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Analysis of NO and NOy in the Low Atmosphere at Mammoth Cave National Park

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ANALYSIS OF NO AND NO\textsubscript{y} IN THE LOW ATMOSPHERE OF
MAMMOTH CAVE NATIONAL PARK

A Capstone Experience/Thesis Project

Presented in Partial Fulfillment of the Requirements for

the Degree Bachelors of Science with

Honors College Graduate Distinction at Western Kentucky University

By

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ABSTRACT

Nitric oxide (NO) and reactive oxides of nitrogen (NO$_y$) are pollutants produced by automobiles and formed naturally from nitrate ions (NO$_3^-$). We are interested in the natural processes and anthropogenic sources of NO and NO$_y$. To better understand NO and NO$_y$ trends in the atmosphere, data from Mammoth Cave National Park (MCNP) was analyzed. The rural location of MCNP leads to the hypothesis that the natural sources of NO to be studied without anthropogenic sources significantly contributing to the overall levels. NO is correlated with factors such as solar radiance and precipitation. There is a correlation between NO levels and solar radiance. Interstate-65 and Bowling Green were identified as possible point sources of pollution in MCNP. The concentration of NO$_3^-$ in wet deposition is compared with NO and NO$_y$ to determine the extent nitrate ions undergo nitrate photolysis which puts NO and NO$_y$ into the atmosphere. Sulfur dioxide (SO$_2$) can scavenge into rain water to form sulfate (SO$_4^{2-}$), so the concentrations in precipitation were analyzed for a negative correlation as well. No correlation was found between ion concentrations in precipitation and trace gases.

Keywords: Atmospheric Chemistry, Nitric Oxide, Mammoth Cave National Park
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My Dad has been one of the most influential people when it came to pursuing science. He inspired my curiosity for science and a love for learning from a very young age. He supported me majoring in physics, and then supported me declaring a second major junior year in ACS chemistry. My mother has helped me get through the last 8 years more than anyone will ever know. When I started taking AP classes in high school she was always there with a warm meal and encouragement. Through college she has been a phone call away. My fiancé, Daniel, has supported me through this entire project, I cannot thank him enough. Without Daniel and my physics friends I would not have made it through my physics degree, especially Jamey, Owen, and Max.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iii</td>
</tr>
<tr>
<td>Vita</td>
<td>iv</td>
</tr>
<tr>
<td>List of Figures</td>
<td>vi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>vii</td>
</tr>
<tr>
<td>Chapters:</td>
<td></td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Methods</td>
<td>8</td>
</tr>
<tr>
<td>3. Atmospheric Data</td>
<td>22</td>
</tr>
<tr>
<td>4. Wet-Deposition Data</td>
<td>34</td>
</tr>
<tr>
<td>5. Conclusion</td>
<td>43</td>
</tr>
<tr>
<td>References</td>
<td>48</td>
</tr>
<tr>
<td>Appendix</td>
<td>50</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Nitrogen cycle and nitrate photolysis ........................................... 3</td>
</tr>
<tr>
<td>1.2</td>
<td>Point source image ........................................................................... 7</td>
</tr>
<tr>
<td>2.1</td>
<td>Google Earth images of the monitoring site ....................................... 9</td>
</tr>
<tr>
<td>2.2</td>
<td>Wet/dry deposition collector ............................................................. 11</td>
</tr>
<tr>
<td>2.3</td>
<td>NO with and without invalid data points ............................................. 14</td>
</tr>
<tr>
<td>2.4</td>
<td>3-D Images of NO, NO\textsubscript{y}, and SO\textsubscript{2} for January 2011 ............................................. 17</td>
</tr>
<tr>
<td>2.5</td>
<td>Removal of points greater than 50 PPB in NO ..................................... 20</td>
</tr>
<tr>
<td>2.6</td>
<td>Average of NO for every month of 2011, including and excluding points greater than 50 PPB ............................................. 21</td>
</tr>
<tr>
<td>3.1</td>
<td>NO averaged for January 2011, and NO versus solar radiance for a single day ............................................. 23</td>
</tr>
<tr>
<td>3.2</td>
<td>Slope and correlation coefficient of NO versus solar radiance everyday for 2011 ............................................. 26</td>
</tr>
<tr>
<td>3.3</td>
<td>Correlation of CO with wind direction ................................................. 29</td>
</tr>
<tr>
<td>3.4</td>
<td>Correlation of NO with wind direction ................................................. 32</td>
</tr>
<tr>
<td>4.1</td>
<td>Correlation of NO with seasonal wet-deposition data ................................ 36</td>
</tr>
<tr>
<td>4.2</td>
<td>Correlation of NO\textsubscript{y} with seasonal wet-deposition data .................. 38</td>
</tr>
<tr>
<td>4.3</td>
<td>Correlation of SO\textsubscript{2} with seasonal wet-deposition data .................. 41</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Directions of possible point sources around Mammoth Cave National Park</td>
<td>31</td>
</tr>
<tr>
<td>4.1 Slopes, correlation coefficients, and p-values for seasonal correlations with NO and SO₂</td>
<td>35</td>
</tr>
<tr>
<td>4.2 Slopes, correlation coefficients, and p-values for yearly correlations with NO and SO₂</td>
<td>39</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

The atmosphere of Earth is one of the reasons it is inhabited while the rest of the solar system is not. The atmosphere is vital to life, but is not completely understood because of its immense complexity. There are mechanisms such as the mechanism of nitrate photolysis in snow that are not fully understood but could have a huge impact on the global environment.\textsuperscript{1-3} The atmosphere is approximately 78\% nitrogen gas (N\textsubscript{2}), 21\% oxygen (O\textsubscript{2}), 0.9\% argon (Ar), and 0.03\% carbon dioxide (CO\textsubscript{2}).\textsuperscript{4} All other gases are considered trace gases, which make up less than one percent of the atmosphere. Trace gases include reactive oxides of nitrogen, volatile organic compounds, ozone, and carbon monoxide.\textsuperscript{4,5} These compounds make up most of atmospheric chemistry because the specific mechanisms of how these compounds get into the atmosphere and how they move from place to place has an impact on the composition of the atmosphere in that area. The composition of the atmosphere has environmental effects, and detrimental health effects.\textsuperscript{4} For example, pollution from a large city can blow from the place of origin to the surrounding areas.\textsuperscript{5} Sulfur dioxide and nitric oxide can react to form acid rain which can be environmentally devastating and hazardous to human health.\textsuperscript{4,6}
Atmospheric chemists are concerned with sources, sinks, and transport phenomena. A source is what produces a specific species. Sinks are where these species react to leave the system they are in, in this case the atmosphere. Sources and sinks can be mapped into a cycle for nitrogen, shown in Figure 1.1. The nitrogen cycle starts will the 78% of the atmosphere that is N\textsubscript{2}. Nitrogen fixing bacteria reduce N\textsubscript{2} to ammonia (NH\textsubscript{3}) in the soil. Ammonia is then oxidized to form nitrite (NO\textsubscript{2}\textsuperscript{-}) and nitrate (NO\textsubscript{3}\textsuperscript{-}) ions. Nitrate and ammonia can be taken into plants and used. This puts nitrogen into the food chain. Nitrogen comes back into the soil through manure and decomposition. Nitrate can also leave the soil through nitrate photolysis, meaning nitrate will break into reactive oxides when exposed to ultraviolet light. Nitrate can break down into nitric oxide (NO), other reactive oxides of nitrogen (NO\textsubscript{y}), which includes HONO, HOONO, HNO\textsubscript{3} among other species. One of the most dangerous sinks for NO in the atmosphere is HNO\textsubscript{3}, or nitric acid.

