The Pennsylvania State University

The Graduate School

College of Earth and Mineral Sciences

BEHAVIOR OF VOLATILE ORGANIC COMPOUNDS SAMPLED IN THE BALTIMORE/DC REGION DURING JULY 2011

A Thesis in

Meteorology

by

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ABSTRACT

Ozone pollution is almost exclusively formed in the troposphere, and excessive mixing ratios occur over generally urban areas with high populations. Volatile Organic Compounds (VOCs), considered to be one of the main precursors to ozone pollution, were collected in canister samples for two sites during NASA’s Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) mission in July 2011. The two sites investigated in this study are located at Edgewood, Maryland, +39° 24’ 36.56” N, -76° 17’ 49.62” W, and Beltsville, Maryland, +39° 3’ 9.59” N, -76° 52’ 42.13” W. Though spatially and temporally limited, the analysis of these VOC measurements was detailed enough in terms of number of species to allow for the analysis of reactivities, VOC variability between collection times, and correlation studies of VOCs with a variety of atmospheric variables. Mixing ratio and reactivity studies were performed to determine relative ozone production potential of the sampled VOCs and their sources. Two case studies for canisters samples collected at the Edgewood site were used to more thoroughly investigate the impact of different air mass sources on locally measured ozone mixing ratios. The air masses measured were found to be highly variable, with the balance of anthropogenic to biogenic species measured in an air mass changing rapidly over short time periods. A diurnal signal was also picked up in the reactivity measurements from isoprene, which contributed approximately 50% of the measured VOC reactivity in midday samples. The methods used in this thesis allow for a selection method to be developed where the most important VOC species are identified and used to focus a data set. For the two sites examined in this paper, biogenics are the most important species category, with isoprene, methyl vinyl ketone, and methacrolein contributing the most reactivity, along with acetaldehyde and benzaldehyde.
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CHAPTER 1

Introduction

1.1 Ozone Pollution in the Troposphere

Tropospheric ozone ($O_3$) is a photochemical secondary pollutant created in the atmosphere from precursor emissions of nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs) under sunlight. Ozone is important in air quality management because it is a strong oxidant and reactive molecule, and can have a profound effect on human health and welfare when high ozone levels aggravate respiratory conditions. These include the development of asthma, reduced lung function across the population, and increased mortality and morbidity. [Bell et al., 2006; Gryparis, 2004; Samet et al., 2000] Additionally, ozone has negative impacts on a variety of natural resources and urban environments, especially as a stressor for foliage in agriculture and forestry [Madden and Hogsett, 2001; Krupa et al., 2000; Taylor, 2001], damage to materials, especially rubbers and unsaturated polymers [Lee et al., 1996], and as a significant greenhouse gas on regional scales [Krupa, 1997].
Figure 1-1. Ozone empirical kinetic modeling approach (EKMA) diagram developed by Kinosian [1982]. The x axis is non-methane hydrocarbons (NMHC) mixing ratios in parts per million carbon, while the y axis is NO\textsubscript{x} mixing ratios in part per million. The isopleth lines are the resulting ozone mixing ratios in parts per million. This graph is a standard EKMAN Diagram produced through modeling studies. The straight lines radiating from the origin are ratio lines of NMHC/NO\textsubscript{x}, indicating different chemical regimes.

Ozone pollution relevant to human health and welfare is almost exclusively formed in the troposphere [Hudman et al., 2004]. Because it is a secondary pollutant, mixing ratios and problem areas are controlled by the amounts of precursor emissions. Clean ozone conditions are ozone mixing ratios in the atmosphere up to 40 parts per billion by volume (ppbv) [Finlayson-Pitts and Pitts, 1997]; above these levels ozone is considered a pollutant, and monitored with threat levels assigned based on atmospheric mixing ratios [Mintz, 2009]. Because the main chemical precursors are NO\textsubscript{x} and VOCs, the rate limiting step for ozone production will be determined by the mixing ratios of these two things. Modeling studies have produced ozone isopleth diagrams to identify NO\textsubscript{x} and VOC limited requiems, such as the one shown in Figure 1-1, from Kinosian.
[1982]. Limiting one or the other of these precursors changes the amounts of ozone that can theoretically be produced within an air mass.

The United States Environmental Protection Agency (EPA) monitors ozone mixing ratios around the United States with commercial instruments, and assesses air quality with the National Ambient Air Quality Standards (NAAQS). The current EPA standards for ozone are an eight-hour average of 0.075 parts per million by volume (ppmv) calculated with a running mean (US EPA), with financial penalties for areas which consistently fail to meet standards [Anderson, 2001]. Air quality is communicated to the public with the Air Quality Index (AQI), which simplifies air pollution mixing ratios into an easily understood threat level [Mintz, 2009]. The break points of AQI are shown in Table 1-1. AQI uses a color code to categorize air quality – green for “good”, yellow for “moderate”, orange for “unhealthy for sensitive groups”, and red for “unhealthy.” Hazardous or code red AQI is used as the benchmark between acceptable and unacceptable air quality for monitoring purposes.

Table 1-1. EPA AQI ozone mixing ratio benchmarks for assessing air quality threat level. These values are based on an 8 hour running average, where the AQI threat level is assessed based on the maximum observed value.

<table>
<thead>
<tr>
<th>Color (Description)</th>
<th>Mixing Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green (good)</td>
<td>0 – 59 ppbv O₃</td>
</tr>
<tr>
<td>Yellow (moderate)</td>
<td>60 – 75 ppbv O₃</td>
</tr>
<tr>
<td>Orange (Unhealthy for Sensitive groups)</td>
<td>76 – 95 ppbv O₃</td>
</tr>
<tr>
<td>Red (Unhealthy)</td>
<td>96 – 115 ppbv O₃</td>
</tr>
<tr>
<td>Purple (Very Unhealthy)</td>
<td>116 – 374 ppbv O₃</td>
</tr>
<tr>
<td>Maroon (Hazardous)</td>
<td>375+ ppbv O₃</td>
</tr>
</tbody>
</table>
Ozone pollution problem areas are generally urban areas with high populations. Amendments made in 1990 to the Clean Air Act of 1963 set mandatory air quality requirements with time tables based on the severity of the pollution [Taylor, 2001; Waxman, 1991]. These amendments put restrictions on NO\textsubscript{x} emissions from automobiles and power plants, and leading to a decrease in ozone pollution levels in the major urban areas most affected (including the urban areas of LA and New York City) [Fiore et al., 1998]. However, according to EPA monitoring ozone levels remain problematically high at many sites in the United States. On the East Coast the United State of America, the Baltimore-Washington, D.C. metropolitan area remains the most problematic in the region; excessive ozone is frequently measured there [Ryan, 1995]. This region has been assigned a moderate 8-hour ozone nonattainment classification, which means that 8-hour ozone levels exceeded the 0.086 ppm level for the third most polluted day of the year [Lefohn et al., 1998; John and Chameides, 1997].

1.2 Ozone Chemistry

The chemistry of the troposphere is summarized thoroughly by Seinfeld and Pandis [2006] and all chemistry in this section is adapted from their work. Ozone is a secondary photochemical species only released directly to the atmosphere under exceptional conditions. It is formed under sunlight by the photolysis of NO\textsubscript{2}. NO\textsubscript{2} and ozone reach a photostationary state in clean conditions, shown in equations 1-1, 1-2 and 1-3; this means that while the chemistry shown in these equations is continually occurring, mixing ratios remain constant. The total amount of ozone in the troposphere can be calculated as the sum of ozone plus NO\textsubscript{2} since the photolysis of is nearly instantaneous under sunlight.

\[
\begin{align*}
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \quad \text{Eq 1-1} \\
\text{O}_2 + \text{O} + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad \text{Eq 1-2}
\end{align*}
\]
However, the steady state equations are insufficient to explain the observed mixing ratios of ozone in the atmosphere. Because the photolysis of NO\(_2\) is the only significant method for producing ozone, the photostationary state must be getting disrupted in a way that produces NO\(_2\) without destroying ozone. This occurs through the oxidation of NO by the hydroperoxyl radical, HO\(_2\). This causes the chemistry to bypass the normal photostationary state and allows ozone to build up. The production of HO\(_2\) begins with the production of the hydroxyl radical (OH) from ozone.

Ozone can be photolyzed in a manner similar to NO\(_2\). When this occurs an energetically excited oxygen atom is produced, noted as O(\(^{1}\)D) and shown in equation 1-4. This excited species has two reaction paths that it can follow after being produced: either it reacts with a chaperone molecule, M (generally O\(_2\) or N\(_2\)), which quenches the excited state, as shown in equation 1-5, or it reacts with water vapor in the atmosphere to produce the hydroxyl radical, shown in equation 1-6. The production of OH through this reaction path is significant but dependent on environmental relative humidity. At 80% relative humidity almost 40% of the O(\(^{1}\)D) atoms will react to form OH radicals [Seinfeld and Pandis, 2006].

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{Eq 1-3} \\
\text{O}_3 + \text{hv} & \rightarrow \text{O}_2 + \text{O}(^{1}\text{D}) \quad \text{Eq 1-4} \\
\text{O}(^{1}\text{D}) + \text{M} & \rightarrow \text{O} + \text{M} \quad \text{Eq 1-5} \\
\text{O}(^{1}\text{D}) + \text{H}_2\text{O} & \rightarrow 2 \text{OH} \quad \text{Eq 1-6}
\end{align*}
\]

OH is extremely reactive but maintains relatively steady atmospheric mixing ratios because it renews itself in catalytic reactions. In the absence of measurements it is generally assumed to be at a constant concentration, which is estimated at a global mean of approximately 1.0 x 10\(^6\) molecules cm\(^{-3}\). The majority of the atmosphere, N\(_2\) and O\(_2\), will not react with OH due to their extremely stable structures. However, VOCs in the atmosphere are readily oxidized by
OH, and the peroxy radical (RO₂) is produced along with water, shown in equation 1-7. The RO₂ radical will rapidly react with NO to produce NO₂, shown in equation 1-8, without the normally related destruction of ozone seen in the photostationary state.

\[
\text{VOC} + \text{OH} \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad \text{Eq 1-7}
\]

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO}^\prime + \text{NO}_2 + \text{HO}_2 \quad \text{Eq 1-8}
\]

Additionally, equation 1-8 produces an HO₂ radical, which can react with another NO molecule to produce NO₂ as well as regenerating an OH radical, equation 1-9. Between equations 1-8 and 1-9, two molecules of NO₂ have been produced. Both NO₂ molecules will immediately photolyze to form ozone, leading to the buildup of ozone in excess of that normally generated by the photostationary state.

