An overview of the causes of tropospheric ozone pollution with regard to meteorological factors in Ypsilanti, Michigan

Stephen Weger
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First Advisor
Dr. Gavin Edwards

Second Advisor
Dr. Evans

Third Advisor
Dr. Heyl-Chegg
AN OVERVIEW OF THE CAUSES OF TROPOSPHERIC OZONE POLLUTION WITH REGARD TO METEOROLOGICAL FACTORS IN YPSILANTI, MICHIGAN.

By

Stephen Weger

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Approved at Ypsilanti, Michigan, on this date __________________

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Dr. Gavin Edwards

________________________________________________
Dr. Evans

________________________________________________
Dr. Heyl-Chegg

________________________________________________
Honors Director:
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Abstract

This thesis presents a study of several meteorological factors and their correlation to tropospheric ozone concentrations in Ypsilanti, Michigan. The meteorological factors studied were air pressure, absolute humidity, temperature, and wind speed and direction. Data was collected from the end of May 2019 to the end of August 2019, on the second story of the Sherzer building at Eastern Michigan University. This thesis also contains a case study, comparing data from Ypsilanti, Michigan to Nanjing, China, to further strengthen the significance of the results found. The study found that the most significant meteorological determinants to tropospheric ozone concentration at Eastern Michigan University were temperature and humidity ($R^2 = 0.90$ and 0.65, respectively). The influence of each meteorological factor, regardless of significance, was also discussed.
Introduction

In the stratosphere, the molecule ozone (O₃) is vital to life as we know it due to its adsorption of harmful ultra-violet radiation (Cunningham & Cunningham, 2015). However, in the troposphere, ozone is an inhibitor of life, not a protector of it. The troposphere is considered the portion of the atmosphere that exists between sea level and from 5 kilometers at the poles to 18 kilometers at the equator, while the stratosphere extends from 10 kilometers to 47 kilometers above sea level (Marshak, 2015). Tropospheric ozone, the type of ozone which will be referenced herein, is responsible for stunted growth and a reduced yield in many crops, as found by Mortenson (1992). Due to a decrease in the productivity of staple crops, food insecurity can worsen. In the developing world, this alone could be enough to ensure civil unrest and in extreme cases, even civil war (Long et al., 2005).

Ozone is particularly hazardous due to the low concentrations required to inflict damage. The World Health Organization (WHO), suggests an 8-hour mean maximum exposure of 100 micrograms per cubic meter (WHO, 2019). The most recent edition of the national ambient air quality standards, which went into effect in December of 2015, set the primary and secondary ozone standard levels to 70 ppbv (EPA, 2015). Wang et al. (2017) found that ambient environmental concentrations of 62 ppb resulted in a decrease in rice productivity from 14-20%. One reason that ozone can cause reduced yield in crops has to do with the oxidative capacity of ozone to create free radicals, which damage the plasma membranes of plants (Wang et al., 2017). Billions of people worldwide depend on rice as a staple crop—therefore, a decrease in productivity in rice can have a profound impact on nutrition worldwide.

Ozone is also responsible for many human health ailments, such as pneumonia, asthma, pulmonary irritation, respiratory mucosal membrane degradation, as well as allergic rhinitis.
hospitalizations (Wang et al., 2017). An unfortunate aspect of ozone pollution is its ability to spread far beyond the source of pollution—in Shenzhen rural and suburban sites are more likely to experience ozone concentrations in excess of WHO guidelines (Huang et al., 2018). This occurs despite the fact that the suburban and urban sites are likely far more responsible for producing ozone than the rural farms.

The present study has three aims. Firstly, to determine which meteorological factors significantly impact ozone concentration. Secondly, to evaluate the Air Quality Egg and its usefulness in the scientific community. And finally, to propose strategies to remediate the ozone problem in southeastern Michigan. This will be accomplished by a thorough study of the ozone concentration, temperature, humidity, incoming solar energy (insolation), air pressure, and wind speed and direction on the Eastern Michigan University (EMU) campus.

A primer on ozone
Ozone requires ultraviolet light in the sequence of formation and decomposition steps (Vanloon & Duffy, 2017). The Chapman sequence, detailed below, describes the synthesis and decomposition of ozone in terms of oxygen-only chemistry. The Chapman sequence is used to describe the production and elimination of ozone in the stratosphere, but it serves as a good framework for understanding ozone synthesis and decomposition in the troposphere.

Synthesis:

\[ \text{O}_2 + \text{hv (} \lambda < 240 \text{ nm)} \rightarrow \text{O} + \text{O} \quad \text{Slow [1]} \]

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \text{Fast [2]} \]

Decomposition:

\[ \text{O}_3 + \text{hv (} \lambda < 315 \text{ nm)} \rightarrow \text{O}_2^* + \text{O}^* \quad \text{Fast [3]} \]
\[ O + O_3 \rightarrow 2\ O_2 \quad \text{Slow [4]} \]

The synthesis of ozone [1] needs higher energy ultraviolet light than the decomposition [3]. M, a neutral and abundant species, likely either N\(_2\) or O\(_2\) (which collectively are >99% of the composition of the stratosphere) is used as a catalyst in [2]. While the final stage of decomposition [4] is highly exothermic, it also requires 18 kJ/mol of activation energy (Vanloon & Duffy, 2017).

