the sampling site was 168,000. A total of 84\% of this traffic was cars, 9.3\% was single unit trucks (i.e., vehicle on a single frame including box trucks, camping and recreation vehicles and motor homes) and 6.7\% was combination unit trucks (i.e., truck-tractors units traveling with a trailer or multiple trailers)\textsuperscript{91}. 
Figure 4.1. The locations of various VOC emission sources, oil refineries (red crosses) and industrial (blue circles) with emission strengths (tons year$^{-1}$) located to the SSW of the Bountiful NATTS sampling site (black star). Green color represents mountains with forested areas. Emission strengths are taken from permits issued by the State of Utah Department of Air Quality. Additionally, included is the location of major roadways and forested areas in the area.

This manuscript presents the results of a positive matrix factorization (PMF) analysis done using historical data (2004–2015) to better understand the sources of formaldehyde in the region. The historical data set measurements collected every sixth day on a 24 h basis. The data set collected in 2019 includes two-hour averaged measurements of formaldehyde and some of its possible
precursors. The more rapid data collection method used in the 2019 study allows for additional conclusions to be made about sources of formaldehyde in the Bountiful region. To better understand the possible variety of formaldehyde emissions, corresponding back-trajectory wind calculations for selected time periods are presented to aid in the understanding of the effects BTEX emission sources on the secondary formation of formaldehyde.

4.4 Methods

4.4.1. PMF Historical Data Analysis (2004–2015 Measurements)
A source apportionment analysis, using Positive Matrix Factorization (PMF), was conducted using 24 h HAPs measurements collected at the Bountiful NATTS location for the time period of 2004–2015. This analysis focused on carbonyls, VOCs, PM$_{2.5}$ and NO$_x$. Historical measurements were collected every 6 days for a 24 h period beginning at midnight. Samples were collected using an instrument designed by ERG (ERG(C):AT/C Sampling System, Massachusetts, USA), which is U.S. EPA’s contract laboratory for the NATTS network. To collect VOCs and carbonyls, air samples were drawn through evacuated canisters and 2,4-dinitrophenylhydrazine (DNPH) sampling cartridges preceded by a potassium iodide-coated O$_3$ scrubber. Following collection, canisters were analyzed for VOCs using U.S. EPA method TO-15 while cartridges were analyzed for carbonyls using U.S. EPA method TO-11A. Over the duration of this sampling campaign, three different instruments were used to measure NO$_x$. These were a Thermo Environmental NO$_x$ (model 42, Massachusetts, USA) analyzer, API (model 200 A/E) analyzer and Teledyne-API (model T200UP, California, USA) analyzer. Measurements were collected in accordance with U.S. EPA air monitoring requirements, with sampler inlets being placed at 4–5 m above ground level. To
avoid airflow interference, a minimum of 2 m was kept between samplers in all horizontal
directions. A minimum of 1 m vertical spacing from supporting structures was also maintained.
PM$_{2.5}$ was measured using a MetOne (Oregon, USA) SASS sampler. The MetOne SASS sampler
was fitted with 47 mm Nylon and Teflon filters, with PM$_{2.5}$ mass being determined by
gravimetrically weighing the Teflon filter. Other filter measurements, which are typically used for
PM$_{2.5}$ speciation analysis, were not used in this study.
The compounds used in the PMF analysis were selected based on data completeness and their
uncertainties. Initially, the raw concentrations for formaldehyde for the entire time period, 2004–
2017, were evaluated to detect weekday vs. weekend trends and seasonal differences. Correlation
coefficients between formaldehyde and other species, such as carbonyls and VOCs, were also used
to understand potential relationships. For formaldehyde, concentrations exceeding 3 ppbv were
separated into different ranges (3–10, 10–15 and 15–36 ppbv). This 3 ppbv threshold was selected
because it is the minimal risk level (MRL) set up by the Agency for Toxic Substances and Disease
Registry (ATSDR) for chronic inhalation causing respiratory problems in humans.$^{93}$
The raw measurements were pre-processed prior to PMF analysis to determine which species to
include in the PMF model. This pre-processing step included identifying and addressing missing
data, data below detection limits, and data with poor or unknown data quality.
The concept of Positive Matrix Factorization (PMF) and the algorithm used in the analysis has
been previously described.$^{34}$ With PMF, the results are constrained so that factor contributions
cannot be negative for any species. The PMF program used in this analysis was EPA PMF v5.0.$^{36}$
One of the advantages of PMF is the ability to account for missing and below detection limit data
as well as perform bootstrap and displacement analysis. The uncertainty in each measurement can
be adjusted to account for aberrations in the data set. In this study, precision measurements were
not available for the measured species. Error estimates were made by establishing an estimated limit of quantitation from the variability of measurements for each species during periods of time when low concentrations were present, and the precision of the measurements was assumed to be 10% for all species. Single missing values in the data set were accounted for by taking the geometric mean of the sample preceding and following the missing data point. The uncertainty for each species for each data point was then taken to be the limit of quantitation plus the concentrations of the species times 0.1. The uncertainty of the fitted parameter, formaldehyde, was taken to be four times the measured value.64

The initial PMF analysis identified three species (carbon disulfide, acetonitrile and dichloromethane) that always appeared in a corresponding factor with only that species and no formaldehyde. This indicated that these species were not related to the formaldehyde factors and they were deleted from the subsequent data set. Likewise, while ozone is formed, in part from formaldehyde, inclusion of ozone in the PMF analysis resulted in a factor with no formaldehyde and ozone was dropped from the data set. Presumably this reflects that while formaldehyde contributes to the formation of ozone, other compounds often dominate ozone formation. NO\textsubscript{X} and PM\textsubscript{2.5} were important species because they should be associated with primary formaldehyde sources. Although data were collected through 2017, starting from 23 February 2015 onward, the NO\textsubscript{X} data had long periods with constant values, indicating an issue with its measurement. Therefore, the data set was truncated to only include measurements from 2004–2015 for the PMF analysis data set. Ultimately, the PMF analysis included twenty species and 578 data points (Table 4.1).
Table 4.1. Twenty species included in the PMF analysis. Uncertainty in the data was calculated as the limit of detection for the species plus the concentration of the species times precision, except for formaldehyde where the uncertainty was taken to be four times the concentration. The detection limit is reported after the species in units of ppbv except for PM$_{2.5}$ ($\mu$g m$^{-3}$).

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Propylene</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Acetone</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Tolualdehydes</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Hexanaldehyde</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Toluene</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>(0.1)</td>
</tr>
<tr>
<td>NO$_X$ (10)</td>
<td></td>
</tr>
<tr>
<td>Trans-Crotonaldehyde</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Benzene</td>
<td>(0.1)</td>
</tr>
<tr>
<td>PM$_{2.5}$ (2)</td>
<td></td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>(0.1)</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>(0.1)</td>
</tr>
<tr>
<td>n-Octane</td>
<td>(0.1)</td>
</tr>
<tr>
<td>m/p Xylene</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Butyraldehyde &amp; isobutyraldehyde</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>(0.1)</td>
</tr>
</tbody>
</table>

EPA PMF v5.0 analysis was conducted in the robust mode by incrementally assuming 4–9 factors as solutions. The resulting data were best described with 5 factors. The final EPA PMF v5.0 solution was further analyzed using the “constrained analysis” option of PMF to optimize the description of Factor 4 (attributed to mobile emissions) with respect to the formaldehyde and acetaldehyde. The Q(true) value for the final solution was 6530, compared to the degrees of freedom of 11,560.

Concentration rose plots were also generated to identify the directions in which sources of formaldehyde are likely to be situated. The plots were created by using the 24 h averaged formaldehyde concentrations, PMF source profiles and same day 24 h average wind direction measurements. The wind measurements were collected for both historical measurements period.

4.4.2. High Temporally Resolved Measurements (2019)

Formaldehyde and related gas-phase species were measured all on an hourly average basis at Bountiful Viewmont High School, Utah (EPA AIRS code: 490110004, see Figure 4.1) the same location that the historic measurements were made. Although measured on an hourly averaged basis the data were converted to two-hour averaged data to increase the signal/noise ratio. The following two-hour averaged data were used in the data analysis:

4.4.2.1. Criteria Gas Phase Species Measurement

O₃ and NOₓ (NO, NO₂) were measured using analyzers which included a photometric ozone analyzer (Teledyne-API (California, USA), Model 400 E), and T series NOx analyzer (Model T200U) equipped with a NO₂ photolytic converter, respectively. The trace gas analyzers were calibrated bi-weekly and automated precision, zero and span (PZS) checks were performed automatically to monitor any drifts. The ambient air was drawn into a manifold at ~10 slpm (standard liters per minute) through ~10 m long 1/2” O.D. PFA tubing to a 6-port glass manifold. The trace gas analyzers sub-sampled from this manifold at 600–700 sccm (standard cubic centimeters per minute).

4.4.2.2. HCHO Measurement

A Broadband Cavity Enhanced Absorption Spectrometer (BBCEAS) instrument was used to measure HCHO and NO₂. The BBCEAS leverages long path lengths (1–5 km) by use of multi-reflections in a short instrument footprint (1–2 m) ⁹⁴. A cage system constructed of carbon-fiber tubes was employed to obtain optical alignment, with structural parts being 3-D printed (laser-
sintering or extruded PLA, depending on the function of the part). Initial tests were performed with a base path of 98.5 cm and 5 cm diameter highly reflective mirrors from Advanced Thin Films (ATFilms) centered at 365 nm, with a second cavity centered at 455 nm. Light was produced by LEDEngin (blue) and Thorlabs (M340D3) LEDs centered at 450 and 340 nm, respectively, and collected at the rear of the cavity onto optical fibers. An Andor Shamrock SR-303i spectrograph with gated, intensified CCD was used as a detector in the UV region (310–400 nm range, ~0.5 nm FWHM). In the visible region, an Avantes (Colorado, USA) AvaSpec-2048L was used as a detector.

Nitrogen and helium were supplied to the cavity to characterize the mirror loss as well as air and NO₂ produced from the reaction of NO with O₃ in a calibration source. The mirror reflectivity was calculated as follows:

\[
R(\lambda) = 1 - d_0 \left( \frac{I_{N2}(\lambda)}{I_{He}(\lambda)} \alpha_{Ray}^{N2}(\lambda) - \alpha_{Ray}^{He}(\lambda) \right) \frac{\alpha_{Ray}^{N2}(\lambda) - \alpha_{Ray}^{He}(\lambda)}{1 - I_{N2}(\lambda)/I_{He}(\lambda)}
\]  

(1)

Where \(d_0\) is the cavity length, \(I\) is the intensity (spectrum) in nitrogen or helium, and \(\alpha\) is the Rayleigh scattering.

Reference spectra were acquired every two hours using an overflow valve controlled by a separate Arduino circuit. Spectra were saved every minute, with signal averaging carried out in post-processing to bring noise in the fitting down. The limit of quantification using this method was 1 ppbv. Spectra were simultaneously fitted for HCHO and NO₂.

For ambient sampling, a 2 m long, ¼” Teflon inlet extended out of the sampling trailer with a 2 µm PTFE filter at the end of the inlet. Air was pulled at a total flow of 1.5 slpm at the inlet, with additional air added as purges over the mirrors. The HCHO fitting window was narrowed to 346–357 nm due to drifts in LED/mirror matching over time at the wings of the mirror reflectivity.
4.4.2.3. BTEX Measurement

A Perkin/Elmer (Massachusetts, USA) GC-FID Clarus 580 made hourly averaged measurements of BTEX. Ambient samples were collected through a 2 m long, ¼”Teflon inlet extended out of the trailer with a 2 µm PTFE filter affixed to the inlet. Air flowing at 200 sccm was pulled through a preconcentrator kept at −30 °C for 45 min. After the collection period, the preconcentrated sample is flash heated and pushed using ultrapure He (99.999%) through an open tubular column for separation and finally detection by flame ionization detection. Built into the sampling protocol was injection of a standard gas mixture (AirGas) containing dichloromethane, benzene, toluene, ethylbenzene and xylenes once a day. Calibration curves affirmed linearity of the instrument response between 0.1 and 20 ppb for these compounds.

4.5 Results and Discussion

The results from the historical data are presented first followed by the results from the high temporally resolved measurements and finally the results from these two studies are compared to one another.


Analysis of the historical data shows that beginning in 2013, the Bountiful station began to experience elevated levels of formaldehyde during the winter (Figure 4.2). Starting winter 2013, high concentrations of formaldehyde were seen throughout the year in all seasons, whereas in Fall 2011, formaldehyde concentrations were not that high as compared to other seasons (winter, spring and summer 2011). Consequently, the year 2013 was used as the starting point for elevated formaldehyde concentrations.
Figure 4.2. Formaldehyde seasonal variations. Winter: December, January and February; Spring: March, April and May; Summer: June, July and August and Fall: September October and November.

Table 4.2 shows the concentration of HCHO sorted by day of the week. This was done in an attempt to detect weekday vs. weekend trends. The formaldehyde concentrations showed no trends between days of the week.

Table 4.2. Proportion of formaldehyde concentration ranges separated by day of week and concentration range. The bottom row in columns 2, 4, 6, and 8 are the sum of the number of days in the analyzed data set that HCHO ranged between <3ppbv, 3–10 ppbv, 10–15 ppbv and 15–36 ppbv. The bottom row in columns 3,5,7 and 9 are the sum of the percentages of time that the concentration ranges occurred between Monday and Sunday.
<table>
<thead>
<tr>
<th>Day</th>
<th>&lt;3 (ppbv)</th>
<th>%</th>
<th>3 – 10 (ppbv)</th>
<th>%</th>
<th>10 – 15 (ppbv)</th>
<th>%</th>
<th>15 – 36 (ppbv)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monday</td>
<td>63</td>
<td>14</td>
<td>48</td>
<td>13</td>
<td>3</td>
<td>10</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>Tuesday</td>
<td>57</td>
<td>13</td>
<td>59</td>
<td>16</td>
<td>3</td>
<td>10</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>Wednesday</td>
<td>64</td>
<td>14</td>
<td>55</td>
<td>15</td>
<td>4</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Thursday</td>
<td>65</td>
<td>15</td>
<td>52</td>
<td>14</td>
<td>5</td>
<td>17</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>Friday</td>
<td>63</td>
<td>14</td>
<td>53</td>
<td>14</td>
<td>5</td>
<td>17</td>
<td>2</td>
<td>33</td>
</tr>
<tr>
<td>Saturday</td>
<td>65</td>
<td>15</td>
<td>54</td>
<td>15</td>
<td>5</td>
<td>17</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>Sunday</td>
<td>65</td>
<td>15</td>
<td>48</td>
<td>13</td>
<td>4</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Number of</td>
<td>442</td>
<td>100</td>
<td>369</td>
<td>100</td>
<td>29</td>
<td>100</td>
<td>6</td>
<td>100</td>
</tr>
</tbody>
</table>

A calculation of correlation coefficients of formaldehyde with other species revealed stronger correlations for formaldehyde with other aldehydes such as: acetaldehyde, butyraldehyde, propionaldehyde, valeraldehyde, trans-crotonaldehyde, benzaldehyde and tolualdehydes ($R^2$ values ranging from 0.9–0.98), indicating their likely shared origin.