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{Eq 1-9}
\]

This ozone production will continue until there is a termination step in the chemical cycles. If there is excess NO₃ in the environment, OH can react with NO₂ to form nitric acid (HNO₃), shown in equation 1-10. This is a termination step, since it prevents the oxidation of VOCs and consumes an NO₂ molecule that otherwise produce ozone. However, this only occurs under highly saturated conditions leading to some interesting behavior around highly NO₃-saturated environments, such as urban centers or power plant plums. In these cases, ozone levels will be attenuated due to this termination step halting the chemical reactions. In contrast, if the area is highly VOC-saturated, ozone production can be halted from radical-radical reactions, which will consume the radicals involved in the oxidation of VOCs. An example is shown in equation 1-11.

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad \text{Eq 1-10}
\]

\[
\text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2 \quad \text{Eq 1-11}
\]
1.3 DISCOVER-AQ Field Campaign

The Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) mission is a multiyear NASA field campaign conducted to investigate air quality dynamics in several areas with poor air quality. The first year of the mission thoroughly sampled over the Baltimore-Washington, DC metropolitan region during July 2011.

The campaign used an enhanced ground monitoring network coupled with intensive aircraft sampling over six Maryland sites: Aldino, Beltsville, Edgewood, Essex, Fairhill, and Padonia. Two aircraft were involved in sampling. The NASA P-3B Airborne Laboratory (P-3B aircraft), flew low spirals over the sites in the boundary layer, and the NASA King Air Airborne Laboratory (Beechcraft B200 Aircraft) flew at high altitude to mimic satellite column measurements. A map of the P-3B aircraft routes is shown in Figure 1-2. In addition to the aircraft measurements, ozonesondes on weather balloons were launched throughout the campaign to obtain total column measurements of ozone at two sites, Beltsville, MD and Edgewood, MD.
Figure 1-2. Map of the 2011 DISCOVER-AQ air quality sites. The bold yellow line is the flight track of the P-3B flight track; circles in the track indicate spiral locations above ground measurements.

The Pennsylvania State University Nittany Atmospheric Trailer and Integrated Validation Experiment (NATIVE) trailer was situated at the Edgewood site and took frequent measurements of ozone, reactive nitrogen, SO₂, and meteorological data. While the main objective of the mission was to improve satellite remote sensing of air quality, the intensive nature of the mission allows for ground-based analysis as well. Although July 2011 was unusually hot, the ozone measurements were much lower than expected. Ground measurements of ozone and precursor species generated a rich data set for investigation of this unexpected behavior, since higher ozone levels are generally associated with higher temperatures at any given location.
Additionally, the Edgewood and Beltsville sites took explicit VOC measurements during the field campaign using vacuum evacuated canisters. Each canister sample was collected for one hour using a specialized pump to conduct a controlled fill. These data are the foundation for this project. Collection methods varied between the sites. The Edgewood site was thoroughly sampled on four days, while the Beltsville site measured one or two samples per day over a greater number of days and meteorological regimes.

1.4 Thesis Overview

Understanding VOC behavior for the DISCOVER-AQ campaign presents challenges, especially with the spatially and temporally scattered sampling. This paper presents an analysis of the VOC behavior for the Edgewood and Baltimore sites using the canister data collected in July 2011. Despite the limited data set, there are some analyses that can be performed to provide greater insight into the behavior of VOCs and their effect on air quality during the mission.

The strength of the data set analyzed in this paper comes from its detailed nature. A large amount of data was collected over a limited number of days, which allows short scale analysis as well as measurements for a large number of species. Previous work collecting VOC data in the Mid-Atlantic region has been done primarily through the photochemical assessment monitors (PAMS) network which is run by the EPA. A doctoral thesis by Raymond Morales through the University of Maryland about the VOC species in the Baltimore/DC region exists, but it has not at this time been published as a paper. A PAMS station is located in Essex, Maryland, and run by the Maryland Department of the Environment (MDE), but very little of the data has been published. A limited number of species (58) have been collected with this kind of monitoring, and the analysis has focused on VOC distributions and associated regimes [Vukovich, 2000].
Additional work has been done with VOCs has been done around the United States in field campaigns, generally with aircraft measurements. These studies analyze a limited number of species above the ground in an attempt to understand how VOCs are affecting ozone mixing ratios in the troposphere. Studies by research groups associated with NOAA, NCAR and NASA have utilized some canister samples when looking at ozone dynamics [Ryerson et al., 2003; Apel et al., 2003; Jobson et al., 1998; Chen et al., 2007]. However, the strength of the data set used in this thesis comes from the detailed nature of the sampling, with many samples collected over a limited number of days. Additionally, very few papers have published VOC studies of this region, with any that have been written looking more at climatological behavior [Russo et al., 2010; Kleinman et al., 2000, Bell and Ellis, 2005].

Chameides et al. [1992] was used as the foundation for this work. Understanding which VOCs control the chemistry in the Baltimore-Washington D.C. metropolitan region, and extracting information about the relative strength of VOC sources and the behavior of ozone as related to VOCs, allows an explicit analysis of the local chemistry. This analysis allows identification of the ozone-pertinent chemical species that form the foundation for future chemical modeling of the region. The methods used in this thesis are a way to narrow down a wide data set and identify which VOC species are important in an individual or conglomerate air sample.

This study will begin by examining the campaign’s complete data set to select the most important chemical species at each site, using mixing ratios and reactivity calculations. This thesis will also attempt to explain the sources and dependencies of the measured VOCs using correlations with both NATIVE measured data and other VOCs. Finally, this paper will examine several canisters to use as case studies for the broader campaign to explain the specifics of how VOCs are impacting local air chemistry. The overall goal of this thesis is to use a temporally limited but very detailed data set to understand some of the VOC dynamics impacting the
polluted Baltimore-Washington, D.C. urban region and demonstrate the methods that can be used to focus a VOC data source.
CHAPTER 2
Methods and Experimental Setup

2.1 Site Descriptions

VOC canister samples were collected at two sites in the Baltimore-DC metropolitan area in July 2011. Both sites were in semirural locations, and canister samples were taken in a mowed meadow surrounded by mixed deciduous and evergreen trees. Both sites were located near industrial zones and high capacity freeways. The Edgewood site is located just south of the I-95 freeway connecting Baltimore, Maryland, to Wilmington, Delaware, while the Beltsville site is located between Washington D.C. and Baltimore, Maryland, between the I-95 freeway and the Baltimore-Washington Parkway. Figure 2-1 shows the relative locations of the sites.
Figure 2-1. Sampling site locations for VOC canister samples in the DISCOVER-AQ field campaign of July 2011

The Edgewood site is located at latitude and longitude +39° 24' 36.56" N, -76° 17' 49.62" W on the Aberdeen Proving Ground. The NATIVE trailer operated by the Pennsylvania State University was the sampling location. Samples were collected at 4 meters above the ground through the general sampling inlets used for the chemical instrumentation housed in the NATIVE trailer. The Beltsville site is located at +39° 3' 9.59" N, -76° 52' 42.13" W and is operated and maintained as a permanent research station by Howard University. The setting is residential, but is in close proximity to a light industrial zone and high capacity roads.
2.2 Sampling Methods

VOC samples were collected in 3.2 L evacuated canisters which were electropolished to prevent loss of sensitive species on the walls. The canisters were evacuated to -25 inches of mercury (in Hg) (-845 mbar) before sampling. The evacuated canisters were connected to a specially designed pump with Teflon tubing. A diagram of the experimental set up is shown in Figure 2-2. Canisters were opened for one hour and slowly brought to pressure; ending pressures were between 10 – 25 pounds per square inch (psi) (690 – 1720 mbar), depending on the sample.

![Diagram of VOC canister setup]

Figure 2-2. VOC canister experimental setup. The evacuated canister has an internal volume of 3.2 L.

Filled canisters were sealed and shipped to Environment Canada in Ottawa, Ontario for analysis. Samples were analyzed with an Agilent 6890 gas chromatograph and an Agilent 5973 MSD quadrupole mass-selective detector, using a 60 meter, 0.32 mm I.D. fused silica capillary column with a 1.0 um film thickness of J&W DB-1 bonded liquid phase. All samples were preconcentrated with an Entech Model 7100 preconcentrator with auto-sampler (Entech Instruments, Inc., Simi Valley, CA), a cryogenic preconcentration technique.

Pre-concentration of the samples was performed on air drawn directly from the sealed canister samples, with all flows controlled with mass flow controllers. A 500 ml sample of air was passed through a glass bead trap maintained at -170°C, then concentrated with a microscale...
purge and trap to remove water resulting in a final sample of 0.5 cc in a cryogenic glass bead trap. This concentrated sample was heated to 25°C and maintained while 50 cc of helium was passed through, sweeping all VOCs into a secondary Tenax trap at -50°C. Following collection in the secondary trap, the VOC’s were back-flushed while heating to 180°C and collected in an open-tubular focusing trap at -160°C. All VOCs in this final trap were rapidly heated to 100°C, and rapidly injected onto the analytical column.

Column temperature was initially -60°C for 3 minutes, then ramped to 250°C at 8°C/min. The GC-MSD was operated in the selected ion monitoring (SIM) mode. Species were identified by retention time and ion relative abundance. Quantification was based on daily 5-point linear regression calibration curves obtained from analysis of an external standard mixture from Scott Environmental Technology Inc.

The sample dates and times are shown in Table 2-1 for Edgewood, Maryland and Table 2-2 for Beltsville, Maryland. The Edgewood site was sampled intensively on July 10, 11, 21, and 22, with approximately six samples each day evenly spaced throughout the day from morning to evening. The Beltsville site took a different approach to sampling, and collected fewer samples over a greater number of days.

**Table 2-1. Edgewood MD Canister Sampling dates, times, pressure, and flow information**

<table>
<thead>
<tr>
<th>Start Date/Time (EDT; UTC-4)</th>
<th>End Date/Time (EDT; UTC-4)</th>
<th>Canister #</th>
<th>Starting vacuum Pressure (in Hg)</th>
<th>Ending Pressure (psi)</th>
<th>Flow Rate (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0700 10 JUL 2011</td>
<td>0830 10 JUL 2011</td>
<td>ARQP002</td>
<td>-25</td>
<td>18.5</td>
<td>90</td>
</tr>
<tr>
<td>1000 10 JUL 2011</td>
<td>1100 10 JUL 2011</td>
<td>ARQP005</td>
<td>-25</td>
<td>18</td>
<td>100</td>
</tr>
<tr>
<td>1300 10 JUL 2011</td>
<td>1400 10 JUL 2011</td>
<td>ARQP020</td>
<td>-25</td>
<td>18</td>
<td>100</td>
</tr>
<tr>
<td>1600 10 JUL 2011</td>
<td>1700 10 JUL 2011</td>
<td>ARQP022</td>
<td>-25</td>
<td>17.8</td>
<td>100</td>
</tr>
<tr>
<td>1900 10</td>
<td>2000 10 JUL</td>
<td>ARQP026</td>
<td>-25</td>
<td>17.5</td>
<td>100</td>
</tr>
<tr>
<td>Start Date/Time (EDT; UTC-4)</td>
<td>End Date/Time (EDT; UTC-4)</td>
<td>Canister #</td>
<td>Starting vacuum Pressure (in Hg)</td>
<td>Ending Pressure (psi)</td>
<td>Flow Rate (sccm)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>------------</td>
<td>----------------------------------</td>
<td>----------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>1103 15 JUL</td>
<td>1203 15 JUL</td>
<td>PMD 140</td>
<td>-26</td>
<td>11</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2.2. Beltsville MD Canister Sampling dates, times, pressure, and flow information
This section summarizes the meteorology of each site for days that canister samples were collected. The means are used for temperature, relative humidity and pressure to give a snapshot comparison between sampled days. Data for the Edgewood site was taken from the Maryland Department of the Environment (MDE) observations at the DISCOVER-AQ Aberdeen Proving Ground location where the NATIVE trailer was located. The Beltsville observations were taken on site.
Figure 2-3. Meteorology summary for Edgewood, Maryland. Meteorological data was taken from MDE instrumentation at the site, and averaged for each day when canister samples were collected. Temperature in degrees Celsius is shown on the top in red, relative humidity in percentage is shown in the middle in purple, and pressure is shown on the bottom in blue.