The anthropogenic gas most responsible for tropospheric ozone formation is NO\(_2\), which forms a hydroxyl radical in six steps (Vanloon & Duffy, 2017). NO\(_2\) is a byproduct of incomplete combustion of gasoline and diesel in automobiles as well as power generation (Vanloon & Duffy, 2017).

\[ N_2 + O_2 \leftrightarrow 2\text{NO} \quad [5] \]
\[ 2\text{NO} + O_2 \rightarrow 2\text{NO}_2 \quad [6] \]
\[ \text{NO} + O_3 \rightarrow \text{NO}_2 + O_2 \quad [7] \]
\[ \text{ROO}^\bullet + NO \rightarrow \text{RO}^\bullet + \text{NO}_2 \quad [8] \]
\[ \text{NO}_2 + \text{hv (λ < 400 nm)} \rightarrow \text{NO} + O \quad [9] \]
\[ O + O_2 + M \rightarrow O_3 + M \quad [10] \]
\[ O_3 + \text{hv (λ < 315 nm)} \rightarrow O_2^* + O^* \quad [11] \]
\[ O^* + \text{H}_2\text{O} \rightarrow 2\cdot\text{OH} \quad [12] \]
\[ \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NO} + 2\cdot\text{OH} \quad [13] \]
Producing nitrogen monoxide from atmospheric nitrogen and oxygen [5] requires a large input of energy as the reaction is highly endothermic. However, it is possible, given the temperatures found in the internal combustion engine, to produce nitrogen monoxide in this manner. This nitrogen monoxide can then follow three reaction pathways. It can be oxidized by molecular oxygen [6], it can react with ozone to form nitrogen dioxide [7], or it can react with a peroxyl or hydroperoxyl radical [8]. The nitrogen dioxide which was just produced can then absorb visible and ultra-violet radiation, which results in the formation of ground state atomic oxygen [9]. Similar to the formation of ozone following the Chapman sequence, atomic and diatomic oxygen in the ground state, in the presence of either N₂ or O₂, react to form O₃ [10]. In the presence of high energy ultraviolet radiation (λ < 315 nm) the ozone photolyzes into excited state mono- and di-atomic oxygen [11]. The excited state oxygen atom the reacts with water to form two hydroxyl radicals [12]. This process is summarized as reacting nitrogen dioxide with water to produce nitrogen monoxide and 2 hydroxyl radicals [13]. In heavily polluted environments, 1 mole each of nitrogen monoxide, nitrogen dioxide, and water combine to form 2 moles of nitrous acid (Vanloon & Duffy, 2017). These 2 moles of nitrous acid then react in visible or ultraviolet light (λ < 400 nm) to form 2 moles of nitrogen dioxide and 2 moles of hydroxyl radicals (Vanloon & Duffy, 2017).

However, anthropogenic sources of pollution can accelerate the process described above (Vanloon & Duffy, 2017).

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad [14] \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \quad [15] \\
\text{O} + \text{O}_3 & \rightarrow 2 \text{O}_2 \quad [16]
\end{align*}
\]
For example, nitrogen dioxide and nitrogen monoxide molecules, such as those occurring from the incomplete combustion observed in automobiles, can also create ozone forming and destroying molecules.

The lowest recorded absolute humidity during this experiment was 5 g/m³. According to the Annual Air Quality report for 2018, the concentration of NO₂ in the troposphere was approximately 20 ppb at the highest concentration (Michigan Department of Environment, Great Lakes, and Energy, 2019). At such a low concentration, the nitrogen dioxide is likely the limiting reagent. Another important factor that is required to produce hydroxyl radicals is ultraviolet radiation [9] [11]. Without the ultraviolet light, the formation of the hydroxyl will terminate at [8]. The hydroxyl radical is a critical component of the synthesis and degradation of ozone, and is responsible for much of the ozone degradation in the absence of ultraviolet radiation.

**Instrumentation**

The Air Quality Egg (Air Quality Egg - Science is Collaboration, N.D.) was used to measure ozone concentrations on Eastern Michigan University’s campus. The Air Quality Egg (AQE) quantifies ozone concentrations by detecting the voltage induced by the presence of ozone molecules in the air. Due to the fact that the intake fan operates at a constant speed, it is then possible to find a concentration of ozone as a function of the voltage recorded. Due to the reliance on a constant input of air, this apparatus is susceptible to influence from wind events. However, the winds observed in this experiment did not have such an effect as the maximum wind speed recorded was only 10 miles per hour. According to the instrument’s manual, the AQE has a temperature accuracy of 0.2 degrees Celsius and the relative humidity is accurate to within 1.8 percent. While there is a lack of empirical studies that confirm the accuracy and precision of the AQE, there is agreement between the measurements given by the air quality egg
and official weather stations (Joseph Ali John, 2016). A previously conducted study at Eastern Michigan University (EMU) determined that the AQE sufficiently matches Airnow (governmental) data (Figure 1; Fahra et al., N.D.). The AQE took measurements every 30 seconds and recorded measurements to a SD card as 5-minute averages.

Figure 1: Comparison of Air Quality Egg data and Airnow (governmental) data from past research at EMU.