4.5.2. PMF Historical Data Analysis (2004–2015 Data)

The most reasonable and physically interpretable solution was achieved for 5 factors. The profiles for the five factors (bars, where Conc refers to fraction of each species in a factor in a log plot) resolved from the PMF model and contribution percentages (dots) from each source factor are shown in Figure 4.3a. Time series factor contributions are presented in Figure 4.3b.
The factors were identified as:

- In Factor 1, the dominant species are formaldehyde, acetaldehyde, butyraldehyde, propionaldehyde and valeraldehyde; these species are related to biomass burning emissions. Biomass burning during the winter may include residential woodburning. Factor 1 was more predominant during the wintertime for most years excluding 2005, 2006 and 2007 when the contributions from this factor were higher during summer. The higher contributions of this factor during these years corresponded to state and regional fires and high PM$_{2.5}$ levels. This factor contains 45% of the formaldehyde.

- Factor 2 is dominated by high concentrations of BTEX, with 40 to 60% of these compounds being present in this factor. These emissions are consistent with expected emissions from the oil refinery complex to the SSW of the sampling site. This factor contains 5.2% of the formaldehyde.

- Factor 3 is attributed to photochemically produced formaldehyde from biogenic emissions and consists mainly of aldehydes, dominated by acetaldehyde, propionaldehyde, acetone and trans-crotonaldehyde, with 85% of the latter species in this factor. Crotonaldehyde is a product of biogenic emissions, and it is not related to industrial emissions. As expected, contributions were more predominant during summertime. This factor contains 34% of the formaldehyde.

- Factor 4 contains 100% of the PM$_{2.5}$ and 34% of the NO$_X$, with the contributions from all other species varying from 4 to 15%. We attribute this factor to mobile emissions. It contains 7.1% of the formaldehyde.
Factor 5, similar to Factor 2 is dominated by high concentrations of BTEX, containing 22 to 65% of these compounds. It also contains 62% of the NO\textsubscript{X}. We attribute this factor to industrial emissions, possibly related to refinery emissions. This factor contains 8.4% of the formaldehyde. The principal difference between Factor 5 and Factor 2 is that Factor 5 contains 62% of the NO\textsubscript{X} while Factor 2 contains no NO\textsubscript{X}. Factor 5 is also much higher in propylene and acetylene. Both factors are probably associated with refinery emissions but reflect contribution from different processes at the refinery. They have been given different names for clarity.
Constrained Factor Profiles

Legend:
- % of Species
- Conc. of Species

(a)
Figure 4.3. (a) PMF factor profile graph shows the concentration in ppbv (logarithmic scale) of each species apportioned to the factor (bars) and the percent of each species apportioned to the factor as a red box (red box); (b) Time series of factor contributions showing the start of each year.
Figure 4.4 illustrates the PMF estimated source contributions during 2004–2015.

![Pie chart showing source contributions]

**Figure 4.4.** PMF estimated source contributions during 2004–2015. Values outside the pie chart represent the average absolute concentration (ppbv) of HCHO attributed to each factor.

**4.5.3. Concentration Rose Plots and Wind Direction of Historical Data (2004–2015 Data)**

To provide more insight on formaldehyde production sources, a concentration rose plot was generated for Factor 2 (Refinery Related) and Factor 5 (Industrial Emissions). Rose plots were generated by binning the measured concentrations of HCHO attributed to these two factors between 0–26 ppbv for the Refinery related factor and 0–8 ppbv for the Industrial Emission related factor. After binning the HCHO values the corresponding wind direction was plotted to generate Figure 4.5. Figure 4.5 shows that both of these factors are primarily present when wind was blowing from the SSW direction. As can be seen in Figure 4.1, five refineries are located to the
SSW of the Bountiful region, and these refineries process a total of 200.5K barrels day$^{-1}$. The wind rose plots coupled with the results of the PMF analysis suggest that both of these factors are associated with refinery and industrial operations. Together they are responsible for 15.7% of the formaldehyde measured in Bountiful. The results of the PMF analysis of the long-term formaldehyde data set are consistent with that observation and suggests that both Factors 2 and 5 are associated with Refinery processes. Figure 4.1 shows the amount of VOCs in tons year$^{-1}$ (tpy) emitted by each refinery and the other industrial permitted sources located to the SSW of the sampling site. Industrial emissions are all within the 0–70 tpy emission range while the refineries are an order of magnitude larger.

![Figure 4.5.](image)

**Figure 4.5.** (a). Concentration rose plot for Factor 2 (Refinery Related) and (b) concentration rose plots for Factor 5 (Industrial Emissions). Values in the legend are in units of ppbv.
4.5.4. High Temporally Resolved Measurements Results (2019)

The analysis presented here is based upon two-hour averaged measurements from the GC-FID and BBCEAS. Figure 4.6 shows two-hour averaged concentrations of BTEX measured between 23 February and 17 April 2019 at the Bountiful, UT site.

![Graphs of BTEX concentrations]

**Figure 4.6.** Two-hour average data for BTEX. Xylene represents a sum of o-,m- and p- xylenes. The hash marks under the x-axis indicates weekends.

The most notable feature of the data in Figure 4.6 is the consistency of the time patterns among the BTEX gases, suggesting they are all dominated by a single source, possibly the refineries to the south and southwest of the sampling site. Additionally, notable is the increase in BTEX concentrations starting around April 3rd and continuing through April 17th. Comparison of the
data shown in Figure 4.6 with the rose plots shown in Figure 4.5 provides supporting evidence for the hypothesis that these species are emitted from sources located to the SSW of the sampling site but unfortunately, the reason for the sudden increase in BTEX beginning on April 3rd is uncertain. An evaluation of the meteorology between 3 April and 17 April shows no unusual wind patterns compared to earlier time periods. The average wind speed from mid-March through 2 April was 4.9 mph whereas it was 4.3 mph between 3 April and 17 April. This suggests there was no major change in the wind speeds during and before the sudden increase in BTEX concentrations. Additionally, analysis of the wind direction shows that predominately the wind blowing from the SSW direction between 23 March and 17 April. Figure 4.7 shows two-hour averaged concentrations of formaldehyde over the duration of the study.

Figure 4.7. (a) shows two-hour average data for formaldehyde from 17th of March to 13th of April (b) 14th of April to 12th of May and (c) 12th of May till 16th of June. The hash marks under the x-axis indicates weekends.
The oxides of nitrogen play a major role in the mechanism for the production of O₃ and HCHO, which is explained in Section 4.5.6. Two-hour averaged concentrations of NOₓ, NO₂ and O₃ are shown in Figure 4.8.

![Figure 4.8](image)

**Figure 4.8.** Two-hour average data for NOₓ, NO₂, and O₃. The hash marks under the x-axis indicates weekends.

### 4.5.5. Relationship Between Formaldehyde and BTEX

Formaldehyde has both primary and secondary sources in the atmosphere. Secondary gas phase HCHO is formed from free radical reactions with a wide variety of VOCs. The most rapid secondary formation is expected to be formed from the photooxidation of ethene, propene and larger terminal alkenes, but HCHO is also formed, albeit more slowly, from the oxidation of alkanes and aromatic compounds.

PMF analysis of the historical data shows that a combination of refinery and industrial emissions account for 13.8% of the HCHO concentrations measured in the Bountiful region (Figure 5). Since
HCHO production from the photooxidation of BTEX is highly variable and depends on the solar flux, ambient temperature, concentration of BTEX and OH radical and meteorological conditions such as wind speed and wind direction, we do not expect the appearance of a formaldehyde peak to routinely follow the appearance of a day-time benzene peak.

A box model using the Master Chemical Mechanism v3.2 and the AtChem online portal (version 1), an open-source box model for the Master Chemical Mechanism was used to assess the lifetime of fossil fuel related emissions (benzene, toluene, ethylbenzene, xylenes, ethene, propene) with respect to the time scale of transport from the refineries to the measurement site. The model was initiated with $2 \times 10^{10}$ molecules cm$^{-3}$ (1ppb) of NO. The hydroxyl radical concentration was held constant at $5 \times 10^6$ molecules cm$^{-3}$ and the model was run for 8-h to roughly simulate the evolution of a plume reacting with OH. Photolysis and other loss processes were not considered. Supplemental Figure A1.2(a) shows that benzene was the slowest to react, as expected from its reaction rate constants, and the results showed that it can serve as a tracer for the refineries if present in the emission plume. All the other compounds modeled reacted faster, with ethene and propene degrading the most rapidly. Supplemental Figure A1.2(b), shows that HCHO is formed as a first-generation oxidation product from both ethene and propene in contrast to the aromatic compounds which do not generate HCHO until the second or more-generation products. In the time series comparing benzene and HCHO (Figure 4.9), when benzene and HCHO are observed together, HCHO is predominantly not from the oxidation of benzene, but from co-emitted species which likely correlate less because a significant portion of them will have reacted away depending on the transport time. Likewise, early morning peaks in benzene would not be expected to correlate with HCHO since OH production will not have been initiated yet and consequently HCHO will not have been produced. Additionally, the plume composition may change to contain less benzene
but even a different mixture of hydrocarbons will still produce HCHO that peaks in the middle of the day along with $O_3$ concentrations. As BTEX and HCHO do not correlate well in time, the Bountiful region does not appear to be primarily impacted from the photooxidation of BTEX to form HCHO but that the formaldehyde observed in this region is most likely from the photooxidation of refinery emitted gases with faster photooxidation reaction times like ethene and propene. Unfortunately, neither ethene nor propene were measured in this study.

![Comparison of the concentrations of ozone and formaldehyde for months of April, May, and June (2019).](image)

**Figure 4.9.** Comparison of the concentrations of ozone and formaldehyde for months of April, May, and June (2019).

### 4.5.6. Relationship Between Formaldehyde and $O_3$

As detailed previously, the formation of HCHO in the atmosphere from the photooxidation of VOCs is complex and dependent on the VOC of interest. Previous work has shown a strong correlation between the emissions from refineries and $O_3$ and HCHO production in air masses
located downwind. The mechanism that is primarily responsible for the production of tropospheric ozone can share some of the same elementary reactions that produce HCHO. As such, if secondary formation of HCHO involves some of the same reactions producing O₃ there should be a correlation observed between these two species. Reactions 1–5 define the well-established mechanism for production of tropospheric O₃ from any hydrocarbon (RH) in the presence of NOₓ.

\[
\text{RH} + \cdot \text{OH} \rightarrow \text{R} \cdot + \text{H}_2\text{O} \tag{2}
\]

\[
\text{R} \cdot + \text{O}_2 \rightarrow \text{RO}_2 \tag{3}
\]

\[
\text{RO}_2 \cdot + \text{NO} \rightarrow \text{NO}_2 + \text{RO} \cdot \tag{4}
\]

\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \tag{5}
\]

\[
\text{O} + \text{O}_2 \rightarrow \text{O}_3 \tag{6}
\]

Reactions 6–9 describe one mechanism for production of HCHO from the photooxidation of C₂H₂ (ethylene), frequently the highest concentration VOC emitted by a refinery, and shares some of the same elementary reactions described by the mechanism that produces tropospheric O₃, reactions 1–5.

\[
\text{C}_2\text{H}_2 \ (\text{RH}) + \cdot \text{OH} \rightarrow \text{HOCH}_2\text{CH}_2 \ (\text{R} \cdot) \tag{7}
\]

\[
\text{HOCH}_2\text{CH}_2 \ (\text{R} \cdot) + \text{O}_2 \rightarrow \text{HOCH}_2\text{HCHO}_2 \ (\text{RO}_2 \cdot) \tag{8}
\]

\[
\text{HOCH}_2\text{HCHO}_2 \ (\text{RO}_2 \cdot) + \text{NO} \rightarrow \text{HOCH}_2\text{HCHO} \ (\text{RO} \cdot) + \text{NO}_2 \tag{9}
\]

\[
\text{HOCH}_2\text{HCHO} \ (\text{RO} \cdot) + \text{O}_2 \rightarrow \text{HO}_2 \cdot + 2 \text{HCHO} \tag{10}
\]

Elementary reactions 2, 3, 4, and 7, 8 and 9 are the same in the two mechanisms. If the hydrocarbon that is being photooxidized is something other than C₂H₂, for example BTEX, the mechanism that describes the oxidation has several additional reactions that delay the formation of HCHO. However, because of the relative high concentration of hydrocarbons that are typically emitted by
refineries and react in a similar fashion to produce tropospheric ozone it is expected that a
correlation between O₃ and HCHO may be observed. Figure 4.9 shows the relationship between
measured concentrations of O₃ and HCHO at the Bountiful sampling site for the months of April,
May and June (2019).

It has been observed that NO can play an important role in the mechanism for the production of
O₃ and HCHO (see reactions (3) and (8)), but HCHO can also be formed in the absence of NO.
When NO concentrations are low, peroxy radicals (RO₂·) can react with other RO₂· radicals to
produce alkoxy radicals (RO·), a product similar to what are produced by the reaction of RO₂· +
NO (reaction 8). This leads to similar product branching ratios and products formed as under high
NOₓ conditions, but without O₃ formation because the needed NO is missing from the mechanism
defined by reactions 1–5, specifically reaction 3. While the HCHO formed might be reduced
because other pathways (e.g., reaction of RO₂· with RO·) may start to contribute, there will still
be HCHO formed while O₃ formation catalyzed by NO will be shut off.

The data plotted in Figure 4.10 were constrained by plotting O₃ and HCHO concentrations when
the wind was blowing between 190–220° and between the hours of 8 am–6 pm (A wind direction
of between 190 and 220° encompasses the range of oil refineries and other industrial sources
located to the SSW of the Bountiful air sampling site, Figure 4.1). Figure 4.10 suggests a
correlation between O₃ and HCHO during the daytime when the wind is blowing from the SSW.

Under conditions in which NOₓ is not limited, the relationship between O₃ and HCHO will be
linear but some scatter is expected in this analysis due to conditions in which NOₓ is limited. Under
these conditions, HCHO concentrations can be higher than the O₃ concentration predicted by a
linear relationship between these two molecules. The NOₓ concentrations varied from 2–67 ppb
during 18–21 April, 1–44 ppb during 10–16 May and 1–35 ppb during 4–14 June. The varying
NO$_x$ concentrations observed during these periods supports the hypothesis that the scatter observed in Figure 4.10 can be attributed to the nonlinear relationship between O$_3$ and HCHO. The non-zero intercept in Figure 4.10 is attributed to background levels of both HCHO and O$_3$ at the sampling site.

**Figure 4.10.** Comparison of ozone and formaldehyde concentrations between the indicated wind direction and time period for the months of April, May and June (2019).

For comparison purposes, Figure 4.11 shows a plot of O$_3$ verses HCHO during daytime when the wind is blowing from between 260–290° (north, northwest). There are no known large points sources for VOC’s or O$_3$ in this direction.
Figure 4.11. Comparison of ozone and formaldehyde concentrations between the indicated wind direction and time period for the months of April, May and June (2019).

When the wind is blowing from the north/northwest towards the sampling site the correlation between $O_3$ and HCHO is not as pronounced as when the wind is blowing from the south, southwest. The absence of a strong relationship between $O_3$ and HCHO in Figure 4.11 is attributed to the absence of VOCs in the air mass that are needed to initiate formation of these two pollutants. By comparison, the data shown in Figure 4.11 are collected when the wind is blowing from the direction of the refineries and providing a higher concentration of VOCs that are used to initiate $O_3$ and HCHO formation.

Examination of Figure 4.12 (blue trace) shows that frequently the peak in HCHO matches the peak in the actinic flux. The peak in HCHO is often observed between 12:00–14:00 h when
photochemical production of OH radical, driving the photooxidation of VOCs and production of HCHO, is at a maximum.

Figure 4.12. Comparison of O3 and HCHO concentrations between March 14 and June 14. The hour of the day in which O3 and HCHO peak are labeled for some of the observed peaks. The hash marks under the x-axis indicates weekends.