The meteorological results for Edgewood are shown in Figure 2-3. Samples for this site were collected on five days over the campaign. For the sampled days, temperatures increased over the campaign, with the final two days of canister sampling, the 21st and the 22nd being the hottest, around 30 degrees Celsius. Temperature results are shown in red. Mean relative humidity, shown in purple, oscillates but remains high at over 60% for all five days. Pressure is shown in blue.
Figure 2-4. Wind rose for 10 July, Edgewood, Maryland. Measurements were taken from MDE instrumentation at the site, and are displayed as points with radial distance from the centre displaying wind speed in meters per second and the point around the circle demonstrating wind direction in degrees. Data for this site was taken in one minute averages.

The Edgewood wind rose for July 10, 2011 is shown in Figure 2-4. The wind roses for the other canister sampled days can be found in Appendix A. Data for this graph was taken from MDE instrumentation located at the Edgewood site, and was available in one minute averages. The radial distance from the center of the graph shows the wind speed in meters per second, while
the angle around the circle is the wind direction in degrees. The graph effectively captures the overall wind pattern for the day. Wind for this day comes predominantly from the south west, with the zero/360 angle indicating north.

Figure 2-5. Meteorology summary for Beltsville, Maryland. Meteorological data was taken from MDE instrumentation at the site, and averaged for each day when canister samples were collected. Temperature in degrees Celsius is shown on the top in red, relative humidity in percentage is shown in the middle in purple, and pressure is shown on the bottom in blue.

The Beltsville meteorological results are shown in Figure 2-5. More days were sampled at this site, although fewer canisters were collected overall. Temperature results for this site are shown in red, and indicate that the high temperatures observed at Edgewood on the 21st and 22nd were not anomalous, and were the two hottest days measured during VOC sampling. Temperatures on the other days remained high. The relative humidity results are shown in purple,
with most days measuring moderately high, but the 25th showing a peak value for the days measured. The pressures are shown in blue, and indicate a generally lowering pressure throughout the days measured.

Figure 2-6. Wind rose for 15 July, Beltsville, Maryland. Measurements were taken from instrumentation at the site, and are displayed as points with radial distance from the centre displaying wind speed in meters per second and the point around the circle demonstrating wind direction in degrees. Data for this site was taken in one hour averages.
The Beltsville wind rose for July 15, 2011 is shown in Figure 2-6. The wind roses for the other canister sampled days can be found in Appendix A. Data for this graph was taken from instrumentation located at the Beltsville site, and was available in one hour averages. The radial distance from the center of the graph shows the wind speed in meters per second, while the angle around the circle is the wind direction in degrees. The graph captures the overall wind pattern for the day. Wind for this day comes predominantly from the South West, with the zero/360 angle indicating north.
CHAPTER 3

Volatile Organic Compound Mixing Ratios and Reactivity

The canister VOC data set analyzed 193 species, organized between polar and nonpolar functional groups. However, only a handful of these are active for ozone production. To determine which VOCs are significant for any given sample, a method is needed for identifying the most reactive molecules. Reactivity calculations are the simplest way to make a quantitative assessment of activity in the atmosphere, with a simple mixing ratio calculation based on rate constants [Chameides et al., 1992]. The data set is analyzed by mixing ratios, sections 3.1-3.3, reactivity with the hydroxyl radical, section 3.4, and Propyl-equivalent mixing ratio, section 3.5. An additional two sections examine how VOC reactivities correlate with ozone mixing ratios, section 3.6, and ozone production efficiency values for the canister samples, section 3.7.

3.1 Mixing Ratios

VOC species with higher mixing ratios are more likely to be reacting in the atmosphere. Higher mixing ratios mean that a species is more likely to be interacting with an atmospheric oxidant and forming the peroxy radicals that go on to form ozone. Determining which VOCs are most prevalent in an air mass can also indicate where the air is originating.

To determine which VOCs are most important for each site, canister samples for each individual species measured in the dataset were analyzed and the median was taken. A cutoff value of 0.05 ppbv was assigned for clarity in presenting the data; median mixing ratios below this value are small and can be dropped from the analysis. The error bars are included to show variation in the mixing ratio values and are constructed from the minimum and maximum VOC
mixing ratios for each VOC species over the campaign. Some VOCs exhibited diurnal cycles or spikes in particular canister samples, which can lead to large variations in mixing ratios, while others remained fairly steady for the entire campaign.

VOCs are organized by emissions source: biogenic, anthropogenic, mixed source and unknown. All VOC types were taken from previously published literature, with the exception of the unknown label, which indicates an unreferenced VOC. Source labels indicate the sector which commonly contributes a specific VOC to the atmosphere (EPA 2005 National Emissions Inventory). For example, propane is a commonly used fuel gas, but in the atmosphere it is often emitted from biogenic sources [Guenther et al., 2000].

Figure 3-1. Median VOC mixing ratios in ppb at Edgewood, Maryland. Median mixing ratios below 0.05 ppbv are excluded from the graph for clarity. The error bars are included to illustrate the variability of the measurements over the campaign, and are constructed from minimum and maximum VOC mixing ratios for each species over the campaign.
The median mixing ratio results for all Edgewood, Maryland canisters are shown in Figure 3-1. Biogenic and mixed source VOCs greatly predominate the VOC mixing ratios in the air, particularly isoprene and its reaction products methyl vinyl ketone (MVK) and methacrolein (MAC) as well as smaller molecules such as ethanol, methanol and acetone. The samples show a variety of anthropogenic species which were evenly concentrated. Biogenic species appear to dominate the mixing ratios of atmospheric chemicals, and appear to correlate with the semi-rural location of the Edgewood site [Biesenthal et al., 1998]

![Beltsville MD VOC Mixing Ratios, Median Values](image)

Figure 3-2. Median VOC mixing ratios in ppb at Beltsville, Maryland. Median mixing ratios below 0.05 ppbv are excluded from the graph for clarity. The error bars are included to illustrate the variability of the measurements over the campaign, and are constructed from minimum and maximum VOC mixing ratios for each species over the campaign.

The median mixing ratio results for the Beltsville, Maryland samples are shown in Figure 3-2. While very similar mixing ratios were observed relative to the Edgewood site, there are some
key differences. First, VOC mixing ratios at Beltsville were generally lower. Second, while the mixing ratio patterns were generally very similar, ethanol is present in larger amounts and is more variable at the Beltsville site than at the Edgewood site, whereas methanol has a large but fairly steady mixing ratio value throughout the campaign. Methanol is generally categorized in this work as a mixed source VOC, although it has significant biogenic sources, while ethanol can be considered an indicator for some anthropogenic activity [Singh et al., 2000].

Table 3-1. Mixing ratio selected species for both sampling sites.

<table>
<thead>
<tr>
<th>Species</th>
<th>Location</th>
<th>Chemical Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butanol (Butyl alcohol)</td>
<td>Beltsville &amp; Edgewood</td>
<td>Alcohol</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>“</td>
<td>Alkane</td>
</tr>
<tr>
<td>2-Methyl-Propanal (Isobutylaldehyde)</td>
<td>“</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>2-Pentanone</td>
<td>“</td>
<td>Ketone</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>“</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Acetone</td>
<td>“</td>
<td>Ketone</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>“</td>
<td>Nitrile</td>
</tr>
<tr>
<td>Acetylene</td>
<td>“</td>
<td>Alkyne</td>
</tr>
<tr>
<td>Acrolein (2-Propenal)</td>
<td>“</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>“</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Butane</td>
<td>“</td>
<td>Alkane</td>
</tr>
<tr>
<td>Butylaldehyde (Butanal)</td>
<td>“</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>“</td>
<td>Haloalkane</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>“</td>
<td>Haloalkane</td>
</tr>
<tr>
<td>Ethane</td>
<td>“</td>
<td>Alkane</td>
</tr>
<tr>
<td>Ethanol</td>
<td>“</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Ethylene</td>
<td>“</td>
<td>Alkene</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>“</td>
<td>Epoxide</td>
</tr>
<tr>
<td>Hexanal</td>
<td>“</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Isobutane (2-Methylpropane)</td>
<td>“</td>
<td>Alkane</td>
</tr>
<tr>
<td>Isoprene (2-Methyl-1,3-Butadiene)</td>
<td>“</td>
<td>Alkene</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>“</td>
<td>Alcohol</td>
</tr>
<tr>
<td>MAC (2-Methyl-2-propenal)</td>
<td>“</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>MEK</td>
<td>“</td>
<td>Ketone</td>
</tr>
<tr>
<td>Methanol</td>
<td>“</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>“</td>
<td>Ester</td>
</tr>
<tr>
<td>MVK</td>
<td>“</td>
<td>Enone</td>
</tr>
<tr>
<td>Pentanal</td>
<td>“</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Pentane</td>
<td>“</td>
<td>Alkane</td>
</tr>
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<td>Alkane</td>
</tr>
<tr>
<td>Compound</td>
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<td>Location</td>
</tr>
<tr>
<td>--------------------------</td>
<td>---------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Propene</td>
<td>Alkene</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>Aromatic Alkene</td>
<td></td>
</tr>
<tr>
<td>1-Butene; 2-Methylpropene</td>
<td>Edgewood Only</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>Aromatic Alkene</td>
<td></td>
</tr>
<tr>
<td>Carbon tetracloride</td>
<td>Haloalkene</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>Aromatic Alkene</td>
<td></td>
</tr>
<tr>
<td>2-Methylbutanal(ISOvaleraldehyde)</td>
<td>Beltsville Only</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>Sulfide</td>
<td></td>
</tr>
<tr>
<td>Limonene</td>
<td>Monoterpene</td>
<td></td>
</tr>
</tbody>
</table>

The mixing ratios between the sites appear to be fairly equivalent, which is expected based on the physical similarity of the sites. The higher mixing ratio of VOCs at the Edgewood site is probably due to its location downwind of Baltimore, Maryland, and the higher mixing ratios of biogenic species may be because of the more rural setting of the Edgewood site. The causes of the other differences are not as clear. The differences in methanol and ethanol may be a result from the Beltsville site’s proximity to the I-5 corridor, while the Edgewood site is more isolated from major roads. Naik et al. [2010] calculated that the US East Coast has industrial and biofuel sources of ethanol, and the increased addition of ethanol to car fuel could be the source of the spikes observed in the canisters samples [Millet et al., 2010], especially at the Beltsville site.