Ambient weather data was collected from an on-campus weather station. The station data included temperature, dew point, UV index, insolation (in watts/square meter), wind speed, and wind direction data for the EMU campus from May to August 2019. The station recorded data in 5-minute intervals.
Methods
The Air Quality Egg was placed on the second story balcony of Sherzer Hall at EMU at the end of May 2019 and was removed at the end of August 2019. The Air Quality Egg was set to take measurements at 30 second intervals and recorded 5-minute averages to an SD card. This data, along with weather station data, were imported into Excel for data analysis. The ozone data collected from the AQE were determined to be too high, and therefore the raw values from the sensor were modified by dividing by nine and subtracting eleven. The relative humidity values obtained from both the AQE and the weather station were converted to absolute humidity values (in units of grams per cubic meter) assuming that the atmospheric pressure remained constant at 1000 hPa. This assumption is reasonable because the actual range of air pressure values varied no more than 25 hPa—less than 2.5 percent variation. This was done in order to reduce the number of variables required in the equation and thus to speed data processing. Mathematical manipulations of raw data included derivations and integrations, as well as significance testing using vassar-stats.net. Four and six hour averages were used when comparing certain meteorological variables to ozone concentration due to a mismatch in time data.

Discussions
The factors influencing ozone that were studied are air pressure, humidity, temperature, wind speed and direction, and insolation. Due to limitations of the AQE, measurements were not taken during periods of heavy rain due to a fear of damaging the sensor. Huang et al. (2018) have determined that rainfall is a relevant meteorological factor for determining ozone concentrations. Due to the fact that the weather station and the AQE’s time data were not synchronized, to evaluate the effect of meteorological factors on ozone 6-hour averages were used to synchronize the time domains of the two instruments. 6-hour intervals were chosen because it provides
enough resolution without becoming too cumbersome to work with. When analyzing the daily insolation, both the total daily accumulation and instantaneous values were used.

*Historic Trends*

Figure 2: Historic data from past measurements made at EMU concerning maximum ozone concentration and the hours above 40 parts per billion by volume ozone. AOT40 means “above threshold of 40 ppbv ozone”.

The maximum ozone concentration and the hours above 40 ppbv (AOT40) have been lower in June as opposed to July (Figure 2). Both the AOT40 and maximum ozone concentrations seem to loosely follow four-year cycles. For example, in July 2012, maximum ozone and AOT40 are large, and decrease until July 2016, when they both increase greatly (Figure 2). Casual observation of the maximum ozone and AOT40 categories in figure 1 reveal a potential correlation, which was determined to be $R^2 = 0.55$. The maximum concentration of ozone, as well as the AOT40, are both higher in July than in June (Figure 2). Insufficient data exists to make any claims about August as compared to June or July.
Air pressure
The range of air pressure values found during this experiment were approximately normally distributed with a mean of 1013.2 hPa and a standard deviation of 4.4 hPa. Anticyclonic conditions, those with high pressures and lower winds, have been found to be supportive of higher ozone concentrations (Wang et al., 2017). However, in the present experiment, this effect was not as well pronounced due to the small spread in air pressure values. Because the weather station and the AQE were not synchronized in their measurements, 6-hour averages of the ozone and pressure values were taken and used to compare the effects of air pressure on ozone concentration.

Figure 3: Graph of the relationship between air pressure and ozone concentration using 6 hour means of each so that they can be related directly despite the ozone and air pressure datasets not matching exactly.
The concentration of ozone appears to follow a parabolic curve with maximum ozone concentration occurring at 1010 hPa (Figure 3). However, this is likely due to the higher concentration of data points in this range as opposed to significant influence from the air pressure. Anticyclonic conditions, which are characterized by high pressure systems where ground-level air diverges and higher altitude air fills the gap, are conducive to increasing tropospheric ozone concentrations (Wang et al., 2017). There are several possible explanations for this phenomenon. Firstly, an increased air pressure in a defined airspace, such as that over Ypsilanti, will result in an increased interaction of adjacent molecules, which would result in increased rates of reaction among the fairly dilute atmospheric components that cause ozone formation (Marshak, 2015). Secondly, the simple correlation of high air pressure and sunny weather could also account for a higher ozone concentration (Marshak, 2015). Conversely, increased mixing can serve to dilute ozone molecules. It is unlikely that the difference in air pressures between two airmasses would cause a significant migration of ozone (Figure 4).

![Graph showing wind speed and air pressure data](image)

**Figure 4**: Wind speed and air pressure data for the duration of the study.
Figure 4 demonstrates that, while the pressure gradient effect discussed above does occur, it is a relatively benign effect. On approximately 8/24/19, this effect is demonstrated—the air pressure decreased from about 1018 hPa to about 1005 hPa over the span of a few hours and caused winds of up to 4 miles per hour. However, given that the present experiment looks at southeastern Michigan as a whole, 4 miles per hour of intermittent wind speed is not sufficient to transport an air mass outside of the Michigan state border.

A meta-analysis of the air pressure and ozone concentration data indicate that an increase in air pressure does not necessarily predict an increase in ozone.

<table>
<thead>
<tr>
<th>Mean air pressure (hPa)</th>
<th>Hours above 40 ppbv</th>
<th>Hours below 40 ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>1003</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>1005</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>1006.5</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>1008.5</td>
<td>0</td>
<td>66</td>
</tr>
<tr>
<td>1010.5</td>
<td>42</td>
<td>126</td>
</tr>
<tr>
<td>1012.5</td>
<td>72</td>
<td>162</td>
</tr>
<tr>
<td>1014.5</td>
<td>18</td>
<td>60</td>
</tr>
<tr>
<td>1016.5</td>
<td>18</td>
<td>42</td>
</tr>
<tr>
<td>1018.5</td>
<td>12</td>
<td>48</td>
</tr>
<tr>
<td>1020.5</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td>1022.5</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>1023.5</td>
<td>0</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 1: Meta-analysis of air pressure and ozone data from figure 4.