Since the formation of formaldehyde is associated with the presence of O3, a secondarily formed pollutant, it suggests that some of the formaldehyde, consistent with the results of the PMF analysis of historical data, is being photochemically produced in the atmosphere from point sources located to the SSW of the sampling site, mostly likely the refineries and industrial sources.

4.5.7. Backwind Trajectory Analysis of High-Resolution Measurements

To identify emission source locations associated with formaldehyde formation at the Bountiful station during April-May 2019, 24 h backward wind trajectories were calculated using the National Oceanic and Atmospheric Administration (NOAA) HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (version 4). For all days except for April 8 and 19, meteorological input data such as wind speed, wind direction was acquired from the High-Resolution Rapid Refresh (HRRR) model with temporal and horizontal grid resolutions of 1 h and 3 km, respectively. Data for April 8 and 19 were acquired from the North America Model (NAM) with a horizontal grid resolution of 12 km since HRRR data were incomplete for these days. Single-
particle backward wind trajectories were calculated for a 24 h duration starting at the Bountiful monitoring station. Given that the atmosphere is well mixed during the study time period, a starting height of half the mixing height (above ground level) was considered. For comparison purposes, trajectories that correspond to select high and low formaldehyde concentration events observed during the 2019 field campaign were calculated. Trajectories start times were selected to match times when high (23.8–32.5 ppbv) and low (≤3 ppbv) formaldehyde concentrations were measured by the BBCEAS. A total of 22 trajectories, equally split between the high and low formaldehyde concentration events, were computed.

Results (Figure 4.13 (a,b)) indicate that trajectories associated with low formaldehyde concentrations had a mixed origin, with no predominant source direction. On the other hand, trajectories associated with peak formaldehyde measurements had a primarily southwesterly component. Given that most refineries and industrial sources in the sampling area fall within the path of the derived back trajectories for the high concentration events, it is likely that precursor emissions from the oil refineries and industrial sources contribute to formaldehyde formation at Bountiful.
Figure 4.13. (a–b) 24 h backwind trajectories at Bountiful monitoring station during (a) high and (b) low formaldehyde concentration events. Red circles represent hourly positions for each trajectory. Green color represents mountains with forested areas.
4.6. Conclusions

Long-term and short-term, high temporal resolution measurements were evaluated to identify the probable source of elevated formaldehyde concentrations in Bountiful, UT. The historical analysis (2003–2017) were analyzed by EPAPMF v5.0 to identify probable sources of formaldehyde. The results indicate that the principal sources are associated with biomass burning and the conversion of biogenic emissions. These two sources accounted for 79% of the formaldehyde. Anthropogenic sources which contributed the other 21% were associated with mobile emissions, and emissions associated with oil refineries and other industrial emissions. Concentration rose plots of these two factors indicated that both are probably associated with oil refinery processes since the emissions from the refineries are an order of magnitude larger than the combination of emissions from other industrial sources. The diel pattern observed for the highly resolved formaldehyde measurements (2019) suggests that formaldehyde concentration is coupled to the actinic flux and that its formation through the photooxidation of VOCs plays an important role. The relationship between O₃ and HCHO supports the importance of formaldehyde being formed as a secondary pollutant. Since the conversion of species like BTEX into HCHO is highly variable and has very slow oxidation rate, the appearance of day-time benzene peak was inconsistent with appearance of formaldehyde peak but this helped in understanding the chemistry of atmospheric oxidation processes in the atmosphere. Back-trajectory wind analysis of low (≤ 3 ppbv) and high (23.8–32.5 ppbv) HCHO cases show a clear dominance of high HCHO originating in trajectories that come from the southwest and pass over the area of the oil refineries in the north Salt Lake City area.
Chapter 5: Absorption Cross-Sections for the 5th and 6th Vibrational Overtones in a Series of Short Chained Alcohols using Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS)

5.1 Contributions

The following chapter is presented in its entirety (with minor changes) from the pre-submitted version of the paper. Nitish Bhardwaj, Callum E. Flowerday, Ryan Thalman, Matthew C. Asplund, Eric T. Sevy and Jaron C. Hansen. Absorption Cross-Sections for the 5th and 6th Vibrational Overtones in a Series of Short Chained Alcohols using Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS). I wrote the paper, collected, and analyzed data. Callum E. Flowerday helped with the collection and analysis of data. Dr. Jaron C. Hansen reviewed and edited the work.

5.2 Abstract

Absorption cross-sections for the 5th (6 ← 0) and 6th (7 ← 0) OH overtones for gas-phase methanol, ethanol, and isopropanol were measured using a slow flow cell and Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS). Measurements were performed in two wavelength regions, 430-490 nm, and 483-549 nm, using two different instruments. The experimental results are consistent with previous computational predictions of the excitation energies for these transitions. Treating the OH stretch as a local mode allowed for calculation of the anharmonicity and bond dissociation energy for each alcohol studied. The anharmonicity constant was measured to be 86 cm⁻¹, 86.9 cm⁻¹, and 86.74 cm⁻¹ for methanol, ethanol, and isopropanol, respectively. The OH bond dissociation energy was measured to be 517.1 kJ/mol (methanol), 508.5 kJ/mol (ethanol), and 501.8 kJ/mol (isopropanol) using a Birge-Sponer plot. The spectroscopically measured values are compared to thermodynamically measured OH bond
dissociation energies. The observed differences in previous measurements of the bond dissociation energies compared to the values reported herein can be explained due to the difference between vertical dissociation energies and dissociation energies. If the OH overtone stretching mode is excited in methanol to either the 5th or 6th overtone, the bimolecular reaction between methanol and O₂ becomes energetically feasible and could contribute to formation of methoxy and HO₂ radical.

**Keywords:** absorption cross-section, vibrational overtones, alcohols, Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS)

### 5.3 Introduction

The study and analysis of vibrational overtones in molecules containing an X-H (where X = O, N, C) bond has attracted the attention of both experimental and computational researchers.¹⁰¹-¹⁰⁴ Vibrational overtone transitions have non-zero intensities because of the anharmonicity factor, which arises due to the anharmonicity of bond potentials and non-linearity of dipole functions. The energy absorption primarily occurs in the vibrational overtone levels of X-H stretching vibrations in the near-IR and visible spectral region.¹⁰² These spectra are often well characterized by the local mode (LM) model, which describes the X-H bond as a set of loosely coupled anharmonic oscillators in a highly vibrationally excited molecule.¹⁰²,¹⁰⁵ These transitions have 4-6 orders of magnitude less intensity than electronic transitions. Although these vibrational transitions are weak and less intense than electronic transitions in the same spectral region, these transitions can still be observed for molecules containing X-H bonds. The X-H vibrational stretching overtone spectra
provide information about the influence of different local environments between bonds and help in understanding the factors affecting the strength of individual chemical bonds.

The study of O-H vibrational overtone transitions is crucial to understanding some photolytic reactions occurring in the atmosphere.\textsuperscript{103} O-H stretching overtone transitions are sharper, narrower, and have well-defined rotational structures compared to most C-H and N-H bonds for similar-sized hydrocarbons.\textsuperscript{102} The relatively narrow bandwidth of O-H stretching overtone transitions explains the weaker coupling of O-H bond vibrations to other vibrational modes in alcohols. Several studies that have analyzed and reported the intensities of different vibrational overtone transitions of various gas-phase atmospheric species commonly found in the atmosphere.\textsuperscript{106-108} The hydroxyl (OH) radical is one of the most predominant species present in the atmosphere and drives the photochemical oxidation of volatile organic compounds (VOCs) present in the atmosphere to form pollutants such as formaldehyde (HCHO).\textsuperscript{109} It has been observed that overtones can play a substantial role in the photochemistry responsible for OH radical production in the atmosphere.\textsuperscript{103,110,111}

Fang et al.\textsuperscript{102} successfully studied the conformers of gaseous ethanol by utilizing its gas-phase vibrational overtone spectra. Philips et al.\textsuperscript{101} successfully measured the 2\textsuperscript{nd} and 3\textsuperscript{rd} overtone intensities for gas-phase ethanol and isopropanol and up to the 4\textsuperscript{th} overtone in methanol. This work was further extended by Lange et al.\textsuperscript{104}, who measured and reported the integrated absorption cross-sections of O-H stretching bands for six alcohols, including methanol, ethanol, 1-propanol, 2-propanol, tert-butyl alcohol, trifluoroethanol, and two acids, namely acetic acid and nitric acid. Recently, Wallberg et al.\textsuperscript{112} reported the absolute intensities of the fundamental and first overtone transition for various alcohols, including methanol, ethanol, 2-propanol, 1-propanol, and tert-butanol.
The measurement of vibrational overtones of alcohols allows for measurement of the vertical bond dissociation energy of the O-H bond by use of the Birge-Sponer plot. This analysis assumes that the sum of successive vibrational energy separations $\Delta G_{v+\frac{1}{2}}$ from the zero-point level to the dissociation limit is the bond dissociation energy (BDE), $D_0$. The area under the plot of $\Delta G_{v+\frac{1}{2}}$, verses $v$ is equal to the sum and therefore $D_0$. When only the $\alpha_0$ anharmonicity constant is considered, successive terms decrease linearly. Due to the experimental difficulties in measuring higher energy terms (e.g., overtones), typically this plot is linearly extrapolated to higher energy terms. Usually, actual Birge-Sponer plots differ from linear plots so the value of $D_0$ is usually overestimated using this analysis method. As a result of possible combination bands in O-H overtones of alcohols it has been speculated that analysis of the BDE measured using this method may suffer from non-linearity and therefore yield overestimate of the BDE.

Historically, the BDEs have been measured by use of three experimental methods: radical kinetics, gas-phase acidity cycles and photoionization mass spectrometry.113 Engelking et al.114 utilized photoelectron spectrometry to investigate the methoxy radical to determine its electron affinity and the vibrational frequencies produced in the detachment process. Additionally, Meot-Ner et al.115 measured the gas-phase acidity difference between water and methanol using pulsed high-pressure mass spectrometry and defined the acidity of methanol at 300 K. Based on the electron affinity/acidity measurements done by Engelking et al.114 and Meot-Ner et al.115, Berkowitz et al.113 reported the OH BDE in methanol to be 104.2 ± 0.9 kcal/mol. Recently, Rayne et al.116 conducted Gaussian calculations and compared their calculated BDE of methanol (104.4 kcal/mole) with that of recommended experimental value (104.2 ± 0.9 kcal/mol) at 298 K.113, 117 Moreover, Ruscic118 published Active Thermochemical Tables (ATcT) thermochemistry for BDEs of methanol, methane and ethane and reported the OH bond dissociation energy in methanol at
298.15 K to be 440.24 kJ/mol or 105.22 kcal/mol. These BDEs values reported for methane, ethane and methanol systems were not measured values but obtained by analyzing and solving a large thermochemical network. These values are claimed to be the most accurate thermochemical values currently available. It is important to note that the BDE values reported in the AtcT are thermochemically measured values and as such are related to values measured using the Birge-Sponer extrapolation plot but are reporting a different value. The vertical bond dissociation energy, $D_o$ measured by use of the Birge-Sponer analysis for the O-H bond assumes that the potential energy surface adheres to the Born-Oppenheimer approximation in that the motion of the atomic nuclei and electrons are separated from one another and that the molecular fragments after breaking the O-H bond do not have a chance to relax and move to a lower energy state as is possible when measuring dissociation energies using thermodynamic techniques.

Absorption spectroscopy has become a widely used approach for the in-situ detection of gas-phase species concentration. Quantification of their concentrations using absorption spectroscopy relies on knowledge of their absorption cross-sections. Absorption spectroscopy has several advantages over other detection techniques that make it important in the detection of gas-phase species. These include in situ real-time measurement and high spatial and temporal resolution. Additionally, if absorption cross-sections are known, standards are not necessary to measure concentrations. Different absorption spectroscopy techniques such as cavity ring-down spectroscopy (CRDS), cavity-enhanced absorption spectroscopy (CEAS), and incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) have been employed to measure trace gas concentrations and absorption cross-sections over different spectral ranges. Broadband cavity-enhanced absorption spectroscopy, first reported in 2003 by Fiedler et al., has emerged as one of the highly sensitive methods for detecting gases. Fiedler et al. used an
incoherent light source (i.e., a short xenon arc lamp) to measure the concentration of molecular oxygen and gas-phase azulene\textsuperscript{27} under atmospheric conditions. Since then, IBBCEAS has been used in the studies for the detection of different gases and their wavelength-dependent cross-sections in the atmosphere.\textsuperscript{25, 94, 95, 119, 120} In IBBCEAS, a broadband incoherent light source is usually used and coupled into a stable optical cavity formed by two highly reflective mirrors. A small fraction of light that leaks from the back end of the optical cavity is then dispersed by a grating and finally detected with the help of a charged-couple device (CCD) or a photo-diode array. In this work, the absorption cross-sections for the 5\textsuperscript{th} and 6\textsuperscript{th} overtones transitions for gas-phase methanol, ethanol, and isopropanol were measured using IBBCEAS. IBBCEAS offers several advantages in terms of selectivity, sensitivity, compactness, mechanical stability, and short integrated time measurements compared to other absorption techniques. Additionally, IBBCEAS has a wide range of practical applications, including (i) simple experimental setup; (ii) does not require any sophisticated and complicated electronic accessories such as fast optical switches, feed-back gates, or loops; (iii) unlike in CEAS, no mode-hop-free scanning is required (iv) unlike diode-lasers which are unable to access short wavelength region, IBBCEAS has the ability to cover a wide range of the electromagnetic spectrum ranging from the short wavelength region of the UV (190 nm) to the infrared region (10 µm); (v) due to the broadband nature of the IBBCEAS technique, many gas-phase species can be detected at the same time.
5.4 Methods

5.4.1 Description of the IBBCEAS instrument setup

Figure 5.1. Schematic of the IBBCEAS experimental setup.

Figure 5.1 shows the experimental setup. The custom-designed and built IBBCEAS instrument consists of a LED light source, optical filters, a collimating lens, a closed cavity made of highly reflective mirrors, and a grating spectrometer. This study used two BBCEAS instruments with different path lengths and LED light sources. Measurement of the 6th overtone (7 ← 0) absorption cross-section for methanol, ethanol, and isopropanol was performed using a blue LED light source coupled into a 98.5 cm long cavity, whereas 5th overtone (6 ← 0) measurements were carried out using a 96.5 cm long optical cavity coupled to a green LED light source. Each optical cavity was constructed slightly differently. The 430-490 nm cavity was a 2” OD PVC tube with nylon mirror mounts. The 483-549 nm cavity was made of a 1” diameter PFA tube with stainless steel mirror mounts. Both had ¼” OD input and output ports for gases to be introduced into and out of the
cavity. A LED light source was used to produce broadband radiation in this system. The light was produced by either blue (LEDEngin) or green LEDs (Thorlabs) centered at 450 and 530 nm, respectively. This light is collimated and introduced into the cavity using a focusing lens. The collimation lenses were f/1 and 2'' diameter (fresnel) in the 430-490 nm cavity and 1” diameter the 483-549 nm cavity. The optical cavity consisted of two 5 cm diameter highly reflective mirrors (reflectivity, R > 99.9%) (Advanced Thin Films (ATFilms)). The light that leaks through the far end of the cavity was collected and focused onto an optical fiber (1000 µm diameter, 2 meter, low-OH, Thorlabs). The absorption cross-sections of these alcohols are measured at a temperature of 25°C and a pressure of 654 torr. A cage system constructed of carbon-fiber tubes was employed to obtain optical alignment, with structural parts being 3-D printed (laser-sintering or extruded PLA, depending on the function of the part). The carbon-fiber tubes for smaller triangle cavity (96.5 cm) were 3/8” diameter and for the larger cavity (98.5 cm), 0.5” diameter carbon-fiber tubes were used. The lengths of carbon-fiber tubes were about 120 cm for both the optical cavities. Spectra were acquired using toroidal imaging optics using a 303 mm focal length Czerny-Turner spectrometer (Andor Shamrock SR-303iA). Attached to the spectrograph is a charged coupled device cooled to -20°C (Andor iDus DU440A-bv). The spectrometer was set at the grating groove density of 1200 l/mm (300 nm blaze) to the spectral range of interest. Wavelength calibration was done using a mercury (Hg) pen lamp with a slit width of 50 µm. With these settings, the collected spectra had a resolution of 1 nm.