Understanding the overall differences between these two sites does not provide a clear picture of how these mixing ratios changed throughout the day. The Edgewood site samples were taken frequently on a small number of days, and can be used to investigate how mixing ratios change diurnally. Canisters were grouped together based on start time, and the mixing ratio median for those canisters were calculated and plotted like the overall median mixing ratio graphs.
Figure 3-3. Time series measurements of two example VOC species presented in concentration ($\mu$g m$^{-3}$) collected at Edgewood, Maryland. The x axis is time in fractional day. Isoprene is shown on the left and demonstrates a distinct diurnal variation, with peak concentrations occurring in midday and falling to low values in the morning and evening samples. Toluene is shown on the right, and exhibits a more random variability in measured concentration.

The mixing ratios of individual species can vary widely between samples, sometimes due to diurnal variability in the sources, sometimes due to changes based on advection of air masses. Figure 3-3 shows the variability of isoprene and toluene in terms of concentration (analogous to mixing ratio, in units of $\mu$g m$^{-3}$). When samples are compared between collection times, as they are in the following graphs, patterns will arise based on the kind of variability that a particular species will have. This is also the cause of the variability error bars that have been included on the median VOC plots throughout this thesis. Species with high variability between canisters due to diurnal changes in the VOC source will show much larger variability error bars.
Figure 3-4. Median VOC mixing ratios in ppb at Edgewood, Maryland, in the 0700 EDT canisters. Species with a median mixing ratio below 0.05 are excluded from the graph for clarity. Error bars are constructed from minimum and maximum VOC mixing ratios for each species over the campaign for canisters sampled at this time.

Figure 3-4 shows the mixing ratio values for the 0700 EDT canister samples. Grouping the canisters by collection time allows more focused analysis on time of day. Differences are quickly apparent between the median values and these morning canisters—notably, a leveling off of the mixing ratios of the species passing the cutoff value of 0.07 ppbv. The dominating species change as well. Isoprene is less abundant, while acetone and methanol dominates the samples. The morning canisters have the most anthropogenic species; this is probably the result of a low boundary layer trapping any overnight emissions close to the ground, resulting in inflated mixing ratios for these early morning samples.
Figure 3-5 shows the results from the 1400 EDT canister samples. Acetone dominates the mixing ratios for these samples, while isoprene is a relatively minor VOC. Methanol, ethanol, and acetaldehyde are all relatively concentrated, but many of the unknown sourced VOCs have vanished, as well as the xylenes in the mixed source VOCs. This can be explained by diurnal VOC oxidation, which is well underway by 1400 EDT. Any species capable of being oxidized can be predicated to decrease in mixing ratio as VOC oxidation occurs.
Figure 3-6. Median VOC mixing ratios in ppb at Edgewood, Maryland, in the 1900 EDT canisters. Species with a median mixing ratio below 0.05 are excluded from the graph for clarity. Error bars are constructed from minimum and maximum VOC mixing ratios for each species over the campaign for canisters sampled at this time.

The final set of samples was collected at 1900 EDT, shown in Figure 3-6. Acetone and methanol are the dominating species based on mixing ratios, with significant contributions from the biogenic species. Many of these species are reaction products from atmospheric oxidation of larger, more complicated VOCs. However, mixing ratios of the main contributing VOCs are generally steady throughout the day. The mixing ratios do not reveal any of the major chemical processes occurring at either site, and generally only reflect the environment in which each site is located. Additionally, while a particular species may be highly concentrated, chemical reactivity and the potential for creating ozone is only partially based on mixing ratios. These aspects of VOC behaviors will be explored in the later part of chapter 3.
3.2 Vertical Variability

A critical factor in understanding VOC behavior in the troposphere is to understand how much the air is connected between the surface, where VOCs are being emitted, and the air aloft. Ozone’s vertical structure is important because of its dual role as a pollutant and protector, with ozone at high altitudes shielding the planet from high energy ultraviolet light [Grenfell et al., 2006] and ozone in the troposphere behaving as a pollutant as discussed in Chapter 1. Understanding whether VOCs on the ground are being mixed to the top of the boundary layer helps us understand how ozone may be produced throughout the boundary layer.

Several species were measured in the P3B aircraft spirals above the sites, including acetaldehyde, acetonitrile, acetone, methanol, toluene, isoprene, the sum of MVK and MAC, xylenes, and monoterpenes. These are all species that were also included in the canister samples. The aircraft did low spirals over the sites, which allows an examination of the vertical distributions of these species over both the Edgewood and Beltsville, Maryland, sites.

The graphs below show data from flights that occurred when canister samples were occurring concurrently. The center line of each plot is the mean value of all spirals for a given height. The grey lines show minimum and maximum mixing ratios for each height. A greater separation between the grey lines indicates greater variability. The shapes of the profiles can be used to evaluate how likely a species is to be well mixed in the boundary layers, with the species having longer atmospheric lifetimes showing a more vertical, less variable profile with altitude. Acetonitrile, acetone and toluene are three examples of long-lived species having well mixed profiles; these can be compared to isoprene, for instance, which has a short atmospheric lifetime of approximately one hour. Species that react quickly will show rapidly decreasing mixing ratios as observations are taken higher up in the atmosphere.
The vertical mixing ratio variability for Edgewood, Maryland, is shown in Figure 3-7. The profiles for the nine relevant species are displayed in a grid for clarity, with mixing ratio represented on the x-axis and altitude on the y-axis. Whereas the majority of the species show fairly well mixed profiles, there are several species that merit more discussion. The methanol
profile shows that there is a significant spike in methanol mixing ratio in the lowest levels of at least one of the spirals. This matches the observation of high methanol mixing ratios and variability in the Edgewood, Maryland, ground samples. The bottom point in the Edgewood methanol profile is a median value of 5.96 ppbv; the ground median value for all canisters was 5.61 ppbv. Comparatively, both the vertical profiles and the ground measurements of methanol show spikes, with the methanol profile spiking to 7.31 ppbv in the lowest level, while the ground measurements have a maximum value of 45.4 ppbv. While the ground variability is much higher, the profile shows that the methanol spikes are visible even above the ground.

The dynamics of isoprene and its reaction products, the sum of MVK and MAC, warrant a closer look as well. Isoprene has a uniquely shaped profile at this site, with large mixing ratios and substantial variability at low altitudes. However, mixing ratios rapidly decrease with increased altitude. This indicates a large isoprene source at the ground, which is expected due to isoprene’s strong biogenic source. Progressively less isoprene gets mixed into higher altitudes, almost certainly because it is being oxidized and reacted away to form reaction products. The measured isoprene reaction products, the sum of MVK and MAC, reinforce this idea, with a peak mixing ratios at a higher altitude then that of isoprene. This indicates that isoprene oxidation is taking place with vertical transport up the column – isoprene is being reacted away and decreasing in mixing ratio, with MAC and MVK increasing vertically as reaction products. Eventually both fall with height, as the more reactive isoprene is reacted away and stops contributing reaction products. MAC and MVK both have a smaller reactivity value then isoprene, which means that they contribute less to the overall atmospheric chemistry.
Figure 3-8. Vertical mixing ratios measured on NASA’s P3B aircraft at Beltsville, Maryland. The black dots indicate the mean mixing ratio at each altitude. The grey lines show the minimum and maximum mixing ratios for those altitudes, showing overall variability of the VOCs measured above the ground.

Figure 3-8 shows the profile mixing ratios for the Beltsville site. While similar to the Edgewood results, there are a few noteworthy differences. The methanol profile lacks the mixing ratio spike at the lowest levels observed in the Edgewood results, explaining the differences observed between the means of both sites. While there is no profile ethanol measured, the high
campaign variability observed at the Beltsville site in the canisters is probably due to a similar spike in concentration above the ground.

The isoprene profile is similar for the Beltsville site, and includes the expected low altitude peak in mixing ratios. The MVK and MAC plot does not show the low altitude spike observed in the Edgewood profiles. The isoprene reaction products are much better mixed over Beltsville, indicating that there may be less OH available above the sites acting as an oxidant.

Species that are capable of being mixed upwards are also capable of being mixed downwards. The source of most of the VOCs, especially the nine being measured by the P3B aircraft, is primarily on the ground. However, as the VOCs are pulled aloft by circulations in the boundary layer, they react and produce secondary products that can be mixed vertically and measured on the ground. Critically, some of the VOC amounts measured on the ground is not necessarily directly emitted, but may be indicative of atmospheric reactions.

3.3 OH Reactivity

While understanding mixing ratios of VOCs is important, it does not provide the entire story for VOC reactions in the local atmosphere. High VOC mixing ratios does not necessarily indicate that a particular VOC is highly reactive or have a high potential for forming ozone. To more completely describe VOC behavior another criteria for assessing this data set is required. OH reactivity values are very useful for this kind of analysis.

The hydroxyl radical, OH, is the major tropospheric oxidant, reacting with most trace gases and forming the foundation of atmospheric reactions. OH is regenerated by many of its reactions through catalytic cycles, so it is generally assumed to be at a constant concentration in the absence of measurements, which for a global mean is estimated at approximately $1.0 \times 10^6$ molecules cm$^{-3}$ [Seinfeld and Pandis, 2006]. OH reactivity is shown in equation 3-4, and is the
product of VOC concentration and the reaction rate of that specific VOC with OH. The reaction rate is a secondary reaction rate, with units of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). A correction factor is included to convert the concentration to ppbv for each \(k_{OH}\) value. The OH reactivity value will therefore be in units of s\(^{-1}\) when the calculation is complete, giving a consumption rate of OH for each VOC present in our samples.

\[
\text{OH reactivity} = [\text{VOC}] \times k_{OH}(\text{VOC}) \quad \text{Eq 3-4}
\]

Calculating the OH reactivities for the data set will allow identification of the most active atmospheric chemicals at the two sites. There are a variety of reaction paths that these molecules can take when oxidized; not all of them lead to ozone production. However, understanding which molecules are most reactive with OH presents a clearer picture of the principal chemistry and allows inactive molecules to be discarded from the analysis.
Figure 3-9. Median OH reactivity values in s\(^{-1}\) at Edgewood, Maryland. Species with a median mixing ratio below 0.005 are excluded from the graph for clarity. Error bars are constructed from minimum and maximum VOC mixing ratios for each species over the campaign for canisters sampled at this time.