\[
\begin{align*}
N_2 + O_2 & \rightarrow 2NO \\
2NO + O_2 & \rightarrow 2NO_2 \\
2NO_2 + H_2O & \rightarrow 2H^+ + NO_3^- + NO_2^- 
\end{align*}
\]

Acid rain will also increase the speed of erosion in karst topographies. From southern Indiana into Tennessee has karst topography, central Kentucky is located in the middle of this region. Karst means there is soluble bedrock. In central Kentucky the bedrock is thick, flat lying limestone. This karst topography is the reason that Mammoth
Nitrogen Fixing Bacteria

Nitrogen Fixing Bacteria

Figure 1.1. The nitrogen cycle including nitrate photolysis. Nitrogen from the air is converted to ammonia, which is oxidized. Nitrate is a photoactive oxide of nitrogen that breaks into nitric oxide and other reactive oxides of nitrogen upon exposure to ultraviolet light.
Cave formed, and is also responsible for the 2014 sink hole in the Corvette plant in Bowling Green Kentucky. This shows the importance of studying levels of NO and NO\textsubscript{y} in western Kentucky. Mammoth Cave is considered a world heritage site, meaning every effort should be taken to preserve it. Inside the cave they do not allow visitors to touch the walls of the cave because the oils on peoples’ hands have eaten away at parts of the cave. The tour guides and park officials are taking measures to preserve the cave, so monitoring acid rain levels is just one more measure being taken to preserve this site.

Acid rain could accelerate the erosion and damage the cave.

According to the National Park Service’s assessment of Mammoth Cave National Park the park is at high risk for acid rain, and a very high risk ecosystem. The report from the National Park Service states that the highest pollution is found near electric power plants, and large population centers. Mammoth Cave National Park is near both of these pollutant risks (Nashville, Bowling Green, Tennessee Valley Authority Paradise Fossil Plant). The National Park Service based their assessment of pollution and risk on oxidized nitrogen and sulfur levels, proximity to populations, and proximity to agriculture. This makes it even more important to monitor the acid rain in and near Mammoth Cave National Park.

Even though NO can be dangerous because of acid rain, it will never be absent from the atmosphere. NO observed at Mammoth Cave National Park follow a diurnal pattern which has been observed by other researchers.\textsuperscript{2,5,10,11} NO levels rise in the morning and sets in the evening with the sun. This is because of nitrate photolysis beginning when the sun rises in the morning, and as the sun sets NO reacts to form other
oxides of nitrogen or settles out of the atmosphere. NO levels are near 0 while the sun is
down, so before the sun rises and after it sets NO is near zero, but NO\textsubscript{y} never sets to zero.
NO\textsubscript{y} levels do not significantly vary during the day and do not follow as regular of a
pattern.

The National Park Service has been collecting data for many years. In 2003,
hourly data collection began of ozone (O\textsubscript{3}), CO, and a few other species. Trace gas data
has been collected every minute since 2009, and wet and dry deposition since the early
2000s. The trace gas data is measured in parts per billion (PPB) and includes NO, NO\textsubscript{y},
O\textsubscript{3}, CO, and SO\textsubscript{2}, among other measurements, such as wind direction, wind speed,
temperature, and solar radiance. The hourly data is the average level within each hour,
and the data collected this way includes all of the species being measured every minute
with the addition of NO\textsubscript{2} and some other elements that weren’t measured every minute.
The wet-deposition data has the concentration in parts per million of the precipitation
gathered. Wet-deposition data is averaged for the week.

The National Park Service was very concerned about the Tennessee Valley
Authority (TVA) Paradise Fossil Plant. Paradise released about 28,000 tons of SO\textsubscript{2},
10,000 tons of NO\textsubscript{x}, and 16,000,000 tons of CO\textsubscript{2} into the atmosphere in 2012.\textsuperscript{12} NO\textsubscript{x} is
not the same as NO\textsubscript{y}. NO\textsubscript{x} is a subset of NO\textsubscript{y} containing the levels of NO and NO\textsubscript{2}. NO\textsubscript{y}
includes both these compounds in NO\textsubscript{x} and many more compounds such as HONO,
HNO\textsubscript{3}, etc. The levels of SO\textsubscript{2} and NO\textsubscript{x} are significantly lower than they have been in
previous years, for example Paradise released 480,000 tons of SO\textsubscript{2} in 1976 and150,000
tons of NO\textsubscript{x} in 1997. CO\textsubscript{2} levels have remained somewhat consistent over the years.
Given the amount of emissions, even though they have decreased significantly over recent years the National Park Service should worry about the pollutants travelling the 80 km to Mammoth Cave National Park, considering Mammoth Cave was assessed to have a very high risk ecosystem. This is the reason that point sources were investigated in this project.

There are two models of how chemicals move in the atmosphere, the general circulation model and the chemical transport model. The general circulation model deals with how everything in the atmosphere moves. This is where the trade winds, the westerlies, and all other major wind currents on the earth come from. The chemical transport model is only concerned with a few species moving from one place to another. Figure 1.2 demonstrates this model using a smoke stack. The smoke diffuses left, right, up, and down in the same direction as the wind as it leaves the smoke stack. This is what is meant by a point source: something such as smoke, exhaust, or anything that is a source being localized to one point, then diffusing out.

The levels of NO and NO$_2$, as well as SO$_2$ and CO will be analyzed using data collected by the National Park Service at Mammoth Cave National Park. These will be used to look at correlations of the wet-deposition data to reveal Mammoth Cave National Park’s acid rain risk. The presence of point sources will be analyzed to determine what species are coming into the park from other locations.
Figure 1.2. Demonstration of a point source using a smoke stack. The smoke spreads up, down, left, and right in the direction of the wind as it leaves the smoke stack.
CHAPTER 2

METHODS

A custom MatLab program was written to analyze data collected at Houchin Meadow Atmospheric Monitoring Center at Mammoth Cave National Park. The MatLab program cleaned, processed, analyzed, and mined data collected at Houchin Meadow Atmospheric Monitoring Center for correlations.

2.1 Site Survey

Atmospheric data is collected from Houchin Meadow Atmospheric Monitoring Center in Mammoth Cave National Park. It is located at 37.1313°N and 86.148°W. The monitoring center is surrounded on three sides by forest as can be seen in Figure 2.1. It is separated by 30 km from Bowling Green, the nearest city, 7 km from the nearest interstate, I-65, and 80 km from the nearest major power plant, Paradise fossil plant. The distance separating the site and the nearest civilization leads to the hypothesis that the site is relatively separated from anthropogenic sources. This would allow the processes that occur naturally to be studied with minimal interference from man-made sources. The extent that the site is isolated from outside influences will be discussed in Chapter 3.

The National Park Service maintains Thermo Fisher Scientific instruments that collect trace gases (NO, NO\textsubscript{y}, CO, and SO\textsubscript{2}). They also have a Prevention of
Figure 2.1. (Top) Google earth images of Houchin Meadow Atmospheric Monitoring Center. (Bottom) Google earth image of Mammoth Cave National Park represented by white rectangle and white oval is TVA Paradise Fossil Plant.
Significant Deterioration (PSD) to measure ozone O₃ on the scale of 0-500 PPB. These instruments gather data for these trace gases every minute of every day of the year. The species collected by the atmospheric instruments are nitric oxide (NO), reactive oxides of nitrogen (NOₓ), ozone (O₃), sulfur dioxide (SO₂), and carbon monoxide (CO). NOₓ is a measurement of all reactive oxides of nitrogen (NO, NO₂, HONO, HNO₃, HOONO, etc).