5.4.2 Workflow of the BBCEAS instrument

The IBBCEAS setup, including LED, spectrometer, and all other components, were allowed to equilibrate for 20 minutes before data collection. The thermal equilibration allowed for temperature stabilization of the IBBCEAS instrument to avoid any fluctuations during spectra
Background spectra were acquired at the beginning, middle, and end of each run to characterize the noise in the CCD detector. This was necessary as the CCD showed non-zero signals even when there was no light impinging on it. A typical trial involved collecting the emission spectra with He (99.99%, AirGas), N₂ (99.99%, AirGas), and then either methanol, ethanol, or isopropyl alcohol flowing through the cell. Alcohols were purchased from Sigma-Aldrich and used without further purification. Their stated purities are methanol (HPLC grade, ≥99.9%), ethanol (anhydrous, gradient grade for liquid chromatography), and isopropanol (HPLC grade, 99.9%). Alcohols were introduced into the cell by use of a stainless-steel 1/4" T fitting (Swagelok) packed loosely with glass wool and then wrapped with heating tape. A 50 mL gastight syringe (Hamilton 85020) mounted on an automated syringe pump (KD Scientific KDS100) was used to pump the alcohol of interest into the stainless-steel T at a controlled rate. The temperature of the stainless-steel T was maintained between 115-130°C. This temperature range ensured the vaporization of the alcohols but was below the thermal degradation temperature. Nitrogen gas was used as a carrier gas to sweep the vaporized alcohol from the T-fitting into the cavity. Conditions were chosen to ensure that the alcohol concentration in the gas phase was at least a factor of two less than the saturated vapor pressure of that alcohol.

Spectra were collected using Andor’s SOLIS 64-bit software program. A Gaussian smoothing function was applied over a range of 1.5 nm after data collection. A study of the fine rotational structures of the alcohols used was beyond the scope of this paper, and hence, no attempt was made to resolve them. Nitrogen and helium were supplied to the cavity to characterize mirror loss. The mirror reflectivity was calculated as follows:
\[
R(\lambda) = 1 - d_0 \left( \frac{I_{N_2}(\lambda) \alpha_{Ray}^{N_2}(\lambda) - \alpha_{Ray}^{He}(\lambda)}{1 - I_{N_2}(\lambda)/I_{He}(\lambda)} \right)
\]

Where \(d_0\) is the cavity length, \(I\) is the intensity (spectrum) in nitrogen or helium, and \(\alpha\) is the wavelength-dependent Rayleigh scattering.

The change in intensity transmitted through the cavity is related to the extinction due to absorption \((\alpha_{abs})\), calculated by the following mathematical relationship\(^{121}\):

\[
\alpha_{abs}(\lambda) = \left( \frac{1 - R(\lambda)}{d_0} + \alpha_{Ray}(\lambda) \right) \left( \frac{I_0(\lambda) - I(\lambda)}{I(\lambda)} \right)
\]

Where \(R(\lambda)\) is the wavelength-dependent mirror reflectivity, \(d_0\) is the cavity length, \(I_0(\lambda)\) is the reference spectrum, \(\alpha_{Ray}\) is the wavelength-dependent Rayleigh scattering extinction, and \(I(\lambda)\) is the measured spectrum for the absorbing species in the cavity. The wavelength-dependent Rayleigh scattering values for both \(N_2\) and \(He\) used were reported by Thalman et al.\(^{95,122}\)

The absorption cross-sections in \(\text{cm}^2/\text{molecule}\) were then calculated for different alcohol flow rates by dividing \(\alpha_{abs}\) by the corresponding concentration in molecules/cm\(^3\) for each flow rate used.

### 5.5 Results & Discussion

#### 5.5.1 Absorption Cross Sections

Figures 5.2 to 5.7 show plots of the absorption cross-sections for the 5\(^{th}\) \((6 \leftarrow 0)\) and 6\(^{th}\) \((7 \leftarrow 0)\) overtone transitions in methanol, ethanol, and isopropanol. These measurements provide information about the shape of the energy well for the OH stretch in each alcohol. The wavelength region between 430-490 nm was used to measure the absorption cross-sections of the 6\(^{th}\) OH overtone transition, whereas the spectral range between 483-549 nm was used for the 5\(^{th}\) OH
overtone absorption cross-section. It is evident in figures 5.2 and 5.3 that the most prominent feature in these spectral ranges is the OH overtone for the 5th and 6th overtone. The individual rotational transitions of the OH overtones are present but unresolved in the observed spectra.

Tables 5.1 and 5.2 show the absorption cross-sections for the 5th (6 ← 0) and 6th (7 ← 0) overtones for each alcohol measured in this study. A trend is observed across the experimental intensities given in Tables 5.1 and 5.2. The overtone cross-section decreases with an increase in the length of the carbon chain attached to the OH moiety. Moreover, as the carbon chain attached to the OH group changes from primary to tertiary, the OH overtone cross section decreases. This is consistent with the findings of Lange et al.104, who measured the absorbance cross-sections of the first three overtones for six alcohols, including methanol, ethanol, 1-propanol, 2-propanol, tert-butyl alcohol, trifluoroethanol. An increase in the length of the carbon chain corresponds to a decrease in the intensity of the overtone transition.

Additionally, authors reported that the change in the intensities of the fundamental transitions for several different compounds was dependent on the electronegativity of the substituent attached to the OH group in the molecules they studied. Although there is a direct relationship of decrease in the OH fundamental intensities as the electronegativity of the group attached to the alcohol increases, the analogous trend is much less apparent for subsequent higher absorption overtone intensities. The absorption cross-section intensities for 5th and 6th OH overtones of alcohols measured in our study were found to be shifted towards a longer wavelength with an increase in the alkyl groups attached to the OH group. Alkane chains are recognized as the least strong polarizing group but still exert some electron-withdrawing capability towards the OH group in which it is attached. As such, there is a measurable decrease in the intensity of the overtone transition with a lengthening of the alkane chain attached to the OH group.
Figure 5.2. Fifth overtone cross-section of methanol determined between 509-515 nm.

Figure 5.3. Fifth overtone cross-sections of ethanol determined between 511-518 nm.
Figure 5.4. Fifth overtone cross-sections of isopropyl alcohol between 514-518 nm.
Figure 5.5. Sixth overtone cross-sections of methanol between 447-454 nm.
Figure 5.6. Sixth overtone cross-sections of ethanol between 448-456 nm.
Tables 5.1 and 5.2 show the values for the measured absorption cross-sections for 5th and 6th overtone of methanol, ethanol, and isopropanol. The wavelength values reported included the absorption cross section peaks of each alcohol studied.
Table 5.1. Fifth overtone cross-sections and band strengths of methanol, ethanol, and isopropyl alcohol determined between 510-517.5 nm.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Measured Methanol Cross-section (E-25 cm²/molecule)</th>
<th>Measured Ethanol Cross-section (E-25 cm²/molecule)</th>
<th>Measured isopropyl alcohol Cross-section (E-25 cm²/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>0.93</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>511.5</td>
<td>2.89</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>513</td>
<td>2.96</td>
<td>1.16</td>
<td>-</td>
</tr>
<tr>
<td>514.5</td>
<td>0.68</td>
<td>0.41</td>
<td>0.61</td>
</tr>
<tr>
<td>516</td>
<td>-</td>
<td>1.01</td>
<td>1.88</td>
</tr>
<tr>
<td>517.5</td>
<td>-</td>
<td>0.61</td>
<td>0.21</td>
</tr>
<tr>
<td>Band Strength</td>
<td>7.46</td>
<td>3.62</td>
<td>2.70</td>
</tr>
</tbody>
</table>
Table 5.2. Sixth overtone cross-sections and band strengths of methanol, ethanol, and isopropyl alcohol were determined between 448-455.5 nm.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Measured Methanol Cross-section (E-26 cm²/molecule)</th>
<th>Measured Ethanol Cross-section (E-26 cm²/molecule)</th>
<th>Measured isopropyl alcohol Cross-section (E-26 cm²/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>449.5</td>
<td>1.29</td>
<td>0.41</td>
<td>-</td>
</tr>
<tr>
<td>451</td>
<td>2.70</td>
<td>1.36</td>
<td>0.34</td>
</tr>
<tr>
<td>452.5</td>
<td>0.46</td>
<td>0.33</td>
<td>2.90</td>
</tr>
<tr>
<td>454</td>
<td>-</td>
<td>0.88</td>
<td>6.83</td>
</tr>
<tr>
<td>455.5</td>
<td>-</td>
<td>0.69</td>
<td>2.42</td>
</tr>
<tr>
<td>Band Strength</td>
<td>4.76</td>
<td>3.67</td>
<td>12.49</td>
</tr>
</tbody>
</table>

Based on the formulas given by Phillips et al.\textsuperscript{101}, band locations of several overtone transitions (up to 9\textsuperscript{th} overtone) were calculated. This reveals information about the center wavelength corresponding to each overtone transition for methanol, ethanol, and isopropanol. The experimental values from our work were compared with the predicted overtone transitions, and good agreement has been observed between the values. Notably, double band profiles were observed for ethanol overtone transitions, as shown in figures 5.3 and 5.6. This can be attributed to the mixture of different conformers of ethanol showing more than one band for 5\textsuperscript{th} and 6\textsuperscript{th} overtone.\textsuperscript{102} Table 5.3 shows the predicted and experimentally determined center wavelength for the 5\textsuperscript{th} and 6\textsuperscript{th} overtone transitions for methanol, ethanol, and isopropanol.
Table 5.3. Comparison of center wavelength predicted from formulas given in Phillips et al. versus the experimental measurements presented here for the 5th and 6th OH overtone transitions of methanol, ethanol, and isopropanol. Two values are reported for ethanol overtone center wavelength due to the double band profile in overtone transitions.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Methanol OH overtone center wavelength (nm)</th>
<th>Ethanol OH overtone center wavelength</th>
<th>Isopropanol OH overtone center wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Predicted</td>
<td>Experimental</td>
<td>Predicted</td>
</tr>
<tr>
<td>0→6</td>
<td>512.2</td>
<td>511.85</td>
<td>515.0</td>
</tr>
<tr>
<td>0→7</td>
<td>450.9</td>
<td>450.5</td>
<td>453.7</td>
</tr>
</tbody>
</table>

5.5.2 Birge-Sponer Plot

Figure 5.8 shows the Birge-Sponer plot for methanol, ethanol, and isopropanol. This plot is used to fit the OH overtone transition energies for an anharmonic oscillator. Mathematically, the fitting of the OH overtone transition energies for anharmonic oscillators is given by the one-dimensional Birge-Sponer equation as follows:

\[ \Delta G_{v,0} = v(A + Bv) \]  

(3)

Where \( \Delta G_{v,0} \) represents the energy difference between the \( v \)th quantum level and the ground state (\( v=0 \)), parameters A-B and B represent the mechanical frequency and anharmonicity of the oscillator, respectively. This type of analysis for determining bond dissociation energies is known
to overestimate this value. This is because this analysis assumes a linear extrapolation towards higher energy terms. Indeed, Phillips et al. speculated that there may be substantial curvature in a Birge-Sponer plot due to existence of combination bands as the energy transitions increased. Inclusion of the high order overtones measured in this work into the Birge-Sponer plot for methanol, ethanol and isopropyl alcohol shows this plot to be linear and not suffering from the issues previously raised.

Integration of the area under the curve of the Birge-Sponer plot yields the vertical bond dissociation energy of the O-H bond for each alcohol. The O-H bond vertical bond dissociation energy in methanol, ethanol and isopropanol were calculated using this plot. Methanol is shown to have the strongest vertical bond dissociation energy of 517.1 kJ/mol, followed by ethanol at 508.5 kJ/mol and finally isopropyl alcohol at 501.8 kJ/mol. The decrease in vertical bond dissociation energy as the length of the carbon chain attached to the OH group increases is consistent with the weak electron-withdrawing effect of the alkane chain attached to the OH group. Additionally, the slope of these plots yields the anharmonicity constants of OH stretch in each alcohol. The anharmonicities calculated for methanol (86.0 cm\(^{-1}\)), ethanol (86.9 cm\(^{-1}\)), and isopropanol (86.74 cm\(^{-1}\)) were found to be similar. This result agrees with the findings of Fang et al.\(^{102}\), who reported that the anharmonicities for all alcohols are essentially identical (86 cm\(^{-1}\)).

Furthermore, the mechanical frequencies of methanol (3856 cm\(^{-1}\)), ethanol (3845 cm\(^{-1}\)), and isopropanol (3815 cm\(^{-1}\)) were calculated using a Birge-Sponer plot. The mechanical frequency of methanol is approximately 11 cm\(^{-1}\) larger than ethanol and again 41 cm\(^{-1}\) larger than isopropanol. This decrease of the mechanical frequency from methanol to isopropanol reflects the decrease of the OH stretch restoring force with the increase in the length of the carbon chain.
Figure 5.8. Birge-Sponer plot for the OH stretch of methanol, ethanol, and isopropanol. The circles with best fit solid line represents methanol, the squares with the best fit dashed line represents ethanol, and the triangles with the best fit dotted line represents isopropanol.

Recent work has highlighted the advantages of plotting the absolute energy of each overtone transition verses the transition. This yields a plot that can be fit with a quadratic equation and thus avoids the introduction of errors because of forcing the linearization of the relationship between the increase in vibrational energy transitions as the value of \( v \) increases.

Methanol(-): \( y = -172x + 3856 \)
Ethanol(--): \( y = -173.8571x + 3844.6667 \)
Isopropanol(..): \( y = -173.4857x + 3815.2 \)
5.5.3 CH₃OH* + O₂ → Products

Recently research has been done to understand the importance of overtone excitations of OH vibrations in atmospherically essential molecules. There have been several studies in which molecules are vibrationally excited to higher overtones to measure the bond dissociation energy of various functional groups in a molecule. In addition, the possibility of chemical reactions occurring because of vibrational overtone excitation has also been explored. These overtone excitations can lead to the dissociation of excited molecules and may result in the formation of new molecules or radicals in the atmosphere. Donaldson et al. showed that the OH vibrational overtone excitation of hydrogen peroxide (H₂O₂) to higher overtones (νOH ≥ 4) allows the H₂O₂+O₂ reaction to overcome the activation energy barrier to form HO₂ + HO₂. This study was important in understanding the potential role of vibrationally excited HOOH in recycling HOₓ when reacted with O₂. Although the contribution of overtone-driven reaction of HOₓ production might not be large, the contribution of this mechanism becomes much more significant at high solar zenith angles, increasing the HOₓ production to about 20-30% by this mechanism.