The mean OH reactivity values for all samples collected at the Edgewood site are shown in Figure 3-9. There are major differences between these results and the results returned from the mixing ratio analysis. A reactivity cutoff value of 0.005 s\(^{-1}\) has been used on this plot to drop unimportant species, which cuts out 81% of the species measured by the canisters; however, 42% of the total calculated reactivity for the campaign is captured in this plot. First, it is apparent that while a handful of species dominate the local air, these are not necessarily the most chemically reactive at these sites. While OH reactivity depends on concentration or mixing ratio, the reaction rate constant is also critical and will change the breakdown of which species are important to ozone production.
Isoprene immediately dominates the mean reactivity values for both sites, particularly at Edgewood. After isoprene, the acetaldehyde and the isoprene reaction products become very important as well. Biogenic species dominate the reactive species. This is expected, based on the semi-rural location and the high summer temperatures driving tree emissions [Kesselmeier and Staudt, 1999]. The species that are the most reactive are also generally the most variable as well. Many of these species have distinct diurnal cycles, especially the biogenic species, due to both temperature and the amount of sunlight available.

There are two anthropogenic species that have also been selected with this method as well, styrene and acrolein. While acrolein has moderate reactivity and variability, styrene shows major variability, indicating that it has distinct spikes in mixing ratio for one or more canister samples. These spikes are likely highly dependent on wind direction, which would be bringing in air masses from industrial regions in the area. Styrene is a polymer precursor, and is a good indicator of anthropogenic activity. The mostly likely source was a trash incinerator located 2.5 km to the south west of the Edgewood site.

There is also a large contribution from acetaldehyde observed in the Edgewood samples. This is noteworthy in this project because acetaldehyde is a major source of formaldehyde. While formaldehyde is not measured in our canister samples, high mixing ratios were measured by the aircraft in the boundary layer. It is not clear where these mixing ratios are coming from, but high reactivity values for a definite precursor may indicate that the formaldehyde observed is an indication of ongoing atmospheric chemistry due to VOC oxidation.
The OH reactivity calculations for Beltsville are shown in Figure 3-10. The immediate difference from the Edgewood site is twofold—first, the reactivities are lower in general, almost certainly due to the fact that Beltsville has lower VOC mixing ratios in general. Second, there are fewer species selected with the reactivity cutoff value of 0.005 $s^{-1}$, due to the fact that the reactivities depend on mixing ratios, and smaller mixing ratios lead to smaller reaction rates. In this case, the reactivity threshold picks up 20% of the total species measured at the site and 36% of the campaigns total calculated reactivity. This is smaller than the values from the Edgewood site, which we calculated above at 29% of the total species measured at the site accounting for 42% of the campaigns total calculated reactivity.
Outside of these excluded species, the results are very similar for the two sites. Isoprene is the species with the highest mixing ratios at both sites, followed by the isoprene reaction products and acetaldehyde. The same pattern in the selected anthropogenic species is present as well, with moderate mixing ratios and variability of acrolein and high variability of styrene, almost certainly from the trash incinerator. The Beltsville site is closer in proximity to a major freeway and industry, but still has more biogenic species selected through the OH reactivity calculations. Biogenic species selected through this method at this site account for 57% of the total OH reactivity calculated from the species selected, with anthropogenic species only contributing 7%.

Table 3-4. OH Reactivity selected species for both sampling sites.

<table>
<thead>
<tr>
<th>Species</th>
<th>Location</th>
<th>Chemical Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butanol (Butyl alcohol)</td>
<td>Beltsville &amp; Edgewood</td>
<td>Alcohol</td>
</tr>
<tr>
<td>1-Butene; 2-Methylpropene</td>
<td></td>
<td>Alkene</td>
</tr>
<tr>
<td>2-Hexanone</td>
<td></td>
<td>Ketone</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td></td>
<td>Alkane</td>
</tr>
<tr>
<td>2-Methylfuran</td>
<td></td>
<td>Aromatic Furan</td>
</tr>
<tr>
<td>3-Methylfuran</td>
<td></td>
<td>Aromatic Furan</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td></td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td>Ketone</td>
</tr>
<tr>
<td>Acrolein (2-Propenal)</td>
<td></td>
<td>Aldehyde</td>
</tr>
<tr>
<td>a-Pinene</td>
<td></td>
<td>Terpene</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td></td>
<td>Aromatic Aldehyde</td>
</tr>
<tr>
<td>b-Pinene</td>
<td></td>
<td>Terpene</td>
</tr>
<tr>
<td>Butane</td>
<td></td>
<td>Alkane</td>
</tr>
<tr>
<td>Butylaldehyde (Butanal)</td>
<td></td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Chloromethane</td>
<td></td>
<td>Haloalkane</td>
</tr>
<tr>
<td>Ethane</td>
<td></td>
<td>Alkane</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>Alcohol</td>
</tr>
<tr>
<td>Ethylene</td>
<td></td>
<td>Alkene</td>
</tr>
<tr>
<td>Hexanal</td>
<td></td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Isobutylaldehyde</td>
<td></td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Isoprene (2-Methyl-1,3-Butadiene)</td>
<td></td>
<td>Alkene</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td></td>
<td>Alcohol</td>
</tr>
<tr>
<td>Limonene</td>
<td></td>
<td>Terpene</td>
</tr>
<tr>
<td>m,p-Xylene</td>
<td></td>
<td>Aromatic Alkene</td>
</tr>
<tr>
<td>MAC (2-Methyl-2-propenal)</td>
<td></td>
<td>Aldehyde</td>
</tr>
</tbody>
</table>
While the original data set includes nearly 200 species, only a handful of these are significant for ozone production and they can be selected using the OH reactivity calculations. The use of an assigned benchmark allows unimportant species to be dropped from the analysis and focus on the most reactive species for the analysis. The benchmark of 0.01 s\(^{-1}\) is still a significant reactivity value; however, it allows identification of the species that are extremely reactive and which will have the most significant contributions to ozone production. Looking at the OH reactivity calculations, biogenic VOC domination is clearly visible at both of these sites, with small contributions from anthropogenic species and a variety of mixed and unknown sourced species.

### 3.4 Propyl-equivalent Mixing Ratios

While OH reactivity is a useful analysis in VOC analysis, OH is extremely reactive and the reactivity calculation will be capturing all potential chemistry from oxidation, not just the ozone pertinent reactions. Additionally, the OH reactivity calculation returns a rate of consumption of the hydroxyl radical in s\(^{-1}\). A more intuitive calculation is necessary to understand the chemistry at the sampled sites.

$$\text{Propyl – Equivalent Concentration} = [\text{VOC}] \frac{k_{\text{OH}(\text{VOC})}}{k_{\text{OH}(\text{C}_3\text{H}_6)}} \quad \text{Eq 3-5}$$
Chameides et al. [1992] uses a secondary reactivity calculation that combines the effects of mixing ratio and OH reactivity – the $k_{\text{OH}}$ value for a specific VOC is normalized by the $k_{\text{OH}}$ value for an arbitrarily chosen VOC. Using these methods, propylene is used as the standardizing species, returning a Propyl-equivalent mixing ratio – calculating the mixing ratio of propylene that we would need to achieve the same oxidation potential of the VOC species that is being examined, an oxidation potential which will depend on mixing ratio. This allows reactivity calculations to be put on a single scale, and clarifies the values returned. While it is very similar to the OH reactivity calculations, this is an easier to understand metric for VOC reactivity.

Figure 3-11. Median Propyl-equivalent mixing ratio values in ppbv at Edgewood, Maryland. Species with a median mixing ratio below 0.008 are excluded from the graph for clarity. Error bars are constructed from minimum and maximum VOC mixing ratios for each species over the campaign for canisters sampled at this time.
The Propyl-equivalent mixing ratios for Edgewood are shown in Figure 3-11. While nearly identical to the OH reactivity values from section 3-4, the units of the results are more easily understood. Using a similar benchmark to drop species with median mixing ratios below the 0.01 ppbv cutoff, a few additional species were added to the unknown and biogenic sourced VOCs. Isoprene and acetaldehyde remain the main components in the local chemistry. Both the OH reactivity calculations and the Propyl-equivalent concentration calculations return styrene, naphthalene and acrolein as the most important anthropogenic species.

![Beltsville MD Propyl-Equivalent Mixing Ratio, Median Values](image)

Figure 3-12. Median Propyl-equivalent mixing ratio values in ppbv at Beltsville, Maryland. Species with a median mixing ratio below 0.008 are excluded from the graph for clarity. Error bars are constructed from minimum and maximum VOC mixing ratios for each species over the campaign for canisters sampled at this time.

Switching our focus to the median Propyl-equivalent mixing ratio values for the Beltsville site, Figure 3-12, we can see the same general pattern repeated from the OH reactivity
calculations. A few species have been added to the unknown and biogenic species selected with the 0.01 ppbv cutoff, but another anthropogenic species appears – naphthalene. This is not a species that is selected at Edgewood, indicating that despite the lower general mixing ratios of VOCs at Beltsville naphthalene is much more important for this site. Generally produced in high mixing ratios from petroleum products, naphthalene has very low variability for this site, indicating that it exists in consistent background mixing ratios. Naphthalene has a short atmospheric lifetime of less than a day [Jia and Batterman, 2010], so a consistent presence in samples throughout the day indicates that the source, most likely incomplete combustion of gasoline, is constant.

Table 3-5. Propyl-equivalent mixing ratio selected species for both sampling sites.