When air pressure is above 1020 hPa, the likelihood of having an elevated concentration of ozone is diminished (Table 1). It is likely that between 1003 and 1008.5 hPa, the air pressure is less than normal, which would cause a low pressure center and therefore would result in higher winds which could transport ozone out of the region. Therefore, it seems that the moderate air pressures—between 1010 and 1018 hPa, constitute enough pressure to prevent a low pressure
center, but are tame enough not to cause migratory winds. In short, this narrow range of mean air pressure values could contribute to causing a stratifying effect in the atmosphere, thereby increasing the number of hours above 40 ppbv ozone.

The relatively narrow spread of air pressure values, as well as the poor correlation, indicates that air pressure alone is not a suitable variable to predict ozone concentration. Likely, air pressure is better as a qualitative metric to support evidence for higher or lower ozone concentrations. A t-test was done to compare the difference in the mean air pressure when the ozone concentration is above 40 ppbv and below 40 ppbv.

<table>
<thead>
<tr>
<th></th>
<th>&gt; 40 ppbv ozone</th>
<th>&lt; 40 ppbv ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>57</td>
<td>232</td>
</tr>
<tr>
<td>Mean air pressure (hPa)</td>
<td>1013.96</td>
<td>1013.03</td>
</tr>
</tbody>
</table>

Table 2: summary of statistics used to perform t-test at vassarstats.net.

According to a t-test performed at vassarstats.net, there is no significant difference between mean air pressure when ozone concentrations are either above or below 40 ppbv (p = 0.151, t = +1.51, df = 287) (Table 2). Therefore, two conclusions can be drawn. Firstly, that the precision of the weather station is not sufficient for a study of ozone concentrations and air pressures. This seems unlikely, however, as the weather station is capable of determining air pressure with a resolution of 0.01 in Hg (0.33 hPa). However, given the difference in mean air pressures is less than 1 hPa, this is still a possibility. The second, and more reasonable conclusion is that air pressure does not impact ozone concentrations to a significant degree on its own. Rather, it works as part of a system, and therefore is more suited as a rough proxy as opposed to a concrete model.
Humidity

As discussed earlier, the hydroxyl radical plays an important role in ozone formation and destruction. While the water is not the limiting reagent in the formation of the hydroxyl radical, an increased concentration will still increase the rate of reaction, as the probability of the collisions occurring that are requisite to form the hydroxyl radical is increased.

![Figure 5: Four-hour mean of ozone concentration and average humidity. Four-hour means were used due to limitations of the processing computer, as well as to demonstrate the general trend clearer.](image_url)

The average humidity and the ozone concentration are decently correlated \((R^2 = 0.65)\); as the average humidity increased the ozone concentration tended to increase as well (Figure 5). A large majority of this phenomena is likely explained in the fact that an increased concentration of water vapor will lead to a greater concentration of the hydroxyl radical. Since, during this study, the concentration of nitrogen dioxide in the atmosphere was not measured, and since the
historical data indicates such a small quantity (20 ppbv) was present, it is likely that nitrogen
dioxide was not responsible for a majority of the hydroxyl radical formation. Vanloon & Duffy,
(2017) notes that at altitudes below 30 kilometers above sea level, the importance of nitrogen
dioxide in creating hydroxyl radicals decreases immensely. This is because, in order to split the
diatomic nitrogen molecule, high energy radiation is required—which is normally absorbed by
the stratospheric ozone layer at around 30 kilometers above sea level (Vanloon & Duffy, 2017).
Due to the positive correlation between ozone concentration and humidity, it is highly unlikely
that the humidity observed caused the formation of clouds. Hertig et al. (2019) observed that in
Augsburg, Germany, increased absolute humidity resulted in a significant decrease in ozone
concentration. The formation of ozone requires ultra-violet radiation, which would be absorbed
by clouds, so the excess humidity in southeastern Michigan likely did not form clouds, or at
least, did not form the type of clouds which absorb ultra-violet radiation.

<table>
<thead>
<tr>
<th>Humidity (g/m³)</th>
<th>10.74</th>
<th>10.69</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insolation (J/m²)</td>
<td>0 J/m²</td>
<td>More than 10 kJ/m²</td>
</tr>
<tr>
<td>N =</td>
<td>10053</td>
<td>12491</td>
</tr>
</tbody>
</table>

Table 3: Summary data used to run t-test at vassar-stats.net.

An analysis of the humidity and insolation data was conducted and it was determined that there
was no significant difference in the humidity present at either 0 kJ/m² or >10kJ/m² of incoming
solar energy (t= +1.35, df = 22543, p = 0.18, Table 3). This is evidence that the humidity present
in the atmosphere above southeastern Michigan did not absorb a significant amount of ultraviolet
radiation.
Figure 6: Absorption of water from 550 to 250nm wavelength radiation. Taken from Mason et al. (2016).

At the wavelengths of 400 nm and 315 nm, the absorbance of water is less than 0.01, which is a transmittance of 97.7% (Figure 6). Therefore, water vapor in the atmosphere does not absorb a significant amount of ultraviolet radiation (Mason et al., 2016).

Since the water in the atmosphere directly above Ypsilanti is not absorbing the ultra-violet radiation, it instead is either scattering it, or emitting it. Since humidity and ozone concentration are directly proportional, the water vapor is not scattering the ultraviolet radiation, as this would instead cause ozone concentration and humidity to be inversely proportional due to a lowering of emitted ultraviolet radiation. Rather, the water vapor emits the ultraviolet radiation, which results in a tropospheric sort of greenhouse effect. Ultraviolet radiation enters through the layer of water
vapor, and if it is not absorbed either in the process of the formation of the hydroxyl radical or in
the formation of ozone, it can be reflected back towards Earth by the layer of water vapor.