The monitoring center also collects wind direction, wind speed, temperature, and solar radiance every minute. The trace gases (NO, NOₓ, O₃, and CO) levels are recorded in parts per billion (PPB) of the atmosphere. Wind direction is recorded in degrees, in integer values of degrees. Wind direction is recorded as the direction that the wind is coming from, so 0° is coming from due north. The degrees increase clockwise. Wind velocity is measured in meters per second. Solar radiance is the intensity that light from the sun is shining on the site. It is measured in watts per square meter by a panel at the inlet of the monitoring center, 10 m above the site. Data every minute has been collected since June, 2009, and is uploaded three months after the data is collected. This project has access to atmospheric data for every minute for the years 2010, 2011, 2012, and 2013. This project will not display data collected in 2013 because this project was conducted in 2013.

In addition to the trace gas detectors there are wet and dry deposition collectors. Figure 2.2 shows the device that is used to collect both wet and dry data. This has a sensor that detects if there is wet precipitation. If there is precipitation the dry bucket is automatically covered allowing all the precipitation to collect in the wet bucket, and vice versa for the dry bucket. This allows snow, rain, freezing rain, and sleet to be analyzed.
Figure 2.2. Device used to collect wet and dry deposition. When the sensor detects precipitation the left bucket is covered. When no precipitation is detected, the right bucket is covered.
separately from dust and other solid particles that settle from the atmosphere. The pH, nitrate, sulfate, calcium, and potassium levels are measured from precipitation collected. The data from this instrument is measured once per week. This allows for the concentrations in precipitation to be roughly correlated with the concentration of trace gases in the atmosphere, which will be discussed in Chapter 4.

2.2 Data Sources and Downloads

The data is stored locally for three months before it is uploaded to one of the National Park Service’s websites. Atmospheric data that is collected every hour or every minute is uploaded to http://ard-request.air-resource.com/, and wet-deposition data is uploaded to http://nadp.sws.uiuc.edu/data/. The data from these websites is open to the public, and can be downloaded. The site must be selected, then the type of data (minutely, hourly, daily, monthly etc) is selected, then the length of time is to be downloaded is selected. This makes it possible to download data for a single day, or a single month, or an entire year. Once the data is downloaded it can be loaded into a custom written MatLab script. Our MatLab script was be written to perform any cleaning or fitting that needs to be done to the data.

The data for every species is downloaded from the website into folders for the years (2010-2012). The months are numbered 1-12 and saved in the comma separate value format that it was downloaded in. The MatLab code calls the folder of the year, and calls each month of the year within a “for” loop. The code breaks the data set into smaller parts that can be analyzed. The species of data are all in individual columns, with each row for every minute within the full data set. These are broken into individual
species that contain all of the data points for the entire month. An example of one of the MatLab scripts used in this project is provided in Appendix A.

2.3 Data Cleaning

The first step to analyzing the data is cleaning it. The data must be cleaned because the instruments run every minute of everyday must periodically calibrate themselves. During the time that the instruments are calibrating themselves the computer records a place holder value for the time that it was down or calibrating. The value that is used is -999. The top panel of Figure 2.3 shows what the data without removing the -999 place holders. The graph range is dominated by -999s, and any usable data is eclipsed by the invalid data points, making any analysis of valid data points impossible visually. The -999 values only account for approximately 20% of the data each month. The exact percentage fluctuates each month. -999 is much higher than the values of NO in PPB. This percentage was determined using a percent coverage calculation. To do a percent coverage calculation all of the NaN values were removed from a data set; then they were divided by the total size of the data set before the NaNs were removed. This gives the number percentage of usable data in each data set. The compliment to the percent coverage is the percentage of invalid data points for a month.

The bottom panel of Figure 2.3 shows the values of NO with -999s removed, and the highest value of NO is less than NO 5 PPB. The bottom graph of Figure 2.3 shows NO rising and falling as the sun rises and sets each day of the month, this is the same graph with -999s removed. -999 data points are replaced with Not a Number (NaN) place holders. NaN’s are recognized by MatLab as invalid points, and does not plot them. The
Figure 2.3. (Top) The raw data for April, 2011 was plotted with -999 values. (Bottom) Data for April, 2011 plotted without -999 values. Diurnal pattern can be seen in bottom graph.
bottom graph in Figure 2.3 shows that the data is clearer once the placeholder values were removed and replaced with NaNs.

2.4 Graph Generation

After the data is cleaned, any graphs of interest for each month are then generated. These could be correlations of solar radiance with NO, correlations of carbon monoxide (CO) with wind direction. This variety of needed graphs necessitated breaking the code into many different MatLab codes. Each code was written for a specific purpose. The cleaning is the same for every program, but the analysis preformed by each code depends on the goal. For example there is one script that only generates wind direction graphs, another that generates graphs of the monthly averages; each type of graph has its own script.

Pollution coming into the park could be a major problem because NO or SO₂ can react to form acid rain. The National Park Service reports that Mammoth Cave National Park is at a very high risk for acid rain, and is at very high risk of pollution coming into the park.⁹ This risk factor concerned the National Park Service at Mammoth Cave National Park about the amount of pollution coming into the park, and where the pollution is coming from. Wind direction is measured in whole degrees. This makes it inconvenient to analyze each degree individually. Wind direction was binned into 10 degree bins, meaning every degree from 0 to 9 is taken to be one point, then 10 to 20, and every ten degrees from that point on. Trace gas data was taken simultaneously with the wind direction. For graphs correlating wind direction with trace gases, the wind direction and species of interest were grouped per minute. The trace gases were put into the bin
with the wind direction. Averaging and integrating the trace gas species based on wind
direction were packaged into subscripts to bin the data and perform any desired function
within the larger MatLab program.

The next correlation of interest is wet deposition with the atmospheric data. Wet-
deposition data is uploaded as the average of each species per week. In order to correlate
the wet deposition with atmospheric data, a new script was written. This script summed
the atmospheric data that was recorded every minute, and divided by the total number of
points that week, excluding NaNs in both cases. The weekly averages were then
correlated with the wet-deposition data.

The data begins as columns of each species/data type with rows of every data
point for each month. This can be redimensioned into time and day for each species as
shown in Figure 2.4, which is a three dimensional representation of the values for NO,
NO\textsubscript{y}, and SO\textsubscript{2} for a month. Each vertical column is a day, the y-axis is the minutes of the
day, and the colors are the concentration. The colors range from dark blue to red. Red is
the maximum concentration of that data set, and the colors follow the spectrum beside the
graph. The very dark blue bands reaching across the graphic are the regular updates
where the instrument was updating or calibrating. This figure illustrates the regular
calibrations very clearly; the bands occur at the same time everyday for the same amount
of time for every species. This also shows that NO\textsubscript{y} and SO\textsubscript{2} maintain more periodic
fluctuations through the month, whereas NO fluctuates similarly each day. This shows
that there is a regular pattern of NO rising at the same time each day and falling around
the same time every day.
Figure 2.4. Three dimensional plot of trace gases, the concentration is represented by color. The x-axis is the days in the month of January 2011, y-axis is the minutes of the day. (Top) NO. (Middle) NO$_y$. (Bottom) SO$_2$. 
2.6 Outlier Removal

After the calibration-period values were removed there were still some data points that appear invalid. Levels of NO above 50 parts per billion are very unlikely without a significant source nearby. Upon closer inspection of the points in question it was found that they are only one minute of unusually high levels before they dropped back to the levels that are expected. The spikes are most often found in the middle of removed (-999) data points or shortly after a series of removed data points. This indicates that these spikes are caused by some malfunction of the equipment, either the detector recording data from a calibration cycle, or that the detector was malfunctioning and recording a bad data point. The instruments are calibrated using a dilution tube where they are flooded with 80%, 60%, 40%, 20% and 0% of the detectors capacity. This means that if a data point was taken during a calibration period that it could detect very high levels. 80% of 500 is 400 PPB. These invalid data points occur a few times a year, they are not a recurring event on a daily basis. When these data points are removed the data becomes clearer as demonstrated in Figure 2.5. Figure 2.5 shows all of the NO values for 2010 on the top graph. There are 3 spikes above 50 PPB, one as high as 180 PPB. The bottom graph shows all of the values for 2010 lower than 50 PPB, the daily cycle of NO can be seen on this graph because the daily levels of NO are expected to be around 3PPB, not 180 PPB. The data for the entire year becomes clearer after these data points were removed.