<table>
<thead>
<tr>
<th>Species</th>
<th>Location</th>
<th>Chemical Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>Beltsville &amp; Edgewood</td>
<td>Aromatic Alkene</td>
</tr>
<tr>
<td>1-Butanol (Butyl alcohol)</td>
<td>&quot;</td>
<td>Alcohol</td>
</tr>
<tr>
<td>1-Butene/2-Methylpropene</td>
<td>&quot;</td>
<td>Alkene</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>&quot;</td>
<td>Alkene</td>
</tr>
<tr>
<td>2-Hexanone</td>
<td>&quot;</td>
<td>Ketone</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>&quot;</td>
<td>Alkane</td>
</tr>
<tr>
<td>2-Methylfuran</td>
<td>&quot;</td>
<td>Furan</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>&quot;</td>
<td>Alkane</td>
</tr>
<tr>
<td>2-Methyl-Propanal (Isobutylaldehyde)</td>
<td>&quot;</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>2-Pentanone</td>
<td>&quot;</td>
<td>Ketone</td>
</tr>
<tr>
<td>3-Methylfuran</td>
<td>&quot;</td>
<td>Furan</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>&quot;</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Acetone</td>
<td>&quot;</td>
<td>Ketone</td>
</tr>
<tr>
<td>Acrolein (2-Propenal)</td>
<td>&quot;</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>a-Pinene</td>
<td>&quot;</td>
<td>Monoterpene</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>&quot;</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>b-Pinene</td>
<td>&quot;</td>
<td>Monoterpene</td>
</tr>
<tr>
<td>Butane</td>
<td>&quot;</td>
<td>Alkane</td>
</tr>
<tr>
<td>Butylaldehyde (Butanal)</td>
<td>&quot;</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Camphene</td>
<td>&quot;</td>
<td>Monoterpene</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>&quot;</td>
<td>Haloalkane</td>
</tr>
<tr>
<td>Ethane</td>
<td>&quot;</td>
<td>Alkane</td>
</tr>
<tr>
<td>Ethanol</td>
<td>&quot;</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Ethylene</td>
<td>&quot;</td>
<td>Alkene</td>
</tr>
<tr>
<td>Hexanal</td>
<td>&quot;</td>
<td>Aldehyde</td>
</tr>
</tbody>
</table>
Understanding how these species change throughout the day is vital for understanding VOC behavior. The chemistry that is important in the morning will not necessarily be the dominant chemistry in the evenings. Similar to the mixing ratio analysis performed in section 3.1, Propyl-equivalent mixing ratios were examined, organized by canister sample start time for the Edgewood site to better illustrate how the VOC chemistry changes throughout the day. The Edgewood site was chosen because of its frequently sampled days, with multiple canister samples for each start time.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Classification</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene (2-Methyl-1,3-Butadiene)</td>
<td>&quot;</td>
<td>Alkene</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>&quot;</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Limonene</td>
<td>&quot;</td>
<td>Monoterpene</td>
</tr>
<tr>
<td>m,p-Xylene</td>
<td>&quot;</td>
<td>Aromatic Alkene</td>
</tr>
<tr>
<td>MAC (2-Methyl-2-propenal)</td>
<td>&quot;</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>MEK</td>
<td>&quot;</td>
<td>Ketone</td>
</tr>
<tr>
<td>MVK</td>
<td>&quot;</td>
<td>Enone</td>
</tr>
<tr>
<td>Pentanal</td>
<td>&quot;</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>Pentane</td>
<td>&quot;</td>
<td>Alkane</td>
</tr>
<tr>
<td>Propane</td>
<td>&quot;</td>
<td>Alkane</td>
</tr>
<tr>
<td>Propyl alcohol (1-Propanol)</td>
<td>&quot;</td>
<td>Alcohol</td>
</tr>
<tr>
<td>Styrene</td>
<td>&quot;</td>
<td>Aromatic Alkene</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>Edgewood Only</td>
<td>Alkene</td>
</tr>
<tr>
<td>1-Hexene; 2-Methyl-1-Pentene</td>
<td>&quot;</td>
<td>Alkene</td>
</tr>
<tr>
<td>1-Nonene</td>
<td>&quot;</td>
<td>Alkene</td>
</tr>
<tr>
<td>2-Heptanone</td>
<td>Beltsville Only</td>
<td>Ketone</td>
</tr>
<tr>
<td>2-Methyl-1-Butene</td>
<td>&quot;</td>
<td>Alkene</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>&quot;</td>
<td>Aromatic Alkene</td>
</tr>
</tbody>
</table>
Figure 3-13. Median values of VOC species selected through Propyl-equivalent mixing ratios in the 0700 EDT canisters at Edgewood, Maryland. Species with a median mixing ratio below 0.008 are excluded from the graph for clarity. Error bars are constructed from minimum and maximum VOC mixing ratios for each species over the campaign for canisters sampled at this time.

Starting with the earliest canisters for the Edgewood site, Figure 3-13, the Propyl-equivalent mixing ratios for the 0700 EDT canisters were examined. Isoprene remains one of the more important VOCs for these samples with a median value of just under 1.5 ppbv, but other VOCs dominate the results. Limonene is significant due to buildup in the shallow boundary layer overnight without photodriven reactions to remove it, while benzaldehyde and acetaldehyde remain relatively reactive with moderately high Propyl-equivalent mixing ratios. Mixing ratios are generally lower than the median values calculated for the Edgewood site. So while more VOCs were selected with the benchmark, the overall maximum reactivity is much generally lower for these samples.
Figure 3-14. Median values of VOC species selected through Propyl-equivalent mixing ratios in the 1400 EDT canisters at Edgewood, Maryland. Species with a median mixing ratio below 0.008 are excluded from the graph for clarity. Error bars are constructed from minimum and maximum VOC mixing ratios for each species over the campaign for canisters sampled at this time.

Figure 3-14 presents the 1400 EDT Edgewood results. Isoprene completely dominates the samples at this time, indicating that in the midday there is a tremendous increase in plant activity. While there are many other species selected, only isoprene contributes in any significant way to the overall reactivity of the air. This situation differs significantly from the median value calculations and either of the other two start-time analysis results. Isoprene is the VOC present in the highest amounts during the daytime, and accounts for 52% of the total Propyl-equivalent concentration in the species selected on this graph. While isoprene is dominant for these samples, the isoprene reaction products (MVK, MAC) do not contribute significantly to the overall
reactivity, with MVK contributing 9% and MAC contributing 5% of the reactivity. This indicates that isoprene has significant mixing ratios, but has not yet begun the reactions that ultimately produce ozone.

Figure 3-15. Median values of VOC species selected through Propyl-equivalent mixing ratios in the 1900 EDT canisters at Edgewood, Maryland. Species with a median mixing ratio below 0.008 are excluded from the graph for clarity. Error bars are constructed from minimum and maximum VOC mixing ratios for each species over the campaign for canisters sampled at this time.

The final start time analysis for the Propyl-equivalent mixing ratios is shown in Figure 3-15, the 7pm canister samples for Edgewood. These results are similar to the morning results in that the selected VOCs have smaller mixing ratios returned. Isoprene continues to be moderately important even as acetaldehyde overtakes it. The isoprene reaction products have become more important as well, indicating at this point that isoprene has been significantly oxidized in the immediate area of the sample.
Overall, the reactivity studies (both OH and Propyl-equivalent mixing ratios) give a very different result from the mixing ratio calculations. The species that dominate the VOC loading for a specific site are not necessarily the VOCs that are important for ozone production. While both techniques identify biogenic VOCs as the most important sources, the study resulted in findings from the anthropogenic and mixed source VOCs that are indicative of the mixed use environment that was sampled during the campaign.

3.5 Reactivity Correlations with Ozone

While the general reactivities for species over the entire campaign have been examined, an important piece of the VOC puzzle is understanding how specific reactivity values correlate with ozone mixing ratios. Strong positive correlations indicate that a specific species had some significant contribution to the mixing ratio of ozone. Scattered or poor correlations indicate poor contributions from that specific VOC. Several interesting will be investigated in this section. Only the Edgewood site will be analyzed due to the reliability and detail of the ozone data taken by the NATIVE instrumentation at the site.
Figure 3-16. Isoprene reactivity in s⁻¹ correlated with median ozone mixing ratios during the canister collection time at Edgewood, Maryland. The points are color coded by canister collection start time. The best-fit line has been added through linear regression. The R² value is 0.4682 and the p value is 0.00032 for this correlation plot.

Isoprene reactivity was correlated with ozone mixing ratios in Figure 3-16. VOC reactivity was calculated for each canister sample, and then correlated with the mean ozone mixing ratio for the hour that the canister was collecting. Isoprene shows a strong positive correlation, with higher isoprene reactivities corresponding to higher mean ozone mixing ratios. Figure 3-20 is color coded by canister start time; coloring by specific dates can be found in Appendix D. The early morning and late evening times generally have both low ozone and low isoprene reactivity, while midday to late afternoon has high values for both. This matches the Propyl-equivalent mixing ratio results, which showed that isoprene reactivity was highest in the midday canisters and much less important for the early morning and late day samples.
Figure 3-17. Styrene reactivity in s⁻¹ correlated with median ozone mixing ratios during the canister collection time at Edgewood, Maryland. The points are color coded by canister collection start time. The best-fit line has been added through linear regression. The R² value is 0.0004623 and the p value is 0.9224 for this correlation plot.

The isoprene reactivity results can be compared to styrene, shown in Figure 3-17. Styrene is an indicator of anthropogenic activity, and has large outlier measurements indicating that it spikes in mixing ratios in some of the samples. Two things become apparent when plotting the styrene reactivity against ozone mixing ratios by start time. First, styrene is generally low in mixing ratio with no general trends associated with ozone mixing ratios, and second there is one canister sample where styrene peaks in reactivity, indicating a similar peak in mixing ratio for that one canister. However, this peak is only associated with moderate mixing ratios of ozone, which suggests that styrene is not the major driver of ozone production in that sample.
Figure 3-18. Limonene reactivity in s$^{-1}$ correlated with median ozone mixing ratios during the canister collection time at Edgewood, Maryland. The points are color coded by canister collection start time. The best-fit line has been added through linear regression. The $R^2$ value is 0.203 and the $p$ value is 0.0310 for this correlation plot.

The reactivity of limonene is compared to ozone mixing ratios in Figure 3-18. Limonene is a terpene and a very important biogenic chemical that has been selected as relevant by the VOC reactivity calculations. However, it is only highly concentrated in the early morning samples, with smaller mixing ratios and reactivity values in the mid – to late day. Plotting limonene reactivity against ozone mixing ratios shows us that this species is mostly important at low ozone mixing ratios, and even returns a generally negative correlation with ozone. Terpene mixing ratios are much higher at night – under high NO$_x$ conditions, limonene mixing ratios are reduced rapidly from reactions with NO$_3$ radicals. [Spittler et al., 2006]
3.6 Ozone Production Efficiency

A final method for understanding VOCs is to understand how much local chemistry is contributing to ozone production in the local air. While many VOCs may be present, or VOCs with high reactivity values, a metric to evaluate how much ozone is being produced locally is required. One possible way of doing this is to evaluate the ozone production efficiency – using ozone and NO\textsubscript{x} data we can calculate the approximate ratio of ozone to NO\textsubscript{x} precursors.