It is hypothesized that pumping methanol to the 4th, 5th, or 6th overtone may enable the methanol + oxygen reaction to overcome the activation energy barrier to form radical products.
Figure 5.9. Potential energy surface for the reaction of CH₃OH* + O₂. The energy levels of the overtones as reported by Phillips et al.¹⁰¹

Figure 9 shows a slice of the potential energy surface for the reaction of CH₃OH + O₂. O₂ can react with vibrationally excited CH₃OH (e.g., CH₃OH*) to extract either a methyl hydrogen or the alcohol hydrogen. Previous work reports that these activation barriers to range between 149 and 188 kJ/mol¹²⁹. Superimposed on the figure are the ν=1-7 energy levels for OH stretch in CH₃OH. As can be seen, exciting CH₃OH via pumping to either the ν=6 or ν=7 OH vibrational level introduces enough energy that the reaction can overcome both the activation barrier and endothermicity of the reaction products. Upon excitation of the OH stretch, several outcomes are possible. Methanol can directly react with O₂ prior to intramolecular vibrational energy redistribution (IVR) if the methanol/O₂ collision rate is faster than IVR, it can be collisionally
deactivated, it can also undergo IVR decreasing the rate of reaction. The various possible outcomes depend on the relative time scales of the different processes.

Rizzo, Perry and co-workers have studied intramolecular energy transfer in highly excited methanol and determined IVR times for the v=5-8 OH stretch levels of 130 fs, 3.2 ps, 240 fs, and 200-300 fs, respectively.\textsuperscript{130-132} While excitation to v=5, 7 and 8 all relax on the order of 100-300 fs, relaxation from v=6 is an order of magnitude longer. Excitation to this state provides the best opportunity for the reaction of methanol and molecular oxygen.

It is interesting to see that the lifetime of the energy that stays in the 6\textsuperscript{th} level (i.e. 5th overtone) is 3.2 ps (picoseconds) and that the lifetime decreases to 240 fs (femtoseconds) when you pump to the 6\textsuperscript{th} overtone, and that the lifetime gets shorter as you pump to higher and higher energy levels. Collision frequencies as a function of pressure for O\textsubscript{2} colliding with CH\textsubscript{3}OH were calculated. In other words, the pressure of O\textsubscript{2} needed to match the collision rate with the rate of IVR for pumping to both the 5\textsuperscript{th} and 6\textsuperscript{th} overtone was computed. A pressure of 50.52 atm yields a collision rate of 3.2 ps which matches the lifetime of CH\textsubscript{3}OH when pumped to the 5\textsuperscript{th} overtone, and a pressure of 673.60 atm is required for O\textsubscript{2} to collide with methanol on the order of 240 fs (for 6\textsuperscript{th} overtone) at 298K.

Rate constants for the CH\textsubscript{3}OH + O\textsubscript{2} reaction have been studied previously using transition state theory at T=1000K.\textsuperscript{133} Abou-Rachid et al\textsuperscript{133} calculated rate constants for the two methanol O\textsubscript{2} reaction pathways and found rate constants of 194 and 70 cm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1} for reaction with the methyl hydrogen and the alcohol hydrogen, respectively. While these reactions would occur at much longer times than the IVR times measured by Rizzo and Parry,\textsuperscript{130, 131} it is important to note that even at T=1000K the population of the excited OH vibrational states is extremely small. The fraction of methanol molecules in the v=5-8 states is 3.5 x 10\textsuperscript{-12}, 6.7 x 10\textsuperscript{-14}, 1.4 x 10\textsuperscript{-15} and 3.8 x
10^{17}$, respectively. Direct excitation of these modes would significantly increase the rate constants of the reaction between methanol and oxygen, especially if the reaction occurs prior to IVR. Even after all the energy from the excitation has been redistributed in the molecule, the reaction rate will be much faster than those calculated at 1000K. Equipartitioning of 5, 6 and 7 quanta of OH stretch using the energy the states measured here, correspond to a vibrational temperature of 3125, 3480, and 3820 K, respectively. Additional efforts are currently underway to investigate the effect of overtone excitation in these molecules on reaction rates, both before and after IVR has set in.

5.6 Conclusions

The absorption cross-sections for the 5th and 6th OH stretching overtones for methanol, ethanol, and isopropanol in the gas-phase are reported. The measured center wavelengths of 511.85 nm (methanol), 512.49 and 516.80 (ethanol), and 516.08 nm (isopropanol) for the 5th OH overtone are in good agreement with previously reported calculated values. The 6th OH overtone values for methanol (450.5 nm), ethanol (450.88, 454.84), and isopropanol (454.4 nm) are also in good agreement with computational predictions. The measurements OH overtone transitions clearly demonstrate an order of magnitude drop in the measured absorption cross-section measurements for the 5th and 6th overtone transitions, which is consistent with what was predicted using formulas given in Phillips et al.\textsuperscript{101} Being the least strong polarizing group, alkanes still possess some electron withdrawing tendencies towards the OH group attached to them. As such, the lengthening of the alkane chain attached to the OH group results in a measurable decrease in the intensity of the overtone transition. Additionally, it was seen that an increase in the carbon chain length of alcohols shifts the center wavelength of OH overtone absorption cross-sections to a slightly higher wavelength. The measured vibrational OH overtones in methanol coupled with the calculated reaction thermodynamics for the biomolecular reaction of vibrationally excited
methanol with $O_2$ shows the reaction to be energetically favorable and could contribute to the formation of $HO_2$ radicals in the atmosphere.
Chapter 6: Detection of Sulfur Dioxide by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS)

6.1 Contributions

The following chapter is presented in its entirety (with minor changes) from the published version of the paper in the journal Sensors. Ryan Thalman, Nitish Bhardwaj, Callum Flowerday, and Jaron C. Hansen. Detection of Sulfur Dioxide by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS). I and Callum Flowerday were involved in SO₂ comparison and ambient measurements experiments and data analysis. Dr. Jaron C. Hansen participated in SO₂ comparison tests and contributed to writing the paper. Dr. Ryan Thalman constructed the instrument, performed data analysis, and wrote the paper.

6.2 Abstract

Sulfur dioxide (SO₂) is an important precursor for formation of atmospheric sulfate aerosol and acid rain. We present an instrument using Broad Band Cavity Enhanced Absorption Spectroscopy (BBCEAS) for the measurement of SO₂ with a minimum limit of detection of 0.75 ppbv (3-σ) using the spectral range 305.5 – 312 nm and an averaging time of 5 minutes. The instrument consists of high reflectivity mirrors (0.9985 at 310 nm) and a deep UV light source (Light Emitting Diode). The effective absorption path length of the instrument is 610 m with a 0.966 m base length. Published reference absorption cross-sections were used to fit and retrieve the SO₂ concentrations and were compared to fluorescence standard measurements for SO₂. The comparison was well correlated, $R^2 = 0.9998$ with a correlation slope of 1.04. Interferences for fluorescence measurements were tested and the BBCEAS showed no interference. Ambient measurements with SO₂ additions responded similarly to standard measurement techniques.
6.3 Introduction

Sulfur dioxide (SO$_2$) is a precursor to formation of atmospheric sulfate aerosol and acid rain.$^{134}$ SO$_2$ is emitted naturally through volcanic eruption,$^{135}$ oxidation of other atmospheric sulfur species,$^{136}$ and is emitted anthropogenically from the oxidation of sulfur from the combustion of coal, and oil.$^{137,138}$ SO$_2$ directly affects health through the respiratory system with elevated risks for high-risk groups.$^{139}$

Further oxidation of SO$_2$ can form sulfate (SO$_4^{2-}$) which in the form of sulfuric acid (H$_2$SO$_4$) contributes to acid rain but also contributes to particulate aerosol in the atmosphere.$^{138}$ Stratospheric injection of SO$_2$ by volcanoes and subsequent formation of stratospheric aerosol has been proven to have a short-term cooling effect on global climate$^{140}$ and therefore is also being considered in some geoengineering scenarios as a possible technique to cool the climate.$^{141,142}$

Even after decreased SO$_2$ emission by the United States and Europe, continued industrialization in other countries has seen an increase in global SO$_2$ emissions since 2000.$^{137}$

Several well-established measurement techniques for SO$_2$ have been used in routine air quality monitoring for decades, including UV fluorescence$^{143,144}$ and the pararosaniline wet chemistry technique,$^{145}$ which are the two Environmental Protection Agency (EPA) Federal Reference and Equivalent Methods.$^{146}$ Other techniques include photo-acoustic spectroscopy,$^{147}$ cavity ring-down spectroscopy,$^{148}$ Long Path Differential Optical Absorption Spectroscopy (LP-DOAS),$^{149,150}$ and Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS).$^{151}$ The LP- and MAX-DOAS techniques are not in situ measurements but leverage the spectroscopic signature of SO$_2$ for quantification. The most applied technique is UV fluorescence with several different manufacturers selling instruments for monitoring. One such instrument, the 43i-Trace Level
Enhanced from Thermo Electron Corp. (TECO, Franklin, MA, USA) has a detection limit of 0.2 ppbv for a 10 second average but can be as low as 0.05 ppbv for a 300 second average with a precision of 1% of the measured concentration of 0.2 ppbv, based on the supplied manufacturer specifications. UV fluorescence uses pulsed UV light to excite the SO2 molecules which then relax to re-emit light at a longer wavelength. The 43i instrument includes a hydrocarbon scrubber to remove most interfering hydrocarbons that also fluoresce when excited with UV light. Known interfering species for fluorescence technique include NO, m-xylene, and H2O.

Broad Band Cavity Enhanced Spectroscopy (BBCEAS) leverages a high finesse optical cavity of a given wavelength to realize long path lengths, similar to LP- and MAX-DOAS but with in situ sampling. Related techniques often add the light source type in front of the acronym (Light Emitting Diode (LED), Interband Cascade Laser (ICL), or Optical Feedback (OF)). BBCEAS and related techniques have been used to measure species including: NO2, NO3, H2O, O3, glyoxal, methyl glyoxal, biacetyl, IO, I2, OIO, ClO, OCIO, ClOCl, BrO, HONO, HCHO, and O4 in the UV and visible regions of the spectrum as well as other compounds in the near-IR and IR using related techniques such as Cavity Ring-down Spectroscopy (CRDS), Integrated Cavity Output Spectroscopy (ICOS), and Cavity Attenuated Phase Shift Spectroscopy (CAPS). SO2 was recently measured using OF-CEAS at 4.035 µm with a detection limit of 130 ppbv and CRDS in the UV with a detection limit of 3.5 ppbv in 10 seconds. Previously SO2 was measured by BBCEAS but in the range of 368 – 372 nm but at concentrations of 0.039 – 1%. Spectroscopic measurements of SO2 in the UV region are based on its highly structured absorption at wavelengths shorter than 320 nm. The structured absorption allows for independent quantification of SO2 from other gases that absorb in the same wavelength window including
NO$_2$, BrO, OCIO, and many organic molecules with broad absorptions in the UV, acetone being just one example (Figure 6.1). This work provides data for a BBCEAS instrument in the range of 305 – 312 nm using SO$_2$ as test molecule and preparing the way for further measurement possibilities of other UV absorbers. The UV spectral region less than 315 nm represents a relatively under-explored region for atmospheric detection of organic and other atmospherically relevant molecules by cavity enhanced methods. In the past this has been limited by both light source availability (cavity ring down spectroscopy requires frequency doubling and a dye laser, LEDs were weak or not available at given wavelengths) and by poor mirror reflectivity. Washenfelder et al. outlined the limitations to UV cavity enhanced spectroscopy which include the lack of bright light sources as well as increasing mirror substrate and coating absorption and scattering losses that limit light throughput and mirror reflectivity. With the introduction of new, brighter LED light sources in the UV, this work explores the possibilities of utilizing the one portion of these UV wavelengths for detection of atmospherically relevant molecules.

6.4 Materials and Methods

The SO$_2$ cavity instrument consists of an optical cavity, mounted in a 3D-printed cage assembly sitting on top of an instrument control box. Figure 6.2 shows a schematic of the instrument including standard dilution and supply as well as gas control valves. The BBCEAS instrument consists of a light source (LED), collimating and focusing optics, the optical cavity and an optical fiber leading to the detector (spectrograph). A UV LED with a center wavelength of 310 nm (Roithner-Lasertechnik GmbH, DUV310-SD353E) was attached to a printed circuit board with an output power of 50 mW collimated by a 25 mm f/1 UV lens. The LED was temperature controlled with a Peltier cooler to 14.0±0.2°C. The Peltier cooler consisted of a temperature controller
(Omega) using a Type K thermocouple held on the front of the printed circuit board (PCB) by a 3D-printed printed brace holding the LED and Peltier cooler to the heat sink, and a small Peltier module mounted directly behind the LED (CUI Devices, CP30138, 15x15x3.8mm) (Figure A2.1 in Appendix 2). The manufacturer specifications state a nominal power output of 93% of initial power after 3000 hours at 25°C ambient temperature and 350 mA.

Figure 6.1. Absorption cross-sections of species absorbing in the 300 - 320 nm range including, SO$_2$\textsuperscript{175}, NO$_2$\textsuperscript{171}, BrO\textsuperscript{172}, OCIO\textsuperscript{170}, acetone\textsuperscript{173}, and HCHO\textsuperscript{176}. The spectral fitting window for the SO$_2$ BBCEAS is shown in blue.

For 6 months of continuous use with the LED actively cooled and driven at 400–500 mA, no noticeable degradation of LED output has been observed. The optical cavity consists of a pair of 2.5 cm diameter high reflectivity mirrors with a center wavelength of 310 nm, a stated maximum reflectivity of 99.9%, and a radius of curvature of 100 cm (Layertec 70 GmbH). Filtered sample air enters and exits the cavity by the mirrors, utilizing the entire cavity length.\textsuperscript{177} The cavity length
was 96.6 ±0.1 cm. The instrument including temperature control, valve control, data acquisition, and LED power supply uses <40W of power (110 VAC).

The instrument temperature was measured by use of the onboard thermocouple which the LabJack U6 data acquisition system includes. Pressure was measured in the cavity airstream using a small pressure sensor (Honeywell, ASDXACX015PAAA5, 0-15 PSI) and the acquired voltages logged on the LabJack. The pressure sensor was inserted into the fitting near the mirror purge. The cavity flow was measured using a Honeywell 0-5 standard cubic centimeters per minute (sccm) flow meter (AWM5101VN) and the analog voltage output of the flow meters was logged using the LabJack. The optical cavity consists of a 0.75 inch outer diameter PFA Teflon tube placed between the mirrors. Light exiting the cavity is focused onto an optical fiber (Thorlabs, 6 x 200 μm round to linear bundle) by a 1-inch f/4 lens and filtered by a 12.5mm diameter bandpass filter (10 nm FWHM, 310 nm, Edmund Optics). The fiber is then directed to the slit of an Andor DU440-BV Spectrograph with a SR-303i CCD camera cooled by a Peltier cooler to -20°C with a 1200 grooves/mm grating. The slit was set at 75 μm for a resolution of 0.25 nm FWHM, which provided a sharp well-defined line function. The fiber assembly only illuminated 100 rows of the 512 row detector, so a portion of the CCD was not read out for each scan in an effort to increase the signal to noise ratio. The CCD was set to an integration time of 0.2 seconds, with a readout time of 0.06 sec. 110 scans were co-added before saving giving a minimum integration time of 30 seconds in these experiments. The optics are all mounted in an optical cage system constructed of carbon fiber
**Figure 6.2.** Schematic of BBCEAS cavity as set up for comparison with the SO$_2$ standard and ambient sampling. Flow is pulled into the system and the total flow of the sample and the overflow are measured by mass flow meters (MFM). BBCEAS measurements are made in parallel with the Thermo Electron Corporation (TECO) 43 series instruments.