Figure 2.6 shows the average values of each month for 2010. The top graph is the average of NO for each month without removing points greater than 50 PPB. The bottom
graph is the same averages after points greater than 50 PPB are removed. Removing points above 50 ppb does not affect the monthly average, which confirms that the overall average of the trace gas levels is not affected by removing these points. This means that these points can be removed with confidence that they are invalid and that removing them will not change the overall average of the data.

The code for MatLab has been written to analyze correlations with wind direction, solar radiance, and wet deposition. These correlations will be discussed in the remaining chapters of this thesis.
Figure 2.5. (Top) Raw data for 2010 without -999 values. (Bottom) Data from 2010 with points greater than 50 PPB removed. The data is visually easier to see.
Figure 2.6. (Top) Monthly average of NO for 2010 with every point except -999s included. (Bottom) Monthly average of NO for 2010 with -999s and values great than 50 PPB removed. Removing outliers does not affect the overall average.
CHAPTER 3

ATMOSPHERIC DATA

The methods described in Chapter 2 are used to analyze the major questions from the National Park Service and those raised by the literature search. The two main questions asked in this chapter are what are the NO patterns observed in Mammoth Cave National Park, and what point sources are there for Mammoth Cave National Park.

3.1 NO Patterns

NO is diurnal, meaning levels rise in the morning and set with the sun. This is because nitrate has photochemical properties. When the sun rises it produces UV light, which breaks nitrate's bonds. This releases NO and other reactive oxides of nitrogen into the atmosphere as were discussed in Chapter 1. Figure 3.1 demonstrates this very clearly: the average level of NO begins to rise around 6 am and begins to fall to zero around 3 pm. Figure 3.1 is the average and standard deviation of NO every minute of every day of the month of January 2011. The month of January was averaged such that the average of the NO value collected at 10:01 every day of January is one point. For each averaged point the standard deviation of all days at that time is calculated, and added and subtracted from the average to give the upper and lower bounds. Average sunrise for January is 7:00 and average sunset is 4:45 pm. The average rise in NO level is consistent with the average sunrise. The decrease in NO levels is finally zero when the
Figure 3.1. (Top) NO was binned into time of day and averaged for the month of January for 2011. Red lines are the standard deviation of this average. Percent coverage is the percentage of usable data out of the possible data. (Bottom) NO correlated with solar radiance for 1/31/2012. The correlation coefficient and slope are calculated.
sun had set. This is consistent with the rising and setting of the sun for this area, implying that solar radiance will be strongly correlated with NO levels.

The red lines above and below the average are the standard deviation. The standard deviation of the average NO in Figure 3.1 is large, which can be accounted for by looking back to Figure 2.5. The levels of NO vary greatly from day to day, but the pattern of NO rising in the morning and falling in the evening is consistent every day. This same pattern is seen in Figure 2.5 where the NO levels are almost zero at night while the sun is down, but increase when the sun rises. Figure 2.5 also shows that the levels vary greatly from day to day; some days are much higher than others, accounting for the large standard deviation. This could be caused by the wind blowing in more NO than other days as will be discussed in Chapter 4, or it could be from greater solar radiance. The cause of the variation is not clear.

The approximate background level of NO is zero. When the sun is not up NO levels are consistently zero. The standard deviation of Figure 3.1 is very low when the sun is down and the level of NO is approximately zero. This means that the average level of NO when the sun is down is approximately zero and there is very little deviation from this. This can also be seen in Figure 2.5, each day when the sun sets the NO level falls to near zero.

This pattern is similar to Day’s observations on a slope in Blodgett Forest Research Station in the Sierra Nevada Mountains in California. Day had very low standard deviation in the average graph solar radiance versus NO concentration. The levels of NO in the graph rise in the morning, and fall in the evening, and the levels observed when the sun is down were approximately 0.01 PPB. One reason Day found
lower standard deviation than was found here could be that they used 30 minute medians, instead of averaging every minute. Another reason could be that Day had a much smaller data set (weekdays) instead of using every day for the month. California may have less variation in the levels of NO, which would also account for the lower standard deviation in Day’s data. The daily pattern, however, is the same here and in Day’s paper. Day’s background level of NO could have been higher because the maximum value in the graph is 0.1 PPB, whereas the maximum in Figure 3.1 is approximately 1 PPB. There is a higher average maximum level of NO in Mammoth Cave National Park than in the Blodgett Forest Research Station.

The bottom panel in Figure 3.1 shows the expected NO pattern because the NO is positively correlated to solar radiance. The more intensely the sun is shining the more nitrate ions are expected to photolyze and releases NO into the atmosphere. In the figure there is a large cluster of low NO levels near zero solar radiance. This was also observed in the top graph of Figure 3.1. When the sun is down, before sun rise and after sunset, the NO levels drop almost to zero on average everyday of the month. This supports that NO is positively correlated to solar radiance. This also gives support to NO being diurnal, because in order for there to be a positive correlation there must be a drop in NO levels when the sun sets.

Since it is expected that NO is positively correlated with solar radiance, the slope of solar radiance with respect to NO for every day of the year can be calculated, along with the correlation coefficient. The NO and solar radiance slope and correlation coefficient can show how much the sun raises the levels of NO every day, and how well the data fits the linear correlation. The top panel of Figure 3.2 is the slope of NO versus
Figure 3.2. (Top) slope of NO vs. solar radiance for each day of the year of 2011 excluding May and June. (Bottom) correlation coefficient of the linear fit of NO versus solar radiance.
solar radiance every day of 2011, and the bottom panel is the correlation coefficient squared every day of 2011. May and June were omitted because of an artifact in the code before the use of NaNs that prevented months starting with a -999 value from being run through this program. May of 2011 only had approximately a week of usable data in it, the detectors are assumed to have been down for most of this month and June. June had approximately a week and a half of usable data. The lack of data available in these months is the reason it is not believed that the omission of May or June will affect the overall data. April ends on the 120th day of the year, so at 120 on the x-axis the data jumps from April 30\textsuperscript{th} to July 1\textsuperscript{st}.

The slopes of solar radiance versus NO concentrations are lower and better correlated to the data on the edges of the graph. The slopes start low in January, and end low in December. The bottom panel of Figure 3.2 resembles Figure 2.6. The average levels of NO are higher in the colder months, and the correlation is better when the levels are higher. Sillman simulated the dependence of NO\textsubscript{x} (NO + NO\textsubscript{2}) and other reactive oxides of nitrogen (peroxyacetyl nitrate (PAN), HNO\textsubscript{3}, RNO\textsubscript{3}) on temperature.\textsuperscript{11} The atmosphere of rural areas from Alabama and Michigan were simulated. NO\textsubscript{x} was consistently the lowest species, and it consistently drops as temperature increases. This indicates that NO and NO\textsubscript{2} levels should drop as temperature rises. This could account for the drop in the average levels of NO in the warmer months from Figure 2.6. A drop in average NO levels could create less variation, and therefore a better correlation between NO and solar radiance, accounting for the pattern seen in Figure 3.2.

Looking at NO and its correlation with solar radiance is only valid if the NO is being generated naturally from nitrate photolysis, and not from anthropogenic
sources. Possible anthropogenic sources will be analyzed by looking at the correlation of NO with wind direction to look for point sources of species coming into the park.