Temperature
During the duration of the study, the temperature had the largest correlation coefficient (R-
squared) amongst any measured variables. There are several reasons this could be the case.
Firstly, the temperature largely following the same diurnal cycle as insolation since the sun is
responsible for a vast majority of the Earth’s energy. Because the insolation detector used in this
experiment was determined to not adequately measure light with wavelengths of less than 400
nm, the temperature will stand in as a proxy for insolation. This should work because during
times of low or no insolation, the temperature will be lower as well. Conversely, during times of
high insulation the temperature should be much higher as a result.

Figure 7: Temperature and ozone are highly correlated (R-squared = 0.90).

Temperature and ozone concentration are highly correlated (Figure 7). This agrees with a study
done by Coates et al. (2016), which determined that in environments with low concentrations of
nitrogen oxides, temperature will exert a small, but noticeable influence on ozone concentration. In all studied cases, ozone concentration increased with an increase in temperature (Coates et al., 2016).

Figure 8: Ozone and temperature data for duration of experiment.

Ozone and temperature are not linearly related (Figure 8, Coates et al., 2016). At 26.20 degrees centigrade, the derivative of the ozone versus time graph was at a maximum, indicating a shift in concavity. This information was used to split the data into two linear series, which are both reasonably correlated. Figure 8 demonstrates that above 26.2 degrees centigrade, each additional degree of ambient temperature will increase the ozone concentration six times as much as below 26.2 degrees centigrade. A t-test performed at vassar-stats.net confirms that the differences between ozone concentrations at temperatures above and below 26.2 degrees centigrade are significant (t = -240.64, df = 23116, p < 0.0001). Interestingly, at temperatures below 26.2
degrees, ozone concentration has more variance, and this variance tends to be in the positive direction. This could be the result of low temperature and high sun days.

Temperature can serve as a proxy for solar radiation, although this negates the effect of all other meteorological effects on total insolation (Varotsos et al., 2019). At solar noon, the maximum amount of solar energy will reach the earth, and thus, the temperature will be at the daily maximum—likewise, at solar midnight, the Earth will have a lack of incoming solar radiation to warm the planet, and therefore the planet will be colder. This is not a perfect model for insolation in many ways, as previously stated, other meteorological conditions influence temperature, such as cloud cover and composition, concentration of greenhouse gases in the atmosphere, as well as even the Milankovich cycles. Secondly, the temperature close to Earth’s surface is influenced by winds which are induced by unpredictable, non-meteorological conditions, such moving traffic and man-made structures causing unnatural deviations in wind speed or direction. However, using temperature as a proxy to insolation could also account for heat pollution in populated areas due to the urban heat island effect, as well as heat emissions from industrial production. Using insolation, in this case, would cause error, as anthropogenic sources are inducing higher concentrations of ozone precursors than would occur normally.

Despite the aforementioned shortcomings, using temperature as a proxy for incoming insolation works well, as an increase in temperature is more closely associated with an increase in ozone concentration than any other meteorological factor studied (Figure 7). While ultraviolet light is a requirement to split ozone molecules, many steps in the process of forming the hydroxyl radical are highly endothermic, such as the initial formation of two moles of nitrogen monoxide from single molecules of diatomic oxygen and diatomic nitrogen, both readily abundant in the atmosphere [5]. This reaction requires 314 kJ/mole of energy in order to run in the forward
direction and produce nitrogen monoxide (Vanloon & Duffy, 2017). Since temperature and energy are directly related, the relative ease with which the reaction [5] is able to proceed is therefore dependent on temperature.

Ozone action days (days when the ambient concentration of ground-level ozone is considered unsafe) have usually occurred on very hot and humid days—perhaps this is because there is more energy in the atmosphere and the ozone producing catalysts are formed at a greater rate than normal. The extra humidity could serve to absorb some of the ultraviolet radiation, thereby reducing the effect of ultraviolet light splitting ozone molecules and resulting in an unstable equilibrium that favors ozone production.

Wind speed and direction
While the prevailing winds can cause increased mixing and therefore increase the rates of reaction involved in either producing or destroying ozone, winds can also transport ozone itself or the radicals which aid in ozone production or destruction. Strong winds will also prevent the formation of an inversion, which occurs when a stable atmosphere forms due to layering of air in the absence of winds. During the course of the present study, only tame winds were recorded, with gusts not exceeding 10 miles per hour.
Wind speed alone is an insignificant factor in determining ozone concentrations (Figure 9). The correlation between wind speed and ozone concentration is only $R^2 = 0.19$, which signifies that the winds are not causing nor preventing a significant amount of mixing. However, given that winds were fairly tame during the experiment, it is possible that the sensitivity of the AQE is too low to accurately quantify such a small change in ozone concentration as would be normally caused by such wind events. The poor correlation notwithstanding, assuming a linear relationship, the mathematical relationship between ozone concentration and wind speed produces the equation: ozone concentration (ppbv) $= 7.08 \times$ wind speed (mph) $+ 23.3$. While the numerical coefficients to the above equation are essentially meaningless, they convey that for an increase in wind speed, the ozone concentration increases. This is interesting, as it suggests that the presence of winds in southeastern Michigan contributes to an increase in ground-level ozone, whereas ground-level winds are typically responsible for decreases in ground-level ozone due to an increase in vertical mixing. The potential causes will be examined next.
While the wind speed, irrespective of direction, is not a significant component of the ground-level ozone concentration’s observed in Ypsilanti, a look into the wind direction revealed a more significant correlation.