Tubes with the braces for the tubes made of 3-D printed parts consisting of Polylactic Acid (PLA) printed on an Ender3 (Creality) printer (See Figure A2.2 in Appendix 2). PLA was used for structural cage supports other than the mirror mounts since PLA is an easy material to print but does not provide an air-tight seal between layers. The 3D printed parts were only used for structural support with stainless-steel tubes inserted into the mirror mounts which sealed via an O-ring to the cavity mirrors. The Teflon tube was held in place between the two stainless steel tubes on each end using a bored-through pipe connection.

The cavity was configured and operated without purge volumes, with the sample being pulled through a particle filter (Pall, 2 $\mu$m pore) in a Teflon filter holder. The reflectivity of the optical
cavity was measured using the differential Rayleigh scattering of He and N\textsubscript{2} gas according to the following equation\textsuperscript{155}:

\[
R(\lambda) = 1 - d_0 \left( \frac{I_{N_2}I_{\text{Ray}}}{I_{He}I_{\text{Ray}}} \right) \frac{\epsilon_{N_2} I_{N_2}(\lambda) - \epsilon_{He} I_{He}(\lambda)}{1 - \epsilon_{Ray}(\lambda)}
\] (1)

where \(d_0\) is the cavity length (96.6 ± 0.1 cm), \(\epsilon_{Ray}\) is the extinction due to Rayleigh scattering of the respective gases\textsuperscript{95, 122} and \(I\) is the spectral intensity in the respective gas (N\textsubscript{2} or He). The measured reflectivity was found to be 99.85\% and the measured reflectivity, effective pathlength and example spectra for N\textsubscript{2} and He are given in Figure A2.3 in Appendix 2.

The measured concentrations were retrieved by non-linear least squares fitting of the cavity extinction as given by Fiedler et al.\textsuperscript{27} and Washenfelder et al.\textsuperscript{157}:

\[
\epsilon(\lambda) = \left( \frac{1 - R(\lambda)}{d_0} + \epsilon_{Ray,\text{Air}}(\lambda) \right) \left( \frac{I_0(\lambda) - I(\lambda)}{I(\lambda)} \right)
\] (2)

where the \(\epsilon(\lambda)\) is the wavelength resolved extinction, \(R(\lambda)\) is the mirror reflectivity, \(d_0\) is the cavity base length, \(\epsilon\) is the extinction due to Rayleigh scattering, \(I_0(\lambda)\) is the reference spectrum, and \(I(\lambda)\) is the measurement spectrum. The reference spectrum was obtained by overflowing the cavity with zero air. The concentrations of the trace gases of interest was retrieved by non-linear least square fitting in IGOR (Wavemetrics) by minimizing the error of the following equation with a 3rd degree polynomial enabling a Differential Optical Absorption Spectroscopy retrieval\textsuperscript{178}:

\[
\epsilon(\lambda) = \sigma_{SO_2}(\lambda)[SO_2] + \sigma_{NO_2}(\lambda)[NO_2] + \text{polynomial},
\] (3)

where \(\sigma(\lambda)\) is the standard absorption cross section for the given gas and [SO\(_2\)] is the retrieved concentration of SO\(_2\)\textsuperscript{170, 175} and [NO\(_2\)].\textsuperscript{171} The absorption cross-sections were convolved to the instrument slit function using the convolution function in QDOAS.\textsuperscript{179} Only SO\(_2\) and NO\(_2\) absorption was retrieved as the absorption cross sections of other gases are either too small or not in large enough concentrations relative to the sensitivity of the instrument to be fitted. Cross-
sections of SO$_2$ and other possible absorbers are shown in Figure 6.1. Because of the fitted polynomial, the retrieval is only sensitive to the structured (differential) cross-section and is insensitive to broad changes in the light source shape, aerosol scatter (if no filter was used) and other broad-band absorbers (many organic compounds that interfere with fluorescence measurements, such as the acetone shown in Figure 6.1). Fitting was carried out from 305.5 – 312 nm using Equation 3 with a 3rd order polynomial and the retrieved concentration was converted to mixing ratio using the measured temperature and pressure.

6.4.1 Comparison of SO$_2$ measurements

Initial testing of the BBCEAS instrument was carried out in comparison to an SO$_2$ standard cylinder (Airgas, 10.14 ppm SO$_2$ in N$_2$, ± 1.4%) diluted using a dilution calibrator (Environics, model 6103) which consists of two mass flow controllers (0–10 liters per minute (lpm) and 0–50 sccm) diluting a small flow of the standard into a large flow of zero air providing a range of SO$_2$ concentrations from zero to 170 ppbv. This range spans the normal operating range of the Thermo instruments as usually deployed (0–200 ppbv). The diluted standard was supplied to an inlet manifold which pulled air at a high flow (>20 lpm) and sampled into the BBCEAS through a 47mm PTFE particle filter (Pall) using a pump at 1.0 lpm. The diluted standard was also sampled by TECO 43c and 43i-TLE SO$_2$ monitors to observe the response of the calibrator and ambient concentrations (See Figure 6.2). Data were logged internally on the 43i and via analog output (0–200 ppbv, 0–10V) for the 43c. Supplied concentrations were provided for a minimum of 10 minutes at each dilution setting to allow for the different settling times of the instruments and ensure enough overlap for averaging for correlation.

Interfering species were tested by introducing known interferences for the fluorescence instruments to the BBCEAS. NO was tested as an interfering species by injection using the same
calibration setup as SO2 with an NO standard of 20.42 ppmv NO (20.43 ppmv total NOx ± 2% in N2). NO is the species reported by the manufacturers to have the largest interfering effect and is the species that is most likely to be encountered in ambient measurements at levels to have a significant influence on the measured SO2 concentrations. Water vapor is considered an interference in stack sampling and m-xylene is a less commonly measured species compared to NO, with a lower reported interference response. Sampling and testing for NO proceeded in the following order: a sampling of ambient conditions, sampling of ambient conditions with standard addition of SO2, sampling of SO2 from the calibration cylinder in Zero Air at varying concentrations, followed by the return to ambient sampling. For xylenes as well as for the broadband absorber acetone, first SO2 was supplied from the dilution calibrator, after which this flow of diluted SO2 standard was flowed separately through the head spaces of two flasks, one containing a mixture of xylenes, the other acetone (Sigma-Aldrich, Spec grade), to observe the change in the retrieved SO2. Water was not tested as an interference, as the manufacturers state that this is only an issue with stack sampling which would be considered close to a condensing environment and can be adjusted for by adding inline dryers.

To evaluate the limit of detection, N2 was continuously flowed through the cavity for 14 hours with a 30 second minimum integration time. Spectra were then averaged over a given number of 30 second spectra to yield a maximum acquisition time of up to 400 minutes for both the spectra and the reference and evaluated with the Beer-Lambert law (absorption = ln(I0/I)) to assess the root mean square noise (RMS) over the fit window.178 Pure photon counting noise follows the relationship RMS = 1/\sqrt{N}, where N is the number of photons collected. To further assess spectral fitting performance with spectral averaging, the data series were also averaged to 1 minute, 5 minute, and 10 minute intervals.
6.5 Results

6.5.1 Comparison to SO$_2$ standard

The BBCEAS followed the response of the SO$_2$ concentration delivered by the dilution calibrator in a linear fashion. Figure 6.3 shows fitted extinctions at a range of different SO$_2$ concentrations and with different averaging times, highlighting unstructured residual features and good matching of the literature cross-section to the data. Figure 6.4 shows the measured SO$_2$ concentrations. Several different measured conditions are highlighted in the figure, including ambient conditions, SO$_2$ standard addition to

![Figure 6.3](image)

**Figure 6.3.** Fits of Eq. 3 (black) relative to the measured extinction (red) in the lower portion of each panel. The difference of the black and red is shown on the upper axis for each panel in blue. A: Ambient sampling [SO$_2$] = 0.5. B: SO$_2$ added to ambient sampling (10.2 ppbv). C: [SO$_2$] = 40.8, D: [SO$_2$] = 89 E: [SO$_2$] = 156 ppbv. F: 5 minutes averaged spectra [SO$_2$] = 91 ppbv.
ambient sampling, and sampling of a SO$_2$ standard at a range of concentration levels. The correlation of the standard dilution from the calibrator with the BBCEAS retrieved concentrations yielded a slope of 1.04 ± 0.05, an offset of 0 ± 1 ppbv, and an $R^2$ value of 0.9998 (Figure 6.5). The absence of any structure in the residuals suggests no systematic error in the fitting routine and means that longer integration times and more acquired photons will lower the detection limit as expected from photon-shot noise. The Rufus et al.$^{175}$ cross-section was used for fitting because the fit residual was improved by 20% at higher concentrations over the use of the Bogumil et al.$^{170}$ cross-section, likely due to the fact that the Bogumil cross-section is a lower resolution than our current instrument. For spectral fitting purposes the reference spectra were averaged from 10 minutes of zero air spectra. The minimum fit residual for the 30 second average is $1.6 \times 10^{-8}$ cm$^{-1}$. The variability of the retrieved concentration at each concentration level indicated a limit of detection of 2.6 ppbv (3-$\sigma$) for a 30 second acquisition. Data under ambient conditions showed that the two instruments followed each other within the operational parameters. Most of the ambient data exhibited no measured SO$_2$ as shown in the ambient portion of Figure 6.4 as well as the longer time period shown in Figure A2.4 in Appendix 2 as well as the correlation of the BBCEAS relative to the 43i-TLE for the same period (Figure A2.5 in Appendix 2).
**Figure 6.4.** Time series of retrieved SO$_2$ concentrations. Panel A shows the 1-$\sigma$ standard deviation of the fit residual for the 30 second, 5 minute and 10 minute data. Panel B shows the measured SO$_2$ from the three instruments under ambient, SO$_2$ + ambient, and calibration conditions as well as the time traces for the 5 and 10 minute averaged data. Vertical red dashed lines separate the different conditions. The jump in the 43i signal at the end of the experiment is due to a flow connection change to that instrument.
6.5.2 Interferences

The fluorescence-based detection instruments reported measured SO$_2$ from NO injected into the sampling line, while the BBCEAS did not measure any NO when 4 ppmv of NO was injected (See Figure A2.6 in Appendix 2). The 43i registered a measured SO$_2$ concentration of 85 ppbv, giving a response of 0.085 ppbv SO$_2$ for every 1 ppbv of NO. This is a likely explanation for some of the baseline drift for the TECO 43i observed under clean conditions for SO$_2$, but with moderate NO$_x$. For xylenes (1ppmv) and acetone (20 ppmv), no change in the measured SO$_2$ was observed for BBCEAS (see Figure 2.7 in Appendix 2).

6.5.3 Signal Averaging Effect on Precision and Accuracy

Signal to noise evaluation was carried out on spectra of N$_2$ with the Andor spectrometer using data from several hours of N$_2$ data. The data show no plateau for up to 20 minutes of integration time and a minimum RMS photon shot noise of 8.7 x $10^{-5}$ (see Figure 6.6). Signal averaging yields 3$\sigma$ detection limits in the fitted spectra of 2.6, 2.25, 0.75, and 0.48 ppbv for integration times of 30 seconds, 1 minute, 5 minutes, and 10 minutes, respectively, as derived from the standard deviation

---

Figure 6.5. Correlation of BBCEAS (boxes) measured SO$_2$ with respect to that measured by the TECO 43i-TLE. The linear fit equation and uncertainties are included in the graph.
of the measurement of the baseline for retrieved concentrations.\textsuperscript{158} The overall uncertainty of the instrument measurement is limited by the fit RMS at low concentrations and by the cross-section uncertainty (5% $1\sigma$) at higher concentrations.\textsuperscript{175} The other contributing uncertainties are the measurement of the spectra (<1% based on the amount of signal acquired), the measurement of the pressure (5%), the measurement of the cavity length (<1%), and the mirror reflectivity (<2%, including the Rayleigh scattering cross-section uncertainty).\textsuperscript{95} The calculated extinction has an uncertainty of 2%, when combined with the absorption cross-section uncertainty this gives an overall uncertainty of 5.4%. The values for the detection limits of several atmospherically relevant species as they can be extrapolated from the 5-minute detection limit for SO\textsubscript{2} are shown in Table 6.1.

Figure 6.6. Signal to noise evaluation for the spectrometer evaluated as the 1-$\sigma$ RMS noise. The RMS noise levels off at longer integration times.
6.5.4 Performance of 3-D printed Cage System

The 3-D printed cage system held up well under movement of the instrument between locations including car trips. Weaknesses in the design include metal screws in plastic threaded holes and flexibility of the parts if exposed to excess heat. The cavity plates tended to crack if the attachment to the carbon tubes was tightened too much, and excess heat (PLA deforms at 60°C) from the LED cooling assembly once melted the cage plate holding the LED in the cage. While these are perhaps barriers for commercialization, the replacement parts were easily reprinted (<$1 each in materials and 6-12 hours of printing) and replaced for the defective parts. Acrylic styrene-acrylonitrile (ASA) printed parts smoothed with acetone vapor was attempted for the mirror mounts, but an airtight seal proved difficult to achieve, lead us to insert stainless-steel tubes.

Table 6.1. Estimated limits of detection for a 5-minute sampling time of atmospherically relevant species that absorb in the same wavelength range as SO₂.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\sigma^*$ (cm² molecule⁻¹)</th>
<th>LOD (ppbv)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>$3.97 \times 10^{-19}$</td>
<td>0.75</td>
<td>Rufus et al.¹⁷⁵</td>
</tr>
<tr>
<td>NO₂</td>
<td>$2.2 \times 10^{-20}$</td>
<td>13.5</td>
<td>Vandaele et al.¹⁷¹</td>
</tr>
<tr>
<td>HCHO</td>
<td>$2.73 \times 10^{-20}$</td>
<td>10.9</td>
<td>Meller and Moortgat¹⁷⁶</td>
</tr>
<tr>
<td>OCIO**</td>
<td>$3.6 \times 10^{-18}$</td>
<td>0.09</td>
<td>Dong et al.¹⁶¹</td>
</tr>
<tr>
<td>BrO**</td>
<td>$6.6 \times 10^{-18}$</td>
<td>0.05</td>
<td>Wilmouth et al.¹⁷²</td>
</tr>
</tbody>
</table>

* The differential cross-section is taken as the maximum peak to peak cross-section in the 306-312 nm at the instrument resolution.