3.2 Point Sources

NO, CO, NO\textsubscript{y}, and SO\textsubscript{2} can all be produced by natural processes, but they are all produced by man-made sources as well. It is important to know to what extent the site is isolated from point sources if the natural processes are being studied at a site. This will be done by correlating CO and NO with the wind direction. CO is produced by automobiles, as is NO\textsuperscript{4}.\textsuperscript{17} CO will be analyzed to assess the sites isolation from exhaust from automobiles. NO will be a general pollution marker because it is produced by industrial processes, such as TVA Paradise Fossil Plant, as well as automobiles.

The top panel of Figure 3.3 is a histogram of the wind direction 2010; it shows that the highest occurrences of wind direction of the year are near 200°, with a smaller peak near 320°. It is binned into ten degree bins, meaning the total number of values between every ten degrees is summed and treated as one data point. Binning wind direction was necessary because wind direction is not quantized, but a continuum. Binning was performed to give a clear picture of the wind direction for the year. For the purpose of correlating the wind direction with species in the atmosphere 10 degrees was enough sensitivity.

While the histogram of the wind direction shows the sum of the wind directions for the year, the middle panel in Figure 3.3 is the integrated CO level as a function of wind direction. CO was binned along with wind direction. Data is recorded every minute, so the CO value was linked to the wind direction for each minute. When the wind directions were binned, so were the CO values. These values were summed for
Figure 3.3. (Top) Histogram of the wind direction for 2010 in ten degree bins. (Middle) Integrated carbon monoxide for 2010 in ten degree bins. (Bottom) Averaged carbon monoxide for 2010 in ten degree bins.
each bin to produce the middle graph. The highest integrated CO is near 200˚ as was the histogram’s highest number of occurrences. The top and middle panels of Figure 3.3 have the same shape; this pattern is observed for every year. The integrated CO levels clearly reflect the histogram of wind direction. The most CO blows in from the direction that the wind blows most. CO following the wind direction means that there is not a large source of CO coming in from another area. This is assuming that if there was a large source of CO it would contribute so much CO that the total CO coming from that direction would be visible in the integrated CO level as a function of wind direction. That is, the CO source would be so significant that that direction would consistently have greater levels of integrated CO.

The bottom panel of Figure 3.3 is the averaged CO level, meaning that the CO was binned into ten degree bins like the middle graph, then summed and divided by the number of points in that bin. This gives the average of the CO coming into the park from each wind direction. The average peak is shifted slightly to the south east from the south. This indicates there is a point source that is putting more CO in the air on average than the rest of the wind. This can be accounted for by observing Table 3.1. There is not a major city to the south east of Mammoth Cave National Park. I-65 wraps around the south east sides of the park. This explains why the average is shifted east from the peak of the histogram. CO coming from the interstate is not isolated to one point, like a factory would be, which is a possible reason I-65 did not appear to be a point source from the integrated CO. The CO from I-65 could be distributed over 5-7 bins of wind direction, whereas a factory or Paradise Fossil Plant would have been within one bin. There is constant traffic on the interstate at all times of the day, and these automobiles are
producing CO at all hours of the day. It is well known that combustion engines produce CO so an increased presence of CO from the direction of a busy road makes sense.

CO was not in the list of pollutants from TVA Paradise Fossil Plant, so NO was analyzed to look for TVA Paradise Power Plant as a point source. Paradise put 10,000 tons of NO\textsubscript{x} in 2012\textsuperscript{12}. NO\textsubscript{x} is the sum of NO and NO\textsubscript{2} levels.

Figure 3.4 shows the analysis of NO data with the wind direction. The top panel is a histogram of the wind direction for 2012. The middle panel is the integrated NO for 2012, and the bottom panel is the average NO. These graphs were generated in the same way as the graphs for CO described above. Integrated NO follows wind direction very

\begin{table}[h]
\caption{Cities and interstates near Mammoth Cave National Park. The direction and distances measured by Google Earth. Direction is measured as the city to Mammoth Cave National Park, so the direction reflects the measurement of wind direction at the site.}
\begin{tabular}{lll}
\hline Locations & Direction in degrees & Distance (km) \\
\hline TVA Paradise Fossil Plant & 282 & 80 \\
Bowling Green & 238 & 30 \\
Nashville & 207 & 126 \\
Louisville & 15 & 128 \\
I-65 & \textasciitilde49-230 & \textasciitilde230 \\
Owensboro & 309 & 113 \\
Elizabethtown & 21 & 68 \\
\hline
\end{tabular}
\end{table}
Figure 3.4. (Top) Histogram of the wind direction in ten degree bins for 2012. (Middle) Integrated nitric oxide in ten degree bins. (Bottom) Averaged nitric oxide in ten degree bins.
closely, just as CO did. The average NO level is not shifted south east as the CO did. It is shifted sharply west, with a thin peak around 240°. This indicates that Bowling Green is a likely point source. The Corvette assembly plant, as well as a Fruit of the Loom plant is located in Bowling Green. Bowling Green’s population was 49,125 in 2000, and increased to 58,000 in 2010.\textsuperscript{18} Bowling Green’s population increased by almost 10,000 people in the last ten years. With this population growth industry has grown rapidly, and can be seen in Mammoth Cave National Park. This may represent the first identification of Bowling Green as a source of pollution at Mammoth Cave National Park.

From the data processed thus far TVA Paradise Fossil Plant cannot be seen at Mammoth Cave National Park. This is not surprising because it is 77 km away from Mammoth Cave National Park where as Bowling Green is almost half the distance at 30 km. The data analyzed thus far has not suggested that TVA Fossil Power Plant is significant source of pollution Mammoth Cave National Park. Bowling Green and I-65 appear to be contributing to the levels of CO and NO respectively in Mammoth Cave National Park.
CHAPTER 4

WET-DEPOSITION DATA

After analyzing the average trends of NO, and the possibility of point sources the contribution to the concentration of NO, nitrate ion found in precipitation still needs to be discussed. SO\textsubscript{2} was correlated with sulfate as well to compare the results of ions with and without photochemical properties.

4.1 NO and NO\textsubscript{y} Correlated with Nitrate Seasonally

It has been shown here and elsewhere that NO is positively correlated to solar radiance. It is theorized that this is from the photolysis of nitrate ions in the soil, organic sources such as leaves, and water\textsuperscript{10,19}. Nitrogen dioxide can also react with sunlight to break apart into oxygen and nitric oxide\textsuperscript{4}. To analyze the impact of nitrate photolysis on the production of NO and NO\textsubscript{y} the correlation of nitrate ions in precipitation and NO in the atmosphere was analyzed. The atmospheric and wet-deposition data were downloaded for the same length of time. The atmospheric data is then averaged for each week of the time period; this is because the wet-deposition data is recorded for each week instead of each minute like the atmospheric data. The averaged data is then correlated with the wet-deposition data.

NO is only one of the reactive oxides of nitrogen in the atmosphere, NO\textsubscript{y} encompasses the rest of the reactive oxides of nitrogen, such as HONO, HOONO, HNO\textsubscript{3},
and NO\textsubscript{2}. This is why NO\textsubscript{y} is also correlated with the wet-deposition data. NO can react to form NO\textsubscript{2}, HONO, and HOONO, all of which are encompassed in NO\textsubscript{y}. This correlation was performed to show correlations with nitrate that would not be included in the NO correlations.