Figure 10: Wind direction (in degrees and without regard to wind speed) and ozone concentration taken as six-hour means. Conversion from degrees to cardinal directions available below in figure 11.

Figure 11: Relationship between ordinal directions and degrees used in Figure 10.
There is a greater likelihood that winds from the south-west will result in higher concentrations of ozone (Figure 10). This is likely because a great deal of pollution is produced in the southern and eastern states surrounding Michigan. Wisconsin is well known for its dairy industries (specifically cheese) and Ohio and Indiana both have very large industrial sectors, which produce steel, automobiles, small appliances, and many more items whose manufacturing create volatile organic compounds, nitrogen oxides, as well as hydroxyl radicals. The dairy industry is notorious for its greenhouse gas emissions; on corn diets cows release an exceptional amount of flatulence, which is composed of methane (study shows potential for reduced methane in cows, 2019). This methane can then react in the atmosphere—much like nitrogen oxides do, to form hydroxyl radicals which cause ground-level ozone (Vanloon & Duffy, 2017).

Further analysis of the effect of winds on ozone concentrations would consider three major concerns. Firstly, it would consider the codependency of wind speed and wind direction on ozone concentration. Secondly, it would determine the relative impact of wind speed on ozone concentration by comparing ozone concentrations at the same wind speed. Thirdly, it would examine Air Resource Laboratory data (provided by NOAA) and determine some potential sources of pollution.

Insolation
Ultraviolet light is a requirement in the formation of ozone, and therefore it follows that the total insolation should correlate to ozone concentration (Vanloon & Duffy, 2017). Days with larger quantities of ultraviolet light should have higher ozone concentrations than days with lower quantities of ultraviolet light.
Figure 12: Total daily insolation and change in ozone throughout the length of the experiment.

The change in the concentration of ozone and the total daily insolation are poorly correlated ($R^2 = 0.33$) (Figure 12). One potential explanation is that the sensor was measuring a broad range of insolation values, and not the specific wavelengths ($\lambda < 400$ nm and $\lambda < 315$ nm) that are of interest to ozone destruction and formation. To confirm this suspicion, the UV index and insolation data were analyzed, and the analysis was redone using the UV index as a proxy for UV insolation.
Figure 13: Relationship between UV index, average insolation, and ozone concentration.

Figure 13 demonstrates that ozone concentration is correlated more with UV index than the insolation data obtained from the weather station ($R^2 = 0.58$). Therefore, the UV index serves as a more accurate proxy when looking to predict future ozone concentrations. The nonlinearity of the concentration of ozone with respect to UV index between UV indexes of 7 and 10 does not follow the expected pattern. Potential reasons for this anomaly as of present remain unknown.

The average ozone concentration does not begin to increase significantly until the UV index is 11, which represents an extreme amount of ultraviolet radiation, as the UV index is reported on a scale from 0-10. Doing a regression analysis for the ozone concentration and the UV index resulted in the following equation: Ozone concentration (ppbv) = 1.49 * UV index + 25.8 ppbv. Interestingly, the average of all ozone concentrations taken during the study was 27.9 ppbv—which is higher than the y-intercept of the regression equation (25.8).
While the correlation of the line-of-best-fit determined previously is low ($R^2 = 0.58$), it demonstrates that the quantity of ultraviolet light available does not readily impact ozone concentrations. Rather, it is extreme concentrations of ultraviolet light which result in a large increase in ozone concentration (Figure 13).

Ironically, incoming solar energy should be what defines the rest of the present meteorological variables—temperature, humidity, and to a lesser extent wind speeds and air pressure. Recall that a vast majority of the Earth’s energy comes from the Sun, and therefore it follows that the Sun, and by extension, its energy, dictates most of the chemical processes on Earth. With this knowledge, it is indeed quite peculiar that insolation does not have a better correlation with ozone concentration. One possible explanation is that the quantity of solar energy present is not as important as having the correct wavelength. This would explain the poor correlation previously discovered.

Diurnal cycles
The diurnal nature of ozone in the troposphere is a well-documented phenomenon. Ozone concentrations typically peak at night and decrease during the day due to the influence of the ultra-violet radiation required to split the diatomic oxygen molecule.
Figure 14: Ozone and time data taken from experimental data obtained on 6/3/19.

The general trend for ozone concentration as a function of time is that ozone is at a minimum around 7:00 and reaches a maximum around 15:00 to 21:00 (Figure 14). This occurs because, in the absence of ultraviolet radiation, ozone will react with any number of readily available chemicals in the atmosphere, such as the hydroxyl radical. Ozone is a highly unstable molecule—it will always attempt to reach a lower energy state.

As the atmosphere is exposed to ultraviolet radiation, the hydroxyl species can form, the diatomic oxygen bonds can break, and the ozone concentration will increase until the sun begins to lower below the horizon. From 18:00 to 21:00, the concentration rises again. This deviates slightly from the perfect, theoretical model—this is likely due to an increase in power consumption which is noted from around 18:00 to 21:00, as this is the time when most people are in their houses making dinner and following their nightly rituals, which could include watching television, playing video games—any number of activities which consume a lot of electricity. This is relevant because a spike in electrical consumption, at least in Michigan, a state predominately powered by coal and natural gas, will result in a spike of volatile organic carbon.
emissions as well as NOx emissions (United States Department Of Energy, 2015). After the sun has fully set, the concentration of ozone decreases because the ozone molecules will react with leftover hydroxyl radicals as well as many other pollutants in the air. Ozone will readily degrade in the atmosphere as it is a highly unstable molecule. The residence time of ozone in the atmosphere is normally on the order of minutes. However, at night, under special conditions, it is possible that ozone can be transported over 100 kilometers from the source, though this is incredibly rare (Downs et al., 2010).