** Short lived species not detectable with an inlet system.
6.6 Discussion

The BBCEAS instrument as currently constructed provides a complementary technique for the measurement of SO$_2$ with similar limits of detection and linearity over a wide range of SO$_2$ concentrations, comparable to what common commercial instruments for ambient monitoring can provide. In the current configuration the 3-$\sigma$ detection limit is 2.6 ppbv for a 30 second integration time and 0.75 ppbv for a 5-minute integration time. The instrument is calibrated with pure gases of N$_2$ and helium, removing the need for standards to be kept in the field for calibration. Known interferences from NO, m-xylene (represented by a mixture of xylenes in this work), and H$_2$O in the instruments utilizing fluorescence detection are avoided using the BBCEAS method as demonstrated for NO and for xylenes. Both of these compounds absorb light further into the UV and fluoresce similar to SO$_2$. Acetone is a broadband absorber which changes the total extinction inside the cavity. While the BBCEAS instrument is insensitive to retrieving concentrations of broadband absorbers (or scattering from aerosol), the instrument was still able to retrieve the SO$_2$ concentration in the presence of the acetone, demonstrating the insensitivity to broadband extinction processes as has been shown previously.$^{155}$ Additionally, it should be noted that early cavity enhanced spectroscopy studies$^{27}$ omitted the scattering term in the extinction calculation (Equation 2) for mirrors of lower reflectivity. Even at low mirror reflectivity, this yields a 4% error in the retrieved trace gas concentrations and should be included as first noted by Washenfelder et al.$^{121}$

The cavity and spectrometer combination demonstrated here allows for signal averaging up to several hours of data with improved limits of detection. This has been previously demonstrated for cavity and DOAS fitting of spectra when the instrument behaves as a white-noise sensor, as has been demonstrated in this work.$^{180}$ The 3-D printed cage performed well and can be utilized for
structural construction of optical cavities at a greatly reduced cost, or for researchers without access to machining and precision design support.
Chapter 7: Conclusions and Future Work

The results of the source apportionment study conducted at the Neil Armstrong Campus, West Valley City, Salt Lake Valley, UT in 2016 were compared with results from the 2015 BYU campus study at Provo, UT in chapter 2. This comparison highlighted the importance of understanding the impact of formation of secondary organic aerosol from wood smoke emitted gases towards the total amount of PM$_{2.5}$ in the atmosphere. Most of the organic markers associated with wood smoke (levoglucosan, stearic acid and dehydroabietic acid) were associated with primary wood smoke emissions, but a fraction of the levoglucosan and stearic acid are also associated with secondary organic material formed from gaseous precursors in wood smoke. The identification of this secondary material was made possible by the collection of hourly averaged data that allowed for the time patterns of black carbon, organic material, and wood smoke marker compounds to be included and compared in a Positive Matrix Factorization (PMF) analysis. The PM$_{2.5}$ factors identified in 2015 Brigham Young University Provo campus included ammonium nitrate (42%), diesel emissions (2.5%), auto emissions (2.9%), ozone related (2.8%), wood smoke (31%) and wood smoke secondary material (19%, or 61% of the primary wood smoke). In the 2016 West Valley City study, PM$_{2.5}$ identified factors included ammonium nitrate (57%), diesel emissions (12%), auto emissions (12%), smelter fugitive emissions (13%), wood smoke (1.8%) and wood smoke secondary material (0.7% or 39% of the primary wood smoke). Wood smoke related material in this 2016 Neil Armstrong study were lower because the sampling site was more removed from the urban areas of the valley. The BYU campus site was surrounded by housing, which means people burn wood during winters, causing emission of gases from wood smoke, leading to the formation of secondary organic aerosols (SOA). I recommended that more source
apportionment studies be conducted to understand the formation of SOA, to better understand the effects of SOA on human health and PM concentrations.

We were able to successfully identify some organic compounds in particulate matter that were unidentified before, with the help of the GC-MS OAM during the 2017-2018 Sevier valley and Uintah basin studies. The GC-MS OAM has been shown to provide invaluable information concerning sources of air pollution by providing an hourly averaged speciated data set. Levoglucosan, a marker of wood smoke, was detected by the instrument during this field study. Since GC-MS OAM is an autonomous instrument, it has the capability to measure on an hourly averaged basis the carbonaceous fraction of aerosols which allows for the measurement of the diurnal pattern of organic components in PM. This data in turn enables better source apportionment analysis. Moreover, the addition of a sorbent trap can enhance the current capability of this instrument to measure volatile organic compounds in addition to semi-volatile organic compounds’ measurements.

An extensive study was conducted in 2019 to identify the probable sources of formaldehyde in Bountiful, Utah. The PMF analysis of the historical data (2003-2017) suggests biomass burning and the conversion of biogenic emissions are the two main sources which accounted for 79% of total formaldehyde emissions. However, the diurnal pattern observed for the highly resolved formaldehyde measurements (2019) suggests that formaldehyde concentrations are coupled to the actinic flux and that its formation through the photooxidation of VOCs plays an important role. This was confirmed through backwind trajectory results which clearly showed the derived back wind trajectories were coming from the direction of oil refineries and industrial sources located primarily to the south, southwest of the Bountiful sampling site. An extensive study of emissions
of volatile organic compounds such as ethene and propene would improve the understanding of
the conversion of these hydrocarbon precursors to formaldehyde formation in the region.

BBCEAS has clearly demonstrated its capability to measure the absorption cross-sections of the
5th and 6th OH vibrational overtones of several short-chained alcohols including methanol, ethanol,
and isopropanol. There have been several studies in which molecules are vibrationally excited to
higher overtones to study the dissociation of the OH bond in a molecule. The idea was to research
the possibility of chemical reactions occurring because of vibrational overtone excitation. These
overtone excitations can lead to the dissociation of excited molecules or increase their reactivity
thus leading to the formation of new molecules or radicals in atmosphere. We believe that pumping
methanol to the 5th and 6th overtone may enable the methanol + oxygen reaction to overcome the
activation energy barrier and endothermicity of the reaction to form radical products. O2 can react
with CH3OH to extract either a methyl hydrogen or the alcohol hydrogen. Previous work reported
these activation barriers to range between 149 and 188 kJ/mol28. Exciting CH3OH via pumping to
either the ν=6 or ν=7 OH vibrational level introduces enough energy that the reaction overcomes
both the activation barrier and endothermicity of the reaction products. In collaboration with Drs.
Sevy and Asplund, reaction rate coefficients are being calculated for the reaction of vibrationally
excited CH3OH* with O2.

BBCEAS has also been able to successfully measure SO2 over a wide range of concentrations with
the limits of detection and sensitivity equivalent with commercial instruments being currently used
for SO2 measurements. This instrument has an advantage over commercially available instruments
that measure SO2 in that it does not suffer from interferences due to water vapor, xylenes or
acetone. Since this instrument can leverage long path lengths depending on the base pathlength of
the instrument, it has the tendency to achieve very low limits of detection, even the ppt level.
Due to the broad absorption lines of SO$_2$ (~1 nm FWHM), the instrument resolution of the Andor spectrograph (0.26 nm) was unnecessarily high. The ideal line width and grating combination would be 0.5 nm with a grating of 600 grooves/mm to maximize light throughput while maintaining a large enough differential absorption cross-section for spectral fitting (Figure 6.6). This improvement in signal to noise would further improve the minimum detection limit and time response for trace level detection of SO$_2$ in the presence of other structured absorbers. This demonstration of workable BBCEAS measurements further into the UV spectral range with lower reflectivity mirrors allows for measurement of a number of molecules of interest (SO$_2$, OH radical) by BBCEAS in the UV and visible light ranges. Continued improvement of higher-powered UV LEDs provided enough light to access detection limit ranges of atmospheric importance (for SO$_2$ 0.5 – 200 ppbv). Other short-lived species may also be detectable by utilizing open-path detection schemes with longer cavity lengths (BrO, OClO, OH radical). Future development of the BBCEAS instrument could be made to lower the power requirements enough to allow the instrument to be mounted on a mobile platform such as an Unmanned Aerial System (UAS) for SO$_2$ source identification for large emitters.

Since OH radical is one of the predominant species in the atmosphere, and responsible for the photochemical oxidation of volatile organic compounds (VOCs) to form pollutants such as formaldehyde, the study of OH radical is crucial to understand the photolytic reactions occurring in the atmosphere leading to the formation of various air pollutants. Based on the success of the custom-built closed cavity BBCEAS that was used to measure HCHO and SO$_2$, we are currently working on designing and building a new instrument for measuring the ambient concentrations of OH radical concentrations. Unlike the previously designed BBCEAS instrument, it will be an open-cavity instrument to quantify OH radical concentrations.
Future work includes construction and characterization of this new open path cavity instrument. Since previously designed instrument has already shown its ability to detect SO$_2$ with a wide range of concentrations as explained in chapter 6, SO$_2$ will be used as a calibration gas to characterize the effects of turbulence and aerosols with the open-cavity design. SO$_2$ will be used as a calibration gas because OH radical’s lowest energy electronic state occurs in the same wavelength region (i.e., 308 nm) that SO$_2$ absorbs (300-310 nm), and the mirrors and data retrieval process for SO$_2$ measurements will be analogous to what is used for OH radical.
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Appendix 1: Supplementary Information for Chapter 4

Supplementary Information for “Sources of Formaldehyde in Bountiful, Utah”

A1.1 Figures

![Figure A1.1](image)

**Figure A1.1.** Comparison of the NO2 concentrations measured by the BBCEAS and the Teledyne Advanced Pollution Instrumentation (API) T series NOx analyzer operated by Utah DAQ during the 2019 air sampling campaign from February 2019 to June 2019.
Figure A1.2. (a) Box modelling of oxidation of BTEX and light alkene compounds as a function of time (hr). (b) Rate of HCHO production as a function of VOC and loss of reactant concentration.
Appendix 2: Supplementary Information for Chapter 6

Supplementary Information for “Detection of Sulfur Dioxide by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS)”

A2.1 Figures

Figure A2.1. LED cooling mount in the cage system.
Figure A2.2. Mechanical drawing of the cage mounting system for the BBCEAS. Cage plates are constructed of 3-D printed plastic parts with pultruded carbon tubes forming the optical cage.
Figure A2.3. Signal intensity in the presence of He and N₂ gas as used in Eq. 1. Panel B: Effective pathlength (1/e) in meters. Panel C: Measured mirror reflectivity in the useable wavelength range.
Figure A2.4. Ambient measurements of SO₂, averaged to 5-minute data for all three instruments.
Figure A2.5. Correlation of ambient data from Figure S3 for BBCEAS measured [SO$_2$] relative to the 43i.
Figure A2.6. Response of BBCEAS vs. fluorescence detection in the presence of NO. 400 ppbv of NO is provided to the instruments with a measured SO$_2$ concentration of 83 ppbv in the Thermo 43i.
Figure A2.7. Interference test for xylenes and acetone. An SO₂ mixture from the calibrator was supplied to the cavity followed by the same mixture flowing through the head space of a flask that had either xylenes or acetone in it at room temperature. The estimated concentrations of the xylenes and acetones were 1 and 20 ppmv respectively.
Appendix 3: Formation of Secondary Organic Material from Gaseous Precursors in Wood Smoke

A3.1 Contributions

The following chapter is presented in its entirety (with minor changes) from the submitted version of the paper to the Journal of Air and Waste Management Association. Delbert J. Eatough, Nitish Bhardwaj, Paul M. Cropper, Robert A. Cary and Jaron C. Hansen. Formation of Secondary Organic Material from Gaseous Precursors in Wood Smoke. I was involved in the collection and analysis of Neil Armstrong and Bountiful data. I also helped with writing and editing the paper. Dr. Jaron C. Hansen reviewed and edited the work. Dr. Delbert J. Eatough wrote the paper.

A3.2 Abstract

The apportionment of the contribution of wood smoke emitted particles to the total concentration of particulate matter in a region has been greatly aided by the development of new analytical methods. These analytical methods quantitatively determine organic marker compounds unique to wood combustion such as levoglucosan and dehydroabietic acid. These markers have generally been determined in 24-hour averaged samples. We have developed an instrument based on the collection of particles on an inert filter, desorption of the organic material in an inert atmosphere with subsequent GC separation and MS detection of the desorbed compounds. The GC-MS Organic Aerosol Monitor (OAM) instrument has been used in three field studies. An unexpected finding from these studies was the quantification of the contribution of secondary organic aerosols from gases present in wood smoke in addition to primary wood smoke emitted particles. The identification of this secondary material was made possible by the collection of hourly averaged
data that allowed for the time patterns of black carbon, organic material, and wood smoke marker compounds to be included and compared in a Positive Matrix Factorization (PMF) analysis. Most of the organic markers associated with wood smoke (levoglucosan, stearic acid and dehydroabietic acid) are associated with primary wood smoke emissions, but a fraction of the levoglucosan and stearic acid are also associated with secondary organic material formed from gaseous precursors in wood smoke. Additionally, this secondary material was shown to be present in each of the three urban areas where wood smoke burning occurs. There is a need for additional studies to better understand the contribution of secondary particulate formation from both urban and wildfires.

A3.3 Implications

This manuscript presents results from three field studies which show that in addition to the formation of primary particulate matter from the combustion of wood smoke and secondary particulate matter is also formed from the gaseous compounds emitted with the wood smoke. This material is identified in the studies of wood combustion reported here by the identification and quantification of specific organic marker compounds related to wood combustion and is shown to and represents a contributor nearly as large as the primary emitted material and better quantifying the impact of wood combustion on airborne fine particulate matter.

A3.4 Introduction

The application of source apportionment to the atmospheric pollution has been recently reviewed. This review points out the infrequency of specific identification of wood smoke emission. The apportionment of the contribution of wood smoke emitted particles to PM$_{2.5}$ has been greatly aided by the development of analytical methods for the quantitative determination of organic marker compounds unique to wood combustion such as levoglucosan. However, these
markers have generally been measured in 24-hour samples. As a result, organic marker compounds in PM$_{2.5}$ have generally not been included in field studies where the source apportionment analysis has been conducted on an hourly averaged basis$^{42-48}$ due to limitations in available sampling techniques.$^{49}$ We have developed an instrument capable of hourly average measurement of PM$_{2.5}$ organic marker compounds based on collection of particles on an inert filter, desorption of the organic material in an inert atmosphere with subsequent GC separation and MS detection, the GC-MS Organic Aerosol Monitor (OAM).$^{14}$ The use of hourly averaged data in a PMF source apportionment greatly improves the ability to sort out sources whose presence is depended on the diurnal cycle of both emissions and conversion processes. For example, the identification of sources associated with the combustion of wood which is generally a night event becomes possible where clear identification of this source based on 24-hour data is more difficult. This instrument has now been used by us in three field studies.$^{8,50,182}$ An unexpected finding from these studies was the quantification of the contribution of secondary organic aerosols from gases present in wood smoke in addition to primary wood smoke emitted particles. The identification of secondary material was made possible by the creation of hourly averaged data which allowed the time patterns of black carbon, organic material, and wood smoke marker compounds to be compared in a PMF analysis. Most of the markers associated with wood smoke (levoglucosan, stearic acid and dehydroabietic acid) are associated with primary wood smoke emissions, but a fraction of the levoglucosan and stearic acid can be associated with secondary organic material formed from gaseous precursors in wood smoke. The findings from these three studies are compared here. Because each of the studies has been published, details of the studies are only outlined.
A3.5 2015 Study on the BYU Campus, Provo, UT (Cropper et al., 2018)

A3.5.1 Overview:
A study was conducted on the Brigham Young University campus during January and February 2015 to identify winter-time sources of fine particulate material in Provo city, Utah Valley, Utah. Hourly average measurements made in the study included:

**Fine particulate mass.** PM$_{2.5}$ mass was measured using an R&P model 8599 FDMS (Filter Dynamics Measurement System) tapered element oscillating microbalance (TEOM) sampler (Chapel Hill, NC). The FDMS TEOM measures all fine particulate mass, including ammonium nitrate and semi-volatile organic material, but does not measure fine particulate water (Grover et al., 2004).

**Fine particulate cations and anions.** A URG model 9000D ambient ion monitor (AIM) was used to measure both gas phase and particulate phase ammonium, sulfate and nitrate species. Dionex IonPac columns were used to quantify both the cation and anion concentrations. Cations analysis were performed with a CS12A-5μm 3x150 mm column, and a AS14A-5μm 3x150 mm column was used for anion analysis. The AIM instrument has already been described in a study involving the composition and secondary formation of fine particulate matter in the Salt Lake Valley (Kuprov et al. 2014). The only ions present in significant concentrations were nitrate, sulfate, and ammonium ions, with reasonable equivalent balance between the anions and the cations. Ammonium nitrate and ammonium sulfate were the species used in the PMF analysis.
**Carbonaceous material.** Black carbon (the absorption measured at 800 nm) and ultraviolet (UV)-absorbing carbon (measured at 325 nm) were determined with a dual-wavelength aethalometer (Anderson Instruments, model RTAA-900). It was intended to measure aerosol carbon with a Sunset Laboratory instrument. However, the instrument did not function properly during much of the study. Therefore, aerosol organic material was estimated from the FDMS-measured PM$_{2.5}$ minus all the measured PM constituents. Fine particulate crustal material was not measured during the study. Based on past measurements along the Wasatch Front,$^{183,184}$ this introduced an error of less than $1 \mu g/m^3$ in the organic material estimate.