Figure 4.1 is the plot of NO versus nitrate ion wet-deposition concentrations every season for the year of 2011. Each season lasts 3 months, winter from December to February, spring from March to May, summer from June to August, and fall from September to November. Few of the graphs appear to be correlated at all. The slope, correlation coefficient, and p-value were determined for each season and listed in Table 4.1. The correlation coefficient is a measure of how well the slope fits the data, and the

<table>
<thead>
<tr>
<th>NO</th>
<th>Slope</th>
<th>Correlation Coefficient</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter '11</td>
<td>29.3016</td>
<td>0.020491</td>
<td>0.95231</td>
</tr>
<tr>
<td>Spring '11</td>
<td>-1,034.2269</td>
<td>-0.47077</td>
<td>0.23905</td>
</tr>
<tr>
<td>Summer '11</td>
<td>-203.2781</td>
<td>-0.51961</td>
<td>0.12372</td>
</tr>
<tr>
<td>Fall '11</td>
<td>652.9042</td>
<td>0.41372</td>
<td>0.23463</td>
</tr>
<tr>
<td>Winter '12</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Spring '12</td>
<td>361.1165</td>
<td>0.83657</td>
<td>0.0096181</td>
</tr>
<tr>
<td>Summer '12</td>
<td>-113.5506</td>
<td>-0.17747</td>
<td>0.64782</td>
</tr>
<tr>
<td>Fall '12</td>
<td>1,156.939</td>
<td>0.01711</td>
<td>0.72744</td>
</tr>
</tbody>
</table>
Figure 4.1. (A) Integrated NO with nitrate for winter 2011. (B) Integrated NO with nitrate for spring 2011. (C) Integrated NO with nitrate for summer 2011. (D) Integrated NO with nitrate for winter 2011.
p-value is the probability of getting the same correlation with randomly generated data. A p-value of less than 0.05 is considered statistically significant. The only statistically significant seasonal correlation was spring 2012, but spring 2011 was not statistically significant. This leads to the conclusion that spring 2012 is an outlier, and that NO is not statistically correlated to nitrate ion concentration in wet deposition.

When NO was determined not to have a statistically significant correlation to nitrate ion, NO\textsubscript{y} was compared to determine if it would give a statistically significant correlation. Graphs for each season of NO\textsubscript{y} correlated with nitrate are shown in Figure 4.2. It can be seen from Figure 4.2 that none of the graphs appear to be correlated with nitrate. Neither NO or NO\textsubscript{y} gave statistically significant correlation. This could be because it is estimated that 1/3 of the NO in the air come from nitrate in the soil\textsuperscript{20}. This could explain why the wet deposition is not well correlated with NO. NO that comes from solid sources, and sources that are settling out of the atmosphere were not considered at all. Also, the concentration of nitrate ion in the surrounding lakes, streams, soil, and vegetation are unknown. The wet-deposition data is a very small percentage of all of the possible sources of nitrate that could contribute to NO in the atmosphere.

4.2 SO\textsubscript{2} Correlation of SO\textsubscript{2} with Sulfate Seasonally

No correlations were found from nitrate with NO and NO\textsubscript{y}, so the correlation of sulfate and SO\textsubscript{2} was analyzed to determine if there was a seasonal correlation. There is not much literature concerning sulfate ions producing SO\textsubscript{2} in the atmosphere, but there are many papers describing SO\textsubscript{2} oxidizing into sulfate\textsuperscript{14, 21}. These correlations
Figure 4.2. (A) Integrated NO$_x$ with nitrate for winter 2011. (B) Integrated NO$_x$ with nitrate for spring 2011. (C) Integrated NO$_x$ with nitrate for summer 2011. (D) Integrated NO$_x$ with nitrate for winter 2011.
were performed to investigate to what degree \(\text{SO}_2\) in the atmosphere of Mammoth Cave National Park is scavenging into the precipitation. If \(\text{SO}_2\) was collecting in the precipitation it would be expected that the levels of \(\text{SO}_2\) would decrease as the concentration of sulfate ions increases in the wet deposition.

Sulfate from wet deposition was downloaded for every season as was \(\text{SO}_2\). The \(\text{SO}_2\) that was recorded every minute was summed every week to correlate with sulfate. The correlations of sulfate with \(\text{SO}_2\) can be seen in Figure 4.3. The correlation coefficients and p-values are displayed in Table 4.2.

From the p-values in Table 4.2 \(\text{SO}_2\) is not statistically correlated to sulfate. One season that was statistically significant according the p-value, fall 2012, but none of the

**Table 4.2.** The table is the slope, correlation coefficient and p-value of each season of 2011 and 2012. The slope if from the linear fit of \(\text{SO}_2\) versus \(\text{SO}_4^{2-}\), the correlation coefficient is how closely this fit represents the data, the p-value is the probability that the same correlation could be obtained from randomly generated data.

<table>
<thead>
<tr>
<th>Season</th>
<th>Slope</th>
<th>Correlation Coefficient</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter ‘11</td>
<td>-78.603</td>
<td>0.0101</td>
<td>0.97627</td>
</tr>
<tr>
<td>Spring ‘11</td>
<td>12,313.811</td>
<td>0.36151</td>
<td>0.37891</td>
</tr>
<tr>
<td>Summer ‘11</td>
<td>269.986</td>
<td>0.09446</td>
<td>0.79521</td>
</tr>
<tr>
<td>Fall ‘11</td>
<td>2,686.866</td>
<td>0.35021</td>
<td>0.32117</td>
</tr>
<tr>
<td>Winter ‘12</td>
<td>5,564.951</td>
<td>0.45515</td>
<td>0.2183</td>
</tr>
<tr>
<td>Spring ‘12</td>
<td>2,165.191</td>
<td>0.41053</td>
<td>0.311237</td>
</tr>
<tr>
<td>Summer ‘12</td>
<td>813.918</td>
<td>0.1822</td>
<td>0.60918</td>
</tr>
<tr>
<td>Fall ‘12</td>
<td>5,450.167</td>
<td>0.65191</td>
<td>0.029857</td>
</tr>
</tbody>
</table>
other seasons were statistically correlated. Only one of the seasons analyzed here has a negative slope. If the SO$_2$ levels were negatively correlated with sulfate they would be expected to have a negative slope. Only one season was negatively correlated, and the p-value was .97. This means that the in one season with a negative slope it had a very high probability of having the same fit with randomly generated data. The data does not support the hypothesis of SO$_2$ being negatively correlated with sulfate. There is a high risk of acid rain in the park, but SO$_2$ is not being oxidized to sulfate in the park. The high p-values also lead to the conclusion that SO$_2$ is not seasonally correlated with sulfate in wet deposition.

4.3 NO and SO$_2$ Correlated with Nitrate and Sulfate Yearly

No seasonal correlation was found between wet deposition sulfate and SO$_2$ or nitrate with NO, so the yearly correlations were assessed. These were assessed because it was hypothesized that because each season only had 12 data points (4 weeks per month, 3 months per season) in them, they could not be representative of the data set as a whole. Integrated NO and SO$_2$ were plotted against nitrate and sulfate for the entire year, and the slope, correlation coefficient, and p-value were all determined. These can be found in Table 4.3.

It can be seen that even though all of the slopes of both species are positive they are not statistically significant. This again does not support the hypothesis that SO$_2$ is negatively correlated with sulfate. Any sulfuric acid rain in the park is most likely coming into the park as acid rain, not being made within the park. The concentrations in
Figure 4.3. (A) SO$_2$ correlated with sulfate for winter 2011. (B) SO$_2$ correlated with sulfate for spring 2011. (C) SO$_2$ correlated with sulfate for summer 2011. (D) SO$_2$ correlated with sulfate for fall 2011.
Table 4.3. Slope, correlation coefficient and p-values for NO correlated with nitrate and SO\textsubscript{2} correlated with sulfate for 2010, 2011, and 2012.