As ozone is produced, NO\textsubscript{x} is consumed (reference to chapter 1.2). Subtracting the amount of NO\textsubscript{x} that is present from the total amount of reactive nitrogen, labeled NO\textsubscript{y} (a measure of NO\textsubscript{x} plus NO\textsubscript{x} oxidation products), and provides a measure of how much nitrogen oxidation is occurring. Taking the ratio between ozone and this difference gives ozone production efficiency (OPE). This calculation was taken from Neuman et al. [2012].

\[
\text{Ozone Production Efficiency} = \frac{[O_3]}{[NO_y] - [NO_x]} \tag{Eq 4-1}
\]

Calculations of OPE were made for each canister sample taken at the Edgewood site using data from the PSU NATIVE trailer. For each canister sample, O\textsubscript{3}, NO\textsubscript{x}, and NO\textsubscript{y} were averaged for the time that the canister was open and collecting air, and these averages were used to make the OPE calculation. One calculation was made for each canister sample. The analysis is restricted to the Edgewood site based on available NO\textsubscript{x} data, which was not taken at the Beltsville site.
Figure 3-19. Mean ozone production efficiency values plotted against mean ozone values for the canister samples at Edgewood, Maryland. The points are color coded by canister collection start time. The best-fit line has been added through linear regression. The $R^2$ value is 0.0249 and the p value is 0.483 for this correlation plot. A version of this plot organized by date can be found in Appendix E.

The OPE results correlated with ozone are shown in Figure 3-19, color coded by canister start time. The results are highly scattered. A high positive correlation would have indicated that measured ozone mixing ratios depended strongly on local chemical production. This does not seem to explain the observations, however. A loose fit to this scattered data actually returns a negative correlation slope. There is apparently only the loosest correlation between OPE and ozone mixing ratios – which indicates that local chemistry is not the most important factor determining ozone mixing ratios, and advection is probably a major factor in ozone mixing ratios at this site. It’s important to approach this analysis with caution, however, as ozone often has a lag between the morning when the precursor species are being emitted, and the afternoon when
mixing ratios peak. Advection is a very important part of this puzzle, but the lag in ozone production will muddy the analysis of plots such as this one.

The VOCs that are being produced in a semi-rural location like this are notable. Biogenic VOCs are a consideration in urban area ozone control. Assuming that the VOCs measured locally are important for ozone production, this indicates that advection is a huge component in ozone production. The reactive air masses are most likely originating away from where the ozone they produce is being measured, and this invites further investigation.

Figure 3-20. Mean ozone production efficiency values plotted against the ratio of NO\textsubscript{x} to NO\textsubscript{y} values for the canister samples at Edgewood, Maryland. The points are color coded by canister collection start time. The best-fit line has been added through linear regression. The $R^2$ value is 0.0307 and the p value is 0.436 for this correlation plot. A version of this plot organized by date can be found in Appendix E.

A similar but separate analysis is to correlate the OPE with the ratio of NO\textsubscript{x} to NO\textsubscript{y} – how much NO\textsubscript{x} is measured for a particular canister sample to how much total reactive nitrogen is
measured. As NO$_x$ reacts away the ratio will decrease, so that smaller values can be viewed as coming from an aged air mass, and therefore less capable of be producing ozone. The results of this calculation for the Edgewood site are shown in Figure 3-20. This shows a loose positive correlation, but the scatter and low correlation indicate that OPE is being influenced greatly by the amount of advection occurring.

![Edgewood 2011 NOx/NOy and O3 Correlation](image)

Figure 3-21. NO$_x$ to NO$_y$ values plotted against mean ozone values for the canister samples at Edgewood, Maryland. The points are color coded by canister collection start time. The best-fit line has been added through linear regression. The $R^2$ value is 0.423 and the p value is 0.00104 for this correlation plot. A version of this plot organized by date can be found in Appendix E.

A final correlation was prepared assuming the ratio between NO$_x$ and NO$_y$ is a ballpark measurement of air mass age, and can be correlated to ozone mixing ratios. The results are shown in Figure 3-11 for the Edgewood site. In this graph, unlike the other two, there is a clear negative correlation. This shows that for higher measured ozone mixing ratios there exists more aged air masses—matching the conclusion that there is a lag between when the reactive nitrogens are being
produced – in the mornings, when the ozone mixing ratios are low – and when the ozone mixing ratios peak in the afternoon, as well as the conclusion that ozone advection may be a key element in understanding the ozone dynamics at the Edgewood site.
CHAPTER 4

Case Studies

The following chapter presents two case studies of canister samples selected to be examined in greater detail. Samples were chosen for case studies based on anomalous behavior of species identified in correlation studies of VOCs from the Edgewood, Maryland, site. Case studies are used to gain a deeper understanding of VOC behavior that cannot be garnered from the general campaign wide analysis, as it allows evaluation of other meteorological variables for each canister sample that is being examined. Canister case studies are undertaken at the Edgewood site exclusively because of the high quality meteorology and chemical data that was collected in the Pennsylvania State University NATIVE Trailer that was at this location.

4.1 Case Study #1: 1000 EDT 22 July 2011

The first canister sample was selected based on the correlation between isoprene and the sum of MVK+MAC, shown in Figure 4-1. Correlation analysis uses VOC values taken from the canister samples at Edgewood, Maryland. This figure correlated the values of isoprene with its major reaction products, which are presented here as the sum of MVK and MAC; the points are colored by when the canister samples were collected during the day. Unusually high mixing ratios of the reaction products compared to isoprene indicate strong isoprene reactivity.
Figure 4-1. Canister sample correlations between isoprene and the sum of MVK and MAC at Edgewood, Maryland. The points are color coded by canister collection start time. The best-fit line has been added through linear regression. The $R^2$ value is 0.191 and the p value is 0.0370 for this correlation plot.

The outlier in this plot in the upper right hand corner colored brown is the 10am EST canister from July 22, which has unusually high MVK mixing ratios correlated with very high isoprene mixing ratios. The rest of the points indicate low to moderate correlation ($R^2 = 0.1911$) with lots of scatter (p value = 0.03701), which reinforces the advection hypothesis—there may not be much local chemistry occurring for most of the samples, because isoprene is not correlating to its oxidation products. Instead, ozone may be being advected in with aged air masses. The outlier point at 1000 EDT 22 July shows unusually high isoprene oxidation, inferred from the uncommonly large values of isoprene oxidation products.
Figure 4-2. The 1000 EDT 22 July mixing ratios for VOCs at Edgewood, Maryland. Mixing ratios below 0.07 ppbv are excluded for clarity. The bars are color coded by VOC species source from the EPA reference.

Figure 4-2 shows the VOC mixing ratios for all VOC’s in the case study sample above 0.07 ppbv. Biogenic species dominate this sample, and isoprene is the biggest contributor. There are a variety of anthropogenic and unknown sourced VOCs as well, but this canister is clearly a mostly biogenic sample. While VOC mixing ratios are not overwhelmingly important for understanding the driving chemistry, they do allow a window into the source of the air mass. The unusually high mixing ratios of isoprene in the sample indicate an air mass with a strong biogenic source in it. This matches the original correlation that showed an unusually large amount of isoprene reaction products as well.
The reactive species for the 22 July 1000 EDT sample were examined in order to understand the ongoing chemistry. Figure 4-3 shows the Propyl-equivalent mixing ratios for the sample. While isoprene was a major contributor to the VOC mixing ratios in the canister, it is also the most reactive VOC measured in this canister. Acetaldehyde and the biogenic isoprene reaction products are mildly significant, while the other VOCs are barely above the cut off mixing ratio. This shows a sample that is not only strongly biogenic but specifically strongly dominated by isoprene.

Figure 4-3. The 1000 EDT 22 July Propyl-equivalent mixing ratios at Edgewood, Maryland. Propyl-equivalent mixing ratios below 0.01 ppbv are excluded for clarity. The bars are color coded by VOC species source from the EPA reference.
Figure 4-4. The 1000 EDT 22 July HYSPLIT ensemble back trajectory for canister case study at Edgewood, Maryland. A 24 run ensemble run for 12 hours is used to show the general uncertainty in the back trajectories. Ending altitude was kept at 500 meters.
To further explain the high isoprene, a NOAA Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) ensemble back trajectory is used to investigate the air source. The model was run backwards for 12 hours in ensemble mode, beginning at an altitude of 500 meters. The model used 24 runs which are overlaid to give an ensemble back trajectory. The results are shown in Figure 4-4 for the Edgewood site. There is a good general agreement in the trajectories, showing the air originating over western Pennsylvania and moving south east over the Alleghenies and rural farmland to the north of Baltimore. This air parcel has missed much of the industry and development present in the Baltimore-Washington D.C. metropolitan area to the south.
Figure 4-5. The 1000 EDT 22 July ozone mixing ratios in ppbv for the case study at Edgewood, Maryland. The red vertical lines bracket the time when the canister was open and collecting air. Ozone values were collected through the NATIVE Trailer run by the Pennsylvania State University, and are one-minute averages. The time is shown on the x-axis in fractional day.
Figure 4-6. The 1000 EDT 22 July ozone production efficiency for the case study at Edgewood, Maryland. The red vertical lines bracket the time when the canister was open and collecting air. Ozone values were collected through the NATIVE Trailer run by the Pennsylvania State University, and are one-minute averages. The time is shown on the x-axis in fractional day.
Figure 4-7. The 1000 EDT 22 July NO$_x$/NO$_y$ ratios for the case study at Edgewood, Maryland. The red vertical lines bracket the time when the canister was open and collecting air. Ozone values and reactive nitrogen data was collected through the NATIVE Trailer run by the Pennsylvania State University, and are one-minute averages. The time is shown on the x-axis in fractional day.

While the strong biogenic marker in the VOC mixing ratios and reactivities are apparent, especially from isoprene, the ozone and reactive nitrogen species measured over the canister sample were also examined. Figure 4-5 shows the ozone mixing ratio measured by the NATIVE instrumentation for the hour that this sample was collected. The ozone values are one minute
averages for the sampled hour. The pattern of the ozone mixing ratios over the one hour sample shows a nearly 12 ppbv rise in mixing ratio before falling to nearly the original ozone levels. Comparing this to calculations of the OPE, in Figure 4-6, a spike in production was observed when the ozone mixing ratios began to rise quickly, indicating that there is localized ozone production occurring.

OPE values fall directly after that, indicating that ozone was produced in a burst then advected away from the site – ozone is falling at the end of the hour even as OPE spikes again. This shows that NOx is getting reacted away during this canister sample in the local environment– the local measurements of the NOx to NOy ratio are steadily decreasing throughout the hour. This appears to indicate locally occurring chemistry, especially when matched with locally increasing ozone. What this indicates is that the local biogenic VOCs are contributing greatly to the locally measured ozone during this sample, spiking the local ozone mixing ratios before this local air is advected away and conditions return to normal.

4.2 Case Study #2: 1600 EDT 21 July 2011

The second canister case study is the 1600 EDT 21 July canister sample. This sample was selected for examination because of unusual behavior in three anthropogenic VOCs measured at Edgewood, Maryland – styrene, benzaldehyde, and toluene. These active anthropogenic species indicate that this sample has a different and distinct source from the first case study. Thus, the 21 July canister sample presents the opportunity to compare a biogenically driven sample to a predominantly anthropogenic sample.