Variations in the diurnal cycle can be observed when there is an inversion which creates a stable air mass that is unlikely to move. In these cases, the diurnal cycle will continue with a positive upwards bias in the concentration of ozone. In extreme cases, there will not be a decrease in ozone production even during the night. These events are exceedingly rare, however, and are usually punctuated by international news headlines (ex: the 2008 Beijing Olympics). The conditions which form an inversion are stable winds, high humidity, and high temperatures. This results in a layering of the atmosphere, with a colder air mass submerged beneath a warmer air mass, and therefore, little vertical or lateral winds.

The meteorological conditions which drive ozone formation and destruction also follow diurnal cycles. These include air pressure, temperature, and insolation. Humidity, while relevant to the reactions which govern the formation and destruction of ozone, does not follow a diurnal cycle.
Figure 15: Temperature, humidity, and air pressure data for 6/3/19.

An increase in air pressure leads an increase in temperature; air pressure increases at 4:00, 9:00, and decreases at 14:00 whereas temperature decreases from 0:00 to 7:00 and increases until 18:00 where temperature begins to decrease (Figure 15). In general, incoming solar energy...
(insolation) will increase from 7:00 until 15:00 where it will decrease until 21:00 (Figure 16). The insolation data shows a lot of discontinuity between the hours of 7:00 and 12:00, which can likely be attributed to the variable weather conditions at this time. For example, a cloud passing overhead would absorb a lot of the insolation and would thus temporarily decrease the insolation until the cloud passes over the sensor.

The general public will usually know when an inversion occurs because these events cause a buildup of ozone which triggers ozone action days in Michigan. To determine the presence of an inversion, the derivative of the ozone versus time function was calculated, and the sections of the graph with slopes that exceeded plus or minus three standard deviations of the average of the derivative were examined. Sometimes, when calculating the derivative, there will be lapses in the original dataset which create extreme slopes in the derivative. None of the 274 instances where the slope of the derivative exceeded plus or minus three standard deviations of the average slope were the result of a lack of data. During the course of this study, no significant inversions were noticed—all 274 instances noted were explained by common meteorological conditions. For the most part, the ozone concentrations followed the expected diurnal cycles.

**Monthly variations**

The concentration of stratospheric ozone varies with the meteorological conditions, as noted in the above section. Therefore, it follows, that since the meteorological conditions are not constant day-by-day that neither is the ozone concentration. Hence, ozone concentrations vary with the seasons.
Figure 17: Ozone concentration data for 6/3/19.

Figure 18: Ozone data from 7/3/19.
Figure 19: Ozone data from 8/3/19.

Maximum ozone concentration was the highest on 8/3/19, followed by 7/3/19, with 6/3/19 exhibiting the lowest maximum ozone concentration of all days (Figures 17, 18, 19). Average ozone concentrations for June, July, and August were 21.4 ppbv, 36.7 ppbv, and 23.5 ppbv, respectively. The monthly variations of meteorological conditions and ozone concentrations mimic those that occur during a single day. Temperature and ozone concentration both start at a minimum in May, reach a maximum in July, and decrease throughout August.
Figure 20: Ozone concentration and temperature data for length of experiment, summarized as 4-hour means for clarity.

Visual inspection of Figure 20 shows that both ozone concentration and temperature behave cyclically on a daily scale as well as monthly. This is largely the result of the Earth’s rotation around the sun, which includes far too many variables to be thoroughly examined here. In short, the Earth, due to its rotation around the sun will experience varying levels of insolation, which in turn dictate the temperature as well as humidity which then determine atmospheric pressure.

Comparison with Nanjing
A study done by Ding et al. (2013) examined the relationship between air pressure, average temperature, average humidity, and rainfall with the average concentration of ozone observed. Due to concerns about the longevity of the AQE, measurements were not taken in the rain—
therefore, the rainfall accumulation and its impact on ozone concentrations will be done only using data from Ding et al. (2013).

<table>
<thead>
<tr>
<th>Month</th>
<th>Avg ozone conc. (ppbv)</th>
<th>Avg Pressure (hPa)</th>
<th>Avg Temp (degC)</th>
<th>Avg Humidity (g/m3)</th>
<th>Rainfall accumulation (mm)</th>
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</thead>
<tbody>
<tr>
<td>January</td>
<td>31.9</td>
<td>1023.7</td>
<td>2.9</td>
<td>3.905</td>
<td>22.6</td>
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<tr>
<td>February</td>
<td>30.4</td>
<td>1021.1</td>
<td>3.0</td>
<td>4.015</td>
<td>77.0</td>
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<td>March</td>
<td>33.5</td>
<td>1016.9</td>
<td>9.0</td>
<td>5.943</td>
<td>83.4</td>
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<td>April</td>
<td>42.8</td>
<td>1007.9</td>
<td>18.0</td>
<td>9.926</td>
<td>60.2</td>
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<tr>
<td>May</td>
<td>40.0</td>
<td>1006.3</td>
<td>21.9</td>
<td>12.705</td>
<td>62.6</td>
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<tr>
<td>June</td>
<td>53.1</td>
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<td>25.5</td>
<td>16.325</td>
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<tr>
<td>July</td>
<td>61.3</td>
<td>999.4</td>
<td>29.4</td>
<td>19.805</td>
<td>184</td>
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<tr>
<td>August</td>
<td>46.4</td>
<td>1002.3</td>
<td>27.0</td>
<td>20.658</td>
<td>291</td>
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<tr>
<td>September</td>
<td>57.2</td>
<td>1009.4</td>
<td>23.1</td>
<td>14.686</td>
<td>13.1</td>
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<tr>
<td>October</td>
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<tr>
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<td>9.131</td>
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<td>1025.9</td>
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<td>4.177</td>
<td>17.0</td>
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</table>