<table>
<thead>
<tr>
<th>Species and Year</th>
<th>Slope</th>
<th>Correlation Coefficient</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO\textsubscript{2} (2010)</td>
<td>13.9372</td>
<td>0.089609</td>
<td>0.63166</td>
</tr>
<tr>
<td>SO\textsubscript{2} (2011)</td>
<td>10.0426</td>
<td>0.048453</td>
<td>0.779</td>
</tr>
<tr>
<td>SO\textsubscript{2} (2012)</td>
<td>19.4746</td>
<td>0.11713</td>
<td>0.47763</td>
</tr>
<tr>
<td>NO (2010)</td>
<td>5.0139</td>
<td>0.2171</td>
<td>0.24161</td>
</tr>
<tr>
<td>NO (2011)</td>
<td>1.9237</td>
<td>0.05271</td>
<td>0.76013</td>
</tr>
<tr>
<td>NO (2012)</td>
<td>5.2455</td>
<td>0.037291</td>
<td>0.82168</td>
</tr>
</tbody>
</table>

the wet-deposition data were not correlated with the concentrations in the atmosphere for either trace gas ion pair. This could be because the wet-deposition data is only a very small faction of all of the sources of nitrate and sulfate in Mammoth Cave National Park.
CHAPTER 5

CONCLUSION

In this project some important questions were asked, such as how the concentrations of ions in precipitation are correlated with their related species in the atmosphere, and what pollutants are coming into Mammoth Cave National Park. A custom written MatLab program was written to clean and plot data collected by the National Park Service to answer these questions, and the graphs generated have been analyzed.

There were many invalid data points in the data that the National Park Service uploaded. These had to be replaced with place holders that the code in MatLab would recognize as invalid. This was accomplished using the not a number (NaN) place holder in MatLab. Then, some of the data points were above reasonable levels, when data points that were unreasonable were removed it did not affect the appearance of the data as a whole. This demonstrated that the data could be further cleaned without affecting the overall average of the data.

The data collected from Mammoth Cave National Park revealed many things about the atmosphere here in Western Kentucky. The National Park Service had some concerns about the 16,000,000 tons of CO$_2$ and 10,000 tons of NO$_x$ produced by Paradise Power Plant every year.$^{12}$ To address this concern the sources of pollution in the Park
were analyzed by correlating CO with the direction that wind was blowing at each point. When this was compared with the wind direction, the integrated CO levels perfectly reflected the direction the wind was blowing. If there was a point source it would be expected that there would be a spike in the CO levels that was not present in the wind direction. Initially, because the CO is highest around 200° every month, Nashville was suspected as a point source. This would make sense because Nashville is a major city with significant industry and a large population and major interstates intersecting within it. Upon further inspection the wind direction is perfectly reflected by the integrated CO. This shows that the most CO is coming in from the direction that the wind blows from most often. That is to say, there is not an overwhelming source of CO coming into the park. The direction the most CO is coming from is the direction that the wind comes from the most frequently.

Then to explore the hypothesis that all of the wind coming into the park has equal amounts of CO the average of the CO was taken over the same time period. When the average is examined the peak is shifted to the left of the integrated values, showing that even though there is not a large source of CO, the wind is carrying more CO from one direction than all of the others. This source is most likely I-65. The wind blows primarily from the southwest, but the peak of the averaged CO is shifted to the south/southeast. I-65 runs closest to Mammoth Cave National Park on the south and south east sides of the park.

Then NO was investigated to look for the plume of TVA Paradise Fossil Plant’s pollution in Mammoth Cave National Park, because NO is contained in NOx. A
histogram was generated to map the wind direction. Then NO was integrated with respect to the wind direction, and NO was averaged with respect to wind direction. From this NO reflected the wind direction, meaning there are not large sources of NO coming into the park. To determine if the wind from all direction had equal amounts of NO in it the averaged graph was analyzed. There was a peak in the average NO coming from 240°. This is the general direction of Bowling Green from Mammoth Cave National Park. This indicated that Bowling Green is putting more NO into the wind blowing into the park than the surrounding areas.

The NO average with respect to wind direction also indicates that TVA Paradise Power Plant is not a significant source of pollution in Mammoth Cave National Park. This is not surprising because Paradise is approximately 50 km farther from Mammoth Cave National Park than Bowling Green is. The two closest sources of pollution to the atmospheric monitoring center were the two sources that were seen in the averaged data of CO and NO.

The next step in this project is to analyze SO₂ with respect to wind direction. If there is no indication that there is SO₂ coming from TVA Paradise Fossil Plant it would further support the hypothesis that TVA Paradise Fossil Plant is not a significant source of pollution in Mammoth Cave National Park. One of the main sinks for SO₂ in the atmosphere is through acid rain. SO₂ is also produced in by burning coal. This could detect coal emissions with minimal automobile detection. Since Paradise is a coal burning power plant this may have been the best way to search for pollution coming from Paradise.
There was an interest in the correlation of NO with nitrate ions in precipitation. To investigate this, tropospheric levels of NO, NO<sub>y</sub>, and SO<sub>2</sub> were plotted against nitrate and sulfate wet deposition concentrations. A positive correlation between nitrate levels in the wet-deposition data and NO in the atmosphere was expected because of NO’s correlation with nitrate in snow.\textsuperscript{1,2} First, the seasonal data was analyzed looking for correlations, and then yearly data was analyzed in the same way. A p-value of less than 0.05 means that the data is statistically significant; none of the yearly data were found to be statistically significant. There were two seasons with p-values less than 0.05; one in the NO correlations, the other in the SO<sub>2</sub> correlations. These were not in the same season or the same year. It is more likely that these are outliers than that these seasons were well correlated. The same season is not well correlated in the other year that was analyzed, nor in the other species analyzed.

NO, NO<sub>y</sub>, and SO<sub>2</sub> are not correlated with the wet-deposition concentration data. This could be because there is only a very small sample of the wet deposition that is being analyzed. None of the nitrate levels in the streams, rivers, lakes, soil, plants, etc., are being taken into consideration when trying to correlate the atmospheric species with their ionic counterparts. This could be the reason that none of the wet-deposition correlations are statistically significant.

In this part of the project the next step will be to examine the total mass of the ions in the wet deposition. This could take into account dilution effects. The more precipitation present the more dilution occurs, so even though the concentration of nitrate
or sulfate ions is low, there may be a large number of them. This may be a more productive way of looking at the same data.

The dry-deposition data has not been analyzed yet. Another of the next steps of this project will be to analyze the dry deposition’s correlation with the atmospheric data. This may give new insight about what is settling out of the air, and give insight about what is entering the atmosphere from the dry deposition. Under a snowpack, the snow-soil interaction is a significantly contributes to the NO put into the atmosphere.\textsuperscript{10} There may be a strong correlation between the ions in dry deposition and the trace gas species entering the atmosphere.

This project will also investigate the correlation NO has with snow. Observing how the average levels of NO change when snow is present will be important because there has never been a study done on the effect of snow on nitrate levels in a rural area with infrequent snow. There have been numerous studies done on nitrates effect on NO levels in areas where there is consistent snow on the ground in the winter.\textsuperscript{1,2,3,10} This information may provide more insight on the levels of NO in this region. It may also contribute to the determination of a mechanism for nitrate photolysis in snow.
REFERENCES