The first VOC of interest is the behavior of styrene, which was discussed in Figure 3-16 as the correlation of styrene in canister samples correlated to ozone mixing rations. Styrene generally only varies a small amount across a range of ozone mixing ratios, with the exception of
one sample, which is discussed in this section. Because the styrene mixing ratios are high but ozone is only moderate compared to the other canister samples, this VOC is most likely not driving ozone production on its own.

Figure 4-8. The benzaldehyde canister values plotted against CO values at Edgewood, Maryland. The points are color coded by canister collection start time. The best-fit line has been added through linear regression. The $R^2$ value is 0.04797 and the p value is 0.3154 for this correlation plot.

The other two species, benzaldehyde and toluene, were selected from a VOC to carbon monoxide (CO) correlation. Figures 4-8 and 4-9 show these results. Carbon monoxide is a reaction product for many atmospheric oxidations, and a strong correlation with CO indicates that a specific VOC may have been engaged in atmospheric reactions. Both benzene and toluene are anthropogenic, and have similar behavior when correlated with CO hour averages for the Edgewood site. Both species show unusually high mixing rations with correspondingly high CO
values for the 1600 EDT 21 July canister sample, which along with the styrene mixing ratios discussed above indicate that there is a large anthropogenic fingerprint in this sample.

Figure 4-9. The toluene canister values plotted against CO values at Edgewood, Maryland. The points are color coded by canister collection start time. The best fit line has been added through linear regression. The R^2 value is 0.2334 and the p value is 0.01954 for this correlation plot.

Examining where the air sampled in this canister originated as well as the behavior of ozone and reactive nitrogens during the canister sample should give some insight into how anthropogenic species are affecting the locally measured ozone mixing ratios. Additionally, this canister sample will be compared to the first case study that occurred only hours earlier. Comparing this air sample that has more anthropogenically generated VOCs to the 1000 EDT 22 July sample is an opportunity to investigate the differences between these two types of samples.
Figure 4-10 shows the VOC mixing ratio results for the 1600 EDT 21 July canister sample. While biogenic species such as isoprene and acetone are important in the sample, methanol dominates the mixing ratios, and a number of anthropogenic species are prominent as well. These include styrene, toluene, and acrolein. Isoprene is not the dominant VOC for this canister at during an afternoon sample, which would ordinarily be dominated by biogenic species, as was typical for the 1400 EDT campaign samples from Edgewood where isoprene contributes 52% of the Propyl-equivalent mixing ratios. These differences indicate a very different chemistry in these samples compared to the first case study.
Figure 4-11. Edgewood, Maryland 1600 EDT 21 July Propyl-equivalent mixing ratios. Propyl-equivalent mixing ratios below 0.01 ppbv are excluded for clarity. The bars are color coded by VOC species source from the EPA reference.

Looking at the reactivity calculations through the Propyl-equivalent concentrations in Figure 4-11, a different picture of the VOC behavior is confirmed. Isoprene is a reactive VOC and highly relevant for this sample, but styrene is also prominent. Toluene, while unusually high compared to CO mixing ratios, does not stand out with this method. The two other main reactive species are acetaldehyde and benzaldehyde. While acetaldehyde is an important reactive species in many of the other canisters and over the entire campaign, benzaldehyde generally has only moderate reactivities for the Edgewood site.
Figure 4-12. Edgewood, Maryland 1600 EDT 21 July HYSPLIT ensemble back trajectory for canister case study. A 24 run ensemble run for 12 hours is used to show the general uncertainty in the back trajectories. Ending altitude was kept at 500 meters.
The wind analysis done through a NOAA HYSPLIT ensemble trajectory is shown in Figure 4-12. The 22 July case study had a back trajectory from the rural north, which was consistent with the biogenic species in the sample. This 21 July case study has a back trajectory that originates in the Washington DC and Baltimore metropolitan region. This explains where the anthropogenic species are coming from – the high populations and industrial development with wooded suburbs in the Baltimore-Washington, DC metropolitan region appear to contribute both industrial and agricultural anthropogenic VOCs to the air mass. This back trajectory also shows greater spread in the ensemble, but with a southerly approach that would bring it over both urban areas. The trash incinerating power plant located to the south west of the Edgewood site is another potential source of anthropogenic species.
Figure 4-13. Edgewood, Maryland 1600 EDT 21 July ozone mixing ratio for the case study. The red vertical lines bracket the time when the canister was open and collecting air. Ozone values were collected through the NATIVE Trailer run by the Pennsylvania State University, and are one-minute averages. The time is shown on the x-axis in fractional day.
Figure 4-14. Edgewood, Maryland 1600 EDT 21 July ozone production efficiency for the case study. The red vertical lines bracket the time when the canister was open and collecting air. Ozone values were collected through the NATIVE Trailer run by the Pennsylvania State University, and are one-minute averages. The time is shown on the x-axis in fractional day.
Figure 4-15. Edgewood, Maryland 1600 EDT 21 July NO$_x$/NO$_y$ ratios for the case study. The red vertical lines bracket the time when the canister was open and collecting air. Ozone values and reactive nitrogen data was collected through the NATIVE Trailer run by the Pennsylvania State University, and are one-minute averages. The time is shown on the x-axis in fractional day.

Figure 4-13 shows the ozone behavior during the 1600 EDT 21 July sampling hour. Mixing ratios are generally steady over the sample, but begin falling during the last quarter or so. However, OPE remains steady throughout the hour as shown in Figure 4-14. This shows the influence of advection on the measured mixing ratios of ozone. The NO$_x$ to NO$_y$ ratio for air mass
age is shown in Figure 4-13. This ratio is low for the entire sample, indicating a fairly aged air mass moving over the Edgewood site where the sample was collected.

This sample was examined because it shows the greatest contributions from anthropogenic VOCS out of all the measured samples. The air mass has an expected source over the developed urban area of DC and Baltimore, due to a mild low pressure forming to the south of the site. This case study indicates that the species of reactive VOCs can change drastically sample to sample, based on the source of the air mass. This leads to the assumption that much of the biogenic species are coming from the immediate environment, but the advection of air masses into the region will be bringing in both biogenic and anthropogenic species, which could potentially impact ozone production.
CHAPTER 5
Conclusions

VOC canister samples were collected in Maryland during July, 2011 as part of NASA’s 2011 DISCOVER-AQ field campaign. Samples were collected in Beltsville, Maryland, and Edgewood, Maryland, for one-hour periods throughout the campaign. The Edgewood samples focused on four intensive days; the Beltsville samples were more scattered for both collection days and sampling times. The data set contained 14 samples from Beltsville and 23 samples from Edgewood.

Analysis of the dataset shows variable VOCs occur for both sites, with the most important species showing variation between samples. Isoprene, arguably the most important VOC at the monitored sites, varied in concentration between 0.19 and 12 ppbv, a variance of 62% which is a moderate and typical spread for the major species analyzed in this study. Analysis was done on both mixing ratios and reactivities, with the most important VOCs in the data examined for both sites. There were some differences between the sites. Higher mixing ratios of VOCs were measured at the Edgewood site in general, which led to higher reactivity values as well. Biogenic species were the major species throughout the campaign for both sites. These biogenic species are especially important during the mid-to late day, which is the peak time for ozone production; however, detailed case studies show that even these patterns are susceptible to large variation. Additionally, using ozone and NOx measured at the Edgewood location it is shown that while VOCs are important for ozone production, advection of polluted air is probably more important.

The case studies of the 1000 EDT 22 July canister and 1600 EDT 21 July canister samples solidify the advection hypothesis. These canister samples were very different, with the
July 22 sample overwhelmingly biogenic and the July 21 sample overwhelmingly anthropogenic. The main difference between the samples where the air is originating in the previous 12 hours, as identified by HYSPLIT model runs. The biogenic sample shows the characteristics of air that is continuously reacting as it moved over the site, while the anthropogenic sample shows air that is already well reacted, indicating that ozone production will be low in this sample, with measured ozone mixing ratios coming from reactions that occurred away from the Edgewood site.

More comprehensive VOC monitoring will allow for better modeling of ozone production over sensitive urban regions as it will eliminate some of the need to make assumptions about the mix of species found in a particular area. While the work presented in this study was temporally limited, the central theme from the analysis is that the VOC mix being measured can be highly variable in time, with changes in advection impacting which species are reactive in a particular area. Additionally, teasing apart the local sources of VOCs from the advection can be difficult as there is wide variation in atmospheric lifetime and reactivity. Having a more comprehensive VOC monitoring network would make it much easier to identify VOC hotspots within an urban region, and ultimately better management of the important ozone precursors.

The data shows the difficulty of making generalizations about the VOCs that are seen at any particular site, because of the wide variability between samples. While the canister samples are a starting point for constructing a model, intensive monitoring will be required to gain a better understanding of VOC behavior and ultimately distribution within a region. The limited scope of the canister sampling in this study makes it difficult to offer much insight into the behavior of ozone over the entire campaign, and this complicates modeling the nearby atmospheric chemistry, although the measured VOCs will be used to initiate photochemical models for comparison with the observed ozone behavior on the sampling days.

However, despite the limitations of the data set used in this study, the analysis used in this paper can easily be used on a larger data set, especially one with greater temporal resolution.
Ozone production is dependent on the mixing ratios and types of VOCs available in an air mass, and understanding which species those are and how they are varying for a site of interest in air quality management is important for untangling ozone production. Instituting regular canister samples or continuous VOC measurements within an area with regular ozone exceedances will allow for much more holistic analysis as well as more reliable air quality modeling within the area.

This is especially relevant when looking at the more complicated problems in our current understanding of ozone chemistry and air pollution dynamics. Understanding ozone production is a difficult problem to solve because it’s a challenging measurement to make, but it’s a subject that will become much more important as ozone pollution continues to improve. As ozone levels drop, the exceedance days are more difficult to predict because they rely on microscale dynamics that are difficult to model. Having a better understanding of ozone production will lead to better management of the industries and areas that are contributing to these events, and will allow targeted reduction of the precursor species that matter for those regions. A full and comprehensive VOC network is essential for this kind of understanding, because VOCs are more difficult to measure than NO\textsubscript{x} and much more variable within a region. Ideally the monitoring network would be both spatially and temporally highly detailed, with data readily supplied to the forecasters and researchers involved in air quality monitoring, with efficient integration into ozone production models.
References


Appendix A

Wind Rose Diagrams for Canister Sampled Days

Edgewood Wind Rose, July 11 2011
Beltsville Wind Rose, July 26 2011
## Appendix B

**VOC Species and OH Rate Constants**

Table A – 1. OH Reactivity values for the VOC data set, reported in cm³ molecule⁻¹ s⁻¹.

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<th>$k_{OH}$</th>
<th>Species</th>
<th>$k_{OH}$</th>
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Table A – 2. All species analyzed in this paper, with source and chemical species.
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Appendix C

Correlations between Ground and Aircraft Measurements
Appendix D

Reactivity Correlations with Ozone by Date
Appendix E

Ozone Production Efficiency by Date