**Gas-phase species.** Concentrations of gas-phase ammonia and nitric acid were obtained from the URG model 9000D AIM ion chromatography (IC) data. The concentrations of NO$_x$ and NO$_2$ were measured using a Thermo model 42NO$_x$ analyzer. Ozone was measured using a Teledyne model 400S ozone monitor. It was recognized that concentrations of CO would be valuable in the PMF analysis, but this gas-phase primary emission species was not measured. However, CO and NO$_x$ were measured at the State of Utah Division of Air Quality North Provo station, located just 1.2 km from the study sampling station. It was assumed that the ratio of CO to NO$_x$ would be the same at the two sampling sites. During the time period used in the PMF analysis, CO and NO$_x$ were linearly related at the North Provo site, with a slope of 111 ppb NO$_x$/ppm CO and $r^2 = 0.916$. This relationship was used to estimate CO at the BYU sampling site using the NO$_x$ concentrations measured at the BYU site.

**Organic Marker Compounds.** Organic marker compounds measured included levoglucosan, dehydroabietic acid, stearic acid, pyrene, and anthracene. Measurements were made using the GC-MS OAM that has been previously described.$^{14}$
A3.5.2 PMF Analysis:

A total of 248 hourly averaged data sets were available for a positive matrix factorization (PMF) analysis of sources of both primary and secondary fine particulate material. A total of nine factors were identified. Details of the PMF analysis have been published.8 Identified factors are shown in Figure A3.1.

![PMF Analysis Chart](image)

**Figure A3.1.** Pie chart of the fraction of the total PM$_{2.5}$ identified with the nine factors. The Chi$^2$ value is that for the final PMF result.

The major factor was identified as secondary ammonium nitrate and 41% on average of the total PM$_{2.5}$ mass was in the form of ammonium nitrate. A smaller, secondary factor was identified and found to be correlated with the production of ozone, with 100% of the ozone contained in this
factor. Additional smaller factors were identified and attributed to diesel and auto traffic based on their time patterns and the presence or lack of significant black carbon. Another small factor contained 100% of the anthracene and appeared during the day on January 19 and 25 and February 12 and 13. The first two days are a Monday holiday and a Sunday and the last two a Thursday and a Friday. This factor is presumable traffic related, but the exact source of the emissions was not further identifiable from the results.

The remaining four factors contained all of the levoglucosan, as indicated in Figure A3.2. The presence of wood smoke emissions was associated with all the levoglucosan, stearic acid, dehydroabietic acid, and pyrene markers. Thirty-four percent of the levoglucosan was present in the Wood Smoke Factor along with 21% of the dehydroabietic acid. This factor accounted for 4.62 $\mu$g/m$^3$ of PM$_{2.5}$ and 3.89 $\mu$g/m$^3$ of the organic material. Two smaller factors associated with wood smoke accounted for 0.13 $\mu$g/m$^3$ of PM$_{2.5}$ and 0.05 $\mu$g/m$^3$ of the organic material and all of the stearic acid, and for 0.39 $\mu$g/m$^3$ of PM$_{2.5}$ and 0.05 $\mu$g/m$^3$ of the organic material and all of the pyrene and 79% of the dehydroabietic acid. The OM factor accounted for 50% of the organic material and for 21% of the levoglucosan. A comparison of the diel patterns of the Wood Smoke and OM factor factors is given in Figure A3.3 and a comparison of their composition is given in Figure A3.4.
Figure A3.2. Distribution of levoglucosan among the four factors where levoglucosan was present.

Figure A3.3. Comparison of the diel patterns of the Wood Smoke and the OM Related Factors. The hash mark under the X axis indicates a weekend. The concentration of BC associated with the Wood Smoke Factor is also given. BC was not present in the Secondary OM Related Factor.
Figure A3.4. Comparison of the Wood Smoke and the OM Factor compositions

The composition of both the Wood Smoke and OM Factors, Figure A3.4 are dominated by levoglucosan and organic material, suggesting that both may be related to emissions from wood smoke. In addition, the black carbon seen in the Wood Smoke factor, Figure A3.3, was not present in the OM Factor, Figure A3.3, suggesting that the OM factor may be secondary in nature. Furthermore, the OM factor was also present dominantly at night, Figure A3.3. These observations all suggest that the OM Factor is a secondary material formed in wood smoke after it is emitted. It is expected, since wood smoke emissions will dominate over regional gaseous organic compounds during winter inversions in the valley, the source of the added SOA will be associated with gaseous wood smoke emissions. These observations were not made in our original publication of this PMF study.\(^8\) However, based on the results of a subsequent study in the Salt Lake Valley we postulate that this factor is secondary organic material formed from gaseous precursors in the emissions from wood smoke.\(^50\)
A source apportionment study was conducted at the Neil Armstrong Academy campus, 5194 Highbury Pkwy, West Valley City, UT 84120, during January and February 2016. Among the objectives of the study was to identify winter-time sources of fine particulate material in West Valley City, Utah. Fine particulate mass and its composition including organic marker and related gas phase species were all measured on an hourly average basis. The following hourly averaged data were used in the Positive Matrix Factorization (PMF) analysis, fine particulate mass, cations and anions, carbonaceous material (NVOM, Nonvolatile Organic Material measured with a Sunset monitor, SVOM, Semi-Volatile Organic material estimated as the FDMS TEOM total PM$_{2.5}$ minus species, Aethalometer measured BC and UV carbon), organic marker compounds, gas phase species including NO$_x$, NO$_2$ and CO and mass spectrometric measurements of gas phase methanol and C$_8$ aromatics.

The location of the Armstrong study is substantially different from that of the BYU study. The BYU was conducted on campus at the edge of a plateau facing the Provo urban area. The campus is surrounded by housing. In contrast, the Armstrong study is an elementary school focused on STEM (science, technology, engineering, and math) education located in the northwestern part of Salt Lake Valley. It is at the northern boundary of the urban area, 7 miles east of the Kennecott Smelter and Refinery and Power Plant, and 9 miles south of the Salt Lake International Airport with shipping and related industry related to the airport to the north and west of the campus. The Great Salt Lake is located 10 miles to the north and west of campus and prevailing winds at the sampling site are from this direction.
A3.6.1 PMF Analysis:

A total of 557 hourly averaged data sets were available for a positive matrix factorization (EPA PMF) analysis of sources of both primary and secondary fine particulate material. A total of seven factors were identified. Details of the PMF analysis have been published. Identified factors are shown in Figure A3.5.

![Armstrong Study PMF Results, µg/m³](image)

Figure A3.5. Pie chart of the fraction of the total PM$_{2.5}$ identified with the seven factors.

The major factor was identified as secondary ammonium nitrate and 56% on average of the total PM$_{2.5}$ mass was in the form of ammonium nitrate. About 12% of the PM$_{2.5}$ mass was identified as diesel fuel related emissions. Another 12% of the PM$_{2.5}$ mass was associated with auto traffic. Both of these sources were assigned to diesel or auto related based on their time patterns and the
presence or lack of significant black carbon. A similar fraction was identified as fugitive emissions from the copper smelter located west of the sampling site based on the presence of SO₂ and wind back trajectories.

The remaining four factors contained all of the levoglucosan, as indicated in Figure A3.6 with 4% being associated with the Diesel Factor. The presence of wood smoke emissions was associated with all the remaining levoglucosan, with 96% of the stearic acid, 96% of dehydroabietic acid, and 92% of the stearic acid.

The factor identified as Wood Smoke, Figure A3.6, is present at an average of 0.39 μg/m³, although it is only sporadically present. It is present only in the evening and tends to be present on weekends. The mass of this factor is not well explained by the PMF results (ratio of components to mass of 0.69). It consists of 20% NVOM, 17% SVOM and 3% ammonium nitrate. These characteristics are all typical of a factor dominated by wood smoke emissions. In addition, the presence of levoglucosan (64% of the total) and dehydroabietic acid (96% of the total) in this profile are also consistent with this assumption. The factor also contains 90% of the adipic acid.

This factor accounted for only 0.38 μg/m³ of PM₂.₅ and 0.26 μg/m³ of the organic material. The much smaller fraction of the Wood Smoke PM₂.₅ in the Armstrong study can be attributed to the location of the sampling site as discussed previously. The two Secondary Wood Smoke factors accounted for 5.2% of the PM₂.₅, 3.0% of the organic material and for 21% of the levoglucosan.
Figure A3.6. Distribution of levoglucosan among the four factors where levoglucosan was present.

Figure A3.7. Comparison of the diel patterns of the Wood Smoke, the Wood Smoke Secondary OM Related Factors and the concentrations of the Ammonium Nitrate factor. Hash marks under the X axis indicate weekends.

A comparison of the diel patterns of the Wood Smoke and the Secondary Wood Smoke OM factors is given in Figure A3.7 and a comparison of their composition is given in Figure A3.8. As expected, one of the other of the two Secondary Wood Smoke factors is always present along with the Primary Wood Smoke Factor. However, the relative amount of the OM2 Factor, compared to the other factors is significantly higher during the time period of February 13 to 15. Also shown Figure A3.7 is the concentrations of the Ammonium Nitrate Factor (divided by 3). This factor was
present at high concentrations (peaking at 60 μg/m³) during the February 13 to 15-time period but was not present at high concentrations during the other time periods when the OM2 factor was present, Figure A3.7. This observation probably accounts for both the high fraction of ammonium nitrate in the Secondary Wood Smoke Factor, Figure A3.8 and for the seemingly high concentrations of the OM2 factor during April 13 to 15. If the Secondary Wood Smoke was formed in a plume of ammonium nitrate, formation of secondary particles on the existing ammonium nitrate particles would be expected. If we assume that this was the case and correct the Secondary Wood Smoke for the non-wood smoke originated material we obtain the composition given in the last pie of Figure A3.8. This composition is more consistent with the Secondary Wood Smoke composition observed in the BYU study. This assumption results in reducing the concentration of Secondary Wood Smoke formed from wood smoke emitted gases to 0.44 μg/m³.

**Figure A3.8.** Comparison of the Primary Wood Smoke and Secondary Wood Smoke Factor compositions and the Secondary Wood Smoke Factor composition adjusted for the effect of ammonium nitrate (see text).
A combined source apportionment – back trajectory analysis study was conducted during February – April 2019 at the Bountiful sampling site located at Bountiful Viewmont High School, 171 W. 1370 N. Bountiful, UT (EPA AIRS code: 490110004).\textsuperscript{182} The focus of this study was not the PMF identification of sources of PM$_{2.5}$, but rather the identification of sources of dichloromethane and formaldehyde. Historic data indicates that this site has elevated concentrations of dichloromethane, with concentrations occasionally seen that would result in increased health impacts on the population with respect to the cancer risk due to exposure to dichloromethane. However, the study did produce data relative to the formation of both primary and secondary wood smoke and that will be the focus of this section of the manuscript. A PMF analysis of PM$_{2.5}$ was conducted to understand the contribution of diesel exhaust to dichloromethane.

\textit{A3.7.1 PMF Analysis:}

The PMF analysis from the Bountiful data set were limited to focus on identification of primary sources of PM$_{2.5}$. This constraint was imposed because potential secondary contributors to PM$_{2.5}$ were not measured during the study. The data available for the PMF analysis was limited to the following:

- PM$_{2.5}$ mass was measured using an R&P Model 8599 FDMS (Filter Dynamics Measurement System) Tapered Element Oscillating Microbalance (TEOM) sampler. The FDMS TEOM measures all fine particulate mass including ammonium nitrate and semi-volatile organic material but does not measure fine particulate water.\textsuperscript{44, 57}

- Two-hour averaged data for a 7 channel aethalometer.
Two-hour averaged data measured with the GC-MS OAM. This included levoglucosan, fluorene, pyrene, stearic acid and anthracene.

A total of 14 parameters and 493 two-hour averaged data sets were available for a positive matrix factorization (EPA PMF) analysis of sources of primary fine particulate material. A total of four factors were identified. This included Primary Wood Smoke, Diesel Emissions, Auto Emissions and PM$_{2.5}$ not accounted for in the PMF analysis. Details of the PMF analysis are available. Identified factors are shown in Figure A3.9.

![Bountiful Study PMF Results, µg/m$^3$](image)

**Figure A3.9.** Pie chart of the fraction of the total PM$_{2.5}$ identified with the four factors.

There are several periods in the data set when concurrent peaks are seen in the missing mass and wood smoke data shown in Figure A3.9. The elliptical circles in Figures A3.10 highlight the more prominent occurrences. It seems reasonable, based on our previous observations, to postulate these are due to secondary aerosol formed from gases emitted during the combustion of wood. The estimation of the ratio of primary to secondary wood smoke is difficult because of the lack of direct apportionment of secondary material in this study, the possible presence of other sources during the time periods highlighted, and the uncertainty of where base lines for the observed peaks should
be drawn. However, if we assume this ratio is roughly constant, as was observed in our previous studies, the best estimate of the ratio may be made for the data on February 27. Integration of these data with the estimate that the wood smoke factor data identify a reasonable base line give a ratio of secondary to primary wood smoke aerosol of 0.79. This gives the diel pattern for the estimated concentrations of secondary wood smoke aerosol shown in Figure A3.11. The remaining aerosol is labeled PM$_{2.5}$ Other in Figure A3.11. This last category will be due to secondary aerosols such as ammonium sulfate or ammonium nitrate. A pie chart of the aerosol composition based on this analysis is shown in Figure A3.12.

![Figure A3.10](image)

**Figure A3.10.** Comparison of the measured concentrations of PM$_{2.5}$, the PM$_{2.5}$ not accounted for in the PMF analysis and the concentrations of the Primary Wood Smoke Factor. Hash marks under the X axis indicate weekends.
Figure 3.11. Diel patterns for measured PM$_{2.5}$, the three factors identified in the PMF analysis and assignment of the remaining unidentified mass into two classes, see text. Hash marks under the X axis indicate weekends.
A3.8 Discussion

A comparison of the concentrations of primary and secondary wood smoke identified in the three studies discussed are given in Figure A3.13.
Figure A3.13. A comparison of the results for primary and secondary wood smoke in studies at BYU, Armstrong and Bountiful.

As indicated, both secondary and primary wood smoke were identified in all three studies with the concentrations of secondary wood smoke being comparable too or slightly less than the concentrations observed for primary wood smoke. The significantly lower concentrations of wood smoke at Armstrong as compared to BYU is attributed to the locations of the two sampling sites relative to the urban population. The lower concentrations seen at Bountiful, compared to BYU can be attributed to the Bountiful study being conducted in the spring, rather than in winter.

While all three studies provide consistent evidence for the formation of secondary wood smoke from the gaseous volatile compounds emitted during the combustion of wood, the results given provide no information on the exact chemistry or the kinetics involved in the formation of secondary wood smoke aerosols. There is a need for the further identification of the chemistry associated with the formation of secondary wood smoke aerosols. Studies of similar chemistry associated with wildfire emission would also appear warranted. A recent publication by Garafaldo
et al\textsuperscript{185} on aging in wildfire plumes indicates the formation of secondary wood smoke particulate matter is seen in the aging plume.