Table 4: Monthly statistics of average ozone concentrations and meteorological data for the period August 2011-July 2012 at Nanjing.

<table>
<thead>
<tr>
<th>Month</th>
<th>Avg ozone conc. (ppbv) (from AQE)</th>
<th>Avg Pressure (hPa) (from station)</th>
<th>Avg Temp (degC) (from AQE)</th>
<th>Avg Temp (degC) (from station)</th>
<th>Avg Humidity (g/m3) (from AQE)</th>
<th>Avg Humidity (g/m3) (from station)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June</td>
<td>21.4</td>
<td>1012.016</td>
<td>23.1</td>
<td>19.6</td>
<td>12.44</td>
<td>9.67</td>
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<td>July</td>
<td>36.7</td>
<td>1014.347</td>
<td>26.7</td>
<td>23.4</td>
<td>16.53</td>
<td>12.1</td>
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<tr>
<td>August</td>
<td>23.5</td>
<td>1013.201</td>
<td>24.7</td>
<td>21.5</td>
<td>14.26</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Table 5: Monthly statistics of average ozone concentrations and meteorological data for the period June 2019-August 2019 at Eastern Michigan University. AQE = Air Quality Egg. "Station" refers to the on campus weather station run by Dr. Kovacs.
The variables most significantly correlated with ozone concentration in the Nanjing study are air pressure, temperature, and humidity, with $R^2$ values of -0.81, 0.77, and 0.77, respectively (Table 4). In the present study concerning Ypsilanti, the variables most significantly correlated with an increase in ozone concentration are temperature and humidity, with $R^2 = 0.90$ and 0.64, respectively (Table 5). Interestingly, in Nanjing, air pressure appears to have a diluting effect on ozone concentration whereas in Ypsilanti air pressure has no significant impact on ozone concentration. The unusually high correlation between ozone concentration and air pressure in Nanjing could be attributed to an increase of pollutants, as the western coast of China is well known for its vast cargo ships and its expansive industry. Therefore, the increased air pressure could be causing the pollutants to mix more, and this could lead to the proliferation of the hydroxyl radical which would readily react in the presence of ozone, thereby decreasing the concentration of ozone.

Interestingly, the Nanjing data has also demonstrated a positive correlation between ozone concentration and humidity (Ding et al., 2013). While the EMU study resulted in a poor correlation ($R^2 = 0.19$) between air pressure and ozone concentration, the data from the Nanjing study produce an $R^2$ of -0.81. Because the correlation is negative between air pressure and ozone concentration in Nanjing, it is likely that the air pressure induced winds which resulted in ozone transport, as opposed to in Michigan, where the air pressure resulted in increased mixing and thus faster rates of ozone formation. Rainfall in Nanjing was not found to significantly impact ozone concentration ($R^2 = 0.35$; Ding et al., 2013).

Conclusion
In summary, the most important meteorological factors that can predict ozone concentration are temperature, humidity and wind speed and direction. An increase in temperature results in an
increase in ozone concentration. Likewise, an increase in humidity results in an increase in ozone concentration. Wind speed and direction can have variable effects on ozone concentrations; winds from the south or south-east result in increases in ozone concentration whereas winds from the north or east result in decreases in ozone concentration. The speed of said winds then determines the magnitude of its effect on ozone concentrations—faster winds result in larger changes in ozone concentration than gentler winds.

The AQE has demonstrated its usefulness in the field of science. For studies which do not require ppbv accuracy, the AQE can be readily adopted and deployed. It is especially useful for taking multiple measurements and covering a larger area than a single, perhaps more accurate (and more expensive) sensor would be able to accommodate. Improvements to the current study would include exploiting the relatively low cost of the AQE to cover a larger section of the EMU campus and then ensemble averaging the data to reduce instrumentally related noise.

*Remediation strategies*

To successfully remediate the tropospheric ozone pollution present in southeastern Michigan, more study is needed on the subject. However, with the findings discussed herein, several recommendations can be made. Firstly, the transition of Michigan’s energy sector to green alternatives would decrease the largest point source emission of VOC’s and nitrogen oxides in the state. Hence, an increase in solar, nuclear, hydro, and wind power would reduce the rate of formation of the precursors to tropospheric ozone production. Secondly, an increase in the monitoring of the tropospheric ozone concentrations would produce more data which could then be utilized in further ozone studies. Further studies will always be needed due to the inherent complexity involved. Thirdly, more observant monitoring of the weather could prevent ozone
action days from occurring by preemptively placing restrictions on running 2-stroke engines, or at least could provide early warning to the elderly and sensitive groups.
References


World Health Organization. *WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide*; *2019*. 