APPENDIX A

Any data that is present is cleared first. Data files are loaded into the script. Every data point is passed through a “for” loop, and every -999 or -9 is replaced with a NaN placeholder. -999 is the placeholder for the atmospheric data, whereas -9 is the placeholder for the wet-deposition data. Each species is labeled according to the column it was in, in a data hierarchy. Data. is the beginning of all data variables that will be cleared at the end of the “for” loop. Anything not beginning with a d will not be cleared. Then various graphs are generated, this script is responsible for generating the graphs correlating wet deposition and the atmospheric levels. Comments in the code are denoted by a %.

```matlab
clear all

file.path = 'C:\Mammoth Cave Data\';
file.ext = 'Yearly Wet Dry Correlation Data\Year 2012 Air.csv';
file.fileName = [file.path file.ext];
data.allData = dlmread(file.fileName, ',', 11, 2);

%%Loading data into script%%
file.pth = 'C:\Mammoth Cave Data\';
file.ex = 'Yearly Wet Dry Correlation Data\Year 2012 Wet.csv';
file.fileNm = [file.pth file.ex];
data.wetData = dlmread(file.fileNm, ',');

%%Cleaning - 999 and -9 out of data%%
for j_ = 1:size(data.wetData, 1)
    for y_ = 1:size(data.wetData, 2)
        if data.wetData(j_, y_) == -9
            data.wetData(j_, y_) = NaN;
        end
    end
end

%%Breaking wet-deposition data into species%%
data.IdCaData = data.wetData(:, 1);
data.CaData = data.wetData(:, 2);
data.IdMgData = data.wetData(:, 3);
```
data.MgData = data.wetData(:,4);
data.IdKData = data.wetData(:,5);
data.KData = data.wetData(:,6);
data.IdNaData = data.wetData(:,7);
data.NaData = data.wetData(:,8);
data.IdNH4Data = data.wetData(:,9);
data.NH4Data = data.wetData(:,10);
data.IdNO3Data = data.wetData(:,11);
data.NO3Data = data.wetData(:,12);
data.IdClData = data.wetData(:,13);
data.ClData = data.wetData(:,14);
data.IdSO4Data = data.wetData(:,15);
data.SO4Data = data.wetData(:,16);
data.pHLabData = data.wetData(:,17);
data.pHFieldData = data.wetData(:,18);
data.pHFVData = data.wetData(:,19);
data.LabCondData = data.wetData(:,20);
data.FieldCondData = data.wetData(:,21);
data.FVCondData = data.wetData(:,22);
data.SvolData = data.wetData(:,23);
data.RGPPTData = data.wetData(:,24);
data.SubPPTData = data.wetData(:,25);
data.allData(end+1,:) = -999;

%%Cleaning atmospheric data%%
for u_=1:size(data.allData,1)
    for z_=1:size(data.allData,2)
        if data.allData(u_,z_)==-999
            data.allData(u_,z_)=NaN;
        end
    end
end

% data.allData(:,10) is a blank column

data.O3Data = data.allData(:,1);
data.O38hrData = data.allData(:,2);
data.SO2Data = data.allData(:,3);
data.NOData = data.allData(:,4);
data.NOYData = data.allData(:,5);
data.NO2Data = data.allData(:,6);
data.COData = data.allData(:,7);
data.SWSData = data.allData(:,8);
data.VWSData = data.allData(:,9);
data.VWDData = data.allData(:,10);
data.SDWDData = data.allData(:,11);
data.tempData = data.allData(:,12);
data.wndspeedscalarData = data.allData(:,13);
data.sunData = data.allData(:,14);
data.stdevwnndirectData = data.allData(:,15);
data.stattempData = data.allData(:,16);
data.notSO2Data = data.allData(:,17);
data.wndvectdirectData = data.allData(:,18);
data.wndvectspeedData = data.allData(:,19);
data.wetnesData = data.allData(:,2);

%%Removing values above 50 from the atmospheric data%%
for u_=1:size(data.NOData,1)
    if data.NOData(u_,:) >= 50
        data.NOData(u_,:) = NaN;
    end
end

%%Taking atmospheric data to correlate with wet-deposition data%%
figure1= figure(1);
%Creating a temporary variable to sort weeks without NaN from weeks with data%
%tempMat=[];
for i_=1:numweek
    if ~isnan(data.NO3Data(i_))
        tempMat=[tempMat;data.NO3Data(i_),data.NOWeeksData(i_)];
    end
end

data.SO2WeeksData=data.summedData(:,1);
data.NOWeeksData=data.summedData(:,2);
data.NOYWeeksData=data.summedData(:,3);

data.corrData = [];
plot1=plot(tempMat(:,1), tempMat(:,2));
set(plot1(1), 'MarkerSize', 25, 'Marker', '.', 'LineStyle', '', 'Color', [0 1 0]);

% Calculating the numbers of weeks
numweek=size(data.allData,1)/168;

if ~isnan(data.SO4Data(i_))
    tempMat2=[tempMat2;data.SO4Data(i_),data.SO2WeeksData(i_)];
end

figure1= figure(1);
%Creating a temporary variable to sort weeks without NaN from weeks with data%
%tempMat=[];
for i_=1:numweek
    if ~isnan(data.NO3Data(i_))
        tempMat=[tempMat;data.NO3Data(i_),data.NOWeeksData(i_)];
    end
end

% Taking atmospheric data to correlate with wet-deposition data%
data.wetdryData=horzcat(data.SO2Data,data.NOData,data.NOYData);

%%Calculating the numbers of weeks%%
numweek=size(data.allData,1)/168;
data.summedData = reshape(data.wetdryData, [168, numweek, 3]);
data.summedData = nansum(data.summedData, 1);
data.summedData = reshape(data.summedData, [numweek, 3]);
data.SO2WeeksData=data.summedData(:,1);
data.NOWeeksData=data.summedData(:,2);
data.NOYWeeksData=data.summedData(:,3);

% Creating a temporary variable to sort weeks without NaN from weeks with data%
%tempMat=[];
for i_=1:numweek
    if ~isnan(data.NO3Data(i_))
        tempMat=[tempMat;data.NO3Data(i_),data.NOWeeksData(i_)];
    end
end

% Creating a graph with nitrate on the x-axis and NO or NOy on the y-axis%
data.corrData = [];
plot1=plot(tempMat(:,1), tempMat(:,2));
set(plot1(1), 'MarkerSize', 25, 'Marker', '.', 'LineStyle', '', 'Color', [0 1 0]);

% Calculating the numbers of weeks
numweek=size(data.allData,1)/168;

[P,S] = polyfit(tempMat(:,1),tempMat(:,2), 1);
data.slopeData= P(1);

[R,A] = corrcoef(tempMat(:,1), tempMat(:,2));

% data.R2Data=(data.corrData(1,2))^2;

 annotation(figure1,'textbox',[0.1494 0.7232 0.2065 0.1866],'
String',[
'\textbf{R} = ' num2str(R(2))],
'\textbf{P} = ' num2str(A(2))],
'Slope = ' num2str(data.slopeData)],'FontSize',30,'FitBoxToText','off','LineStyle','none');

xlabel('NO_3^-(PPM)','$\text{NO_3^-(PPM)}$','FontSize',30);
ylabel('NO (PPB)','FontSize',30)

for i_=1:52
    if ~isnan(data.SO4Data(i_))
        tempMat2=[tempMat2;data.SO4Data(i_),data.SO2WeeksData(i_)];
    end
end

52
end

figure2=figure(2);
plot2=plot(tempMat2(:,1), tempMat2(:,2));
set(plot2(1),'MarkerSize',25,'Marker','.','LineStyle','none','Color',[0 1 0]);
[L,U] =polyfit(tempMat2(:,1),tempMat2(:,2), 1);
data.slopeData2= L(1);
[K, E] = corrcoef(tempMat2(:,1),tempMat2(:,2));
% data.R2Data2=(data.corrData2(1,2))^2;
annotation(figure2,'textbox',[0.1494 0.7232 0.2065 0.1866],'
\textbf{String}', [{'P = ' num2str(E(2))},{'R = ' num2str(K(2))},{'Slope = ' num2str(data.slopeData2)}],'
\textbf{FontSize}',30,'FitBoxToText','off','LineStyle','none');
xlabel('SO_4^{-2} (PPM)\),'\textbf{FontSize}',30)
ylabel('SO_2 (PPB)','\textbf{FontSize}',30)