Air Quality & Boundary Layer Undergraduate Experiment (AQUABLUE): AOS 404 Measurements Class Project (Spring 2018)

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Abstract

Surface ozone transport and distribution is an important area of research in the Midwest due to the harmful effects of ozone both on humans and the environment. In particular, lakeshore environments can be at risk of significant ozone exposure due to the role of lakes as conducive creators and transporters of ozone and its precursors from anthropogenic sources at greater length scales than on land. Considering that northeastern lakeshore environments in Wisconsin often exceed legal ozone concentration limits, set at 70 parts per billion, it is prudent to try to identify sources of both ozone and other pollutants for the purposes of policy making as well as environmental preservation. Our experiment used in situ instruments, Windsonds, and Wisconsin DNR data to identify correlations between maxima in pollutants and recorded values of wind speed, direction, radiation, temperature, and humidity. Our findings suggest that the mechanisms for ozone creation and transportation during winter and spring months are not consistent with the mechanisms during summer, when the lake serves as a key creator and transporter of ozone as well as other pollutants.

1. Introduction

Ozone distribution throughout the atmosphere is an important area of research due to its positive role in the upper atmosphere but negative role in the lower atmosphere. In the upper levels of the stratosphere, ozone serves as in important chemical in preventing harmful ultraviolet radiation from reaching the surface. In the upper atmosphere, ozone is formed through a cyclic process of dissociating molecular oxygen by means of absorption of radiation into two oxygen atoms, one of which can then join together with an oxygen molecule to form ozone. Ozone is highly absorptive to radiation between 0.2 and 0.31 μm (Petty, 2006), and can use radiation within this range to dissociate into molecular and atomic oxygen which can then repeat the process (Crutzen, 1970).

Though ozone is beneficial in the upper levels of the atmosphere, at the surface it is a harmful pollutant and a key contributor to the formation of photochemical smog. The formation of ozone near the surface is typically done through the combination of precursor molecules, volatile organic compounds (VOC) and nitrogen oxides (NOx), with solar radiation. These precursor compounds are typically emitted by industrial processes (Petty 2004) and can thus be dispersed in high concentrations from urban areas. In addition, atmospheric processes such as inversions can prevent ozone from being dispersed vertically, creating regions of high concentration of ozone at the surface (García-Yee et al. 2017).

Due to the negative effects of tropospheric ozone, considerable research has been done to investigate the mechanisms by which ozone is distributed from surface sources. In the states surrounding Lake Michigan, cities such as Milwaukee, Chicago, and Gary have been identified as sources of large amounts of precursors, and hence sources of ozone advection. The Lake Michigan Ozone Study established that ozone pollution in northeastern Wisconsin and northwestern Michigan was due to synoptic transport of precursors over Lake Michigan. These precursors originated primarily from Chicago and Gary, and upon being transported over the lake, they were exposed to large amounts of solar radiation. The high stability of the air over the lake surface mitigated convection, which was conducive to both the formation and transportation of ozone from southern anthropogenic sources towards northern lakeshore environments (Dye et al. 1995).

Ozone formation and transportation during winter is less understood than during the summer, when the Lake Michigan Ozone Study was conducted. The role of snow and changing planetary albedo has been identified as an additional factor in the solar radiation component of ozone formation (Carter and Seinfeld 2012). Our investigation sought to identify whether the lake is still a large contributing factor to ozone pollution in northeastern Wisconsin. Our expectation was that peak ozone events would be correlated to southeasterly winds, which could be traced back to anthropogenic sources on the southern shore of the lake.

For our project, we also explored the relationship between fine particulates and wind direction. Fine particulates are small (<2.5μm) aerosols that can cause health problems when inhaled over an extended period of time. Major sources include automobiles, burning of organic material, unpaved roads, and heavy industry (Laden et al, 2000). While larger aerosols can cause respiratory illnesses when inhaled, $PM_{2.5}$ are of particular interest because they are small enough to go through the lung tissue and into the bloodstream. This allows them to affect the health of all organs in the body. Exposure to elevated levels of $PM_{2.5}$ increases the risk for many chronic diseases, such as chronic obstructive pulmonary disease (COPD), and heart disease (Schwartz et al, 1996). Even relatively low amounts of fine particulates have been shown to increase the risk of premature death, while cases of extreme air pollution such as the Great London Smog of 1952 can be truly disastrous. Historic levels of sulfur dioxide turned into suspended droplets of sulfuric acid, which people then breathed in. The London event lasted only five days, yet an estimated 12,000 people died directly from it (Hunt et al, 2003). Identifying sources of fine particulates is an important part of clean air regulation, and much research continues to be done on this topic.

2. Methods & Instrumentation

In order to adequately measure the effects of the low-level flow on the advection of ozone and other particulate matter, ozone concentration and other meteorological variables were gathered at two stations along Lake Michigan: Harrington Beach State Park in Belgium, Wisconsin and Kohler-Andrae State Park in Sheboygan, Wisconsin. Ozone and temperature data are from the Wisconsin DNR (available at https://dnrx.wisconsin.gov/) with hourly measurement frequency during the time period (March 9 -- April 19).

2.1. HOBO Weather Stations

HOBO weather stations were erected to measure various meteorological variables at both sites. The variables that were gathered by these stations include: Wind speed and direction, temperature, dew point temperature, and solar insolation. These instruments are useful as they can be rapidly deployed due to their relatively small and lightweight construction, while simultaneously being effective at withstanding nearly all environmental conditions it may come to experience.

2.2. DustTraks

We used two DustTrak Aerosol Monitor 8520s for this experiment. Both were placed several feet above the nearest significant obstruction and as close to the lake as reasonably possible. Since DustTraks are not waterproof, both were placed inside weatherproof enclosures and insulated to prevent the possibility of low temperatures from affecting the instruments. A vinyl hose ran from the intake on both instruments to the outside to minimize sample contamination. Both DustTraks were plugged into a 120v power supply to ensure they remained running for the duration of the study. The units were set to measure $PM_{2.5}$ and record measurements every minute. This provided 3-4 weeks of data, which were then be downloaded to a computer and compared to recorded wind direction from the DNR’s instruments.

2.3. Windsonds

Along with the ground-based measurements that were done as a part of the AQUABLUE experiment, Windsond weather balloons were launched along the Lake Michigan shore to take measurements in the boundary layer. The boundary layer is the layer most affected by surface properties and processes. Windsonds are a compact radiosonde device, which can take all the same measurements that a regular radiosonde is capable of (temperature, relative humidity, pressure, altitude, and wind speed/direction). The sonde is housed in a simple styrofoam cup with a plastic lid. Along with the meteorological sensors, the Windsond is equipped with a GPS locator that sends exact coordinates to the receiver, which allows for easy retrieval. The exact location of the Windsond can also be displayed in Google Earth via a KML file. The radio has the capability to be connected to a laptop, which allows the user to view real-time data displays in the Windsond software as the Windsond is rising. In the software, the user can select the altitude at which the Windsond is to cut itself down, which it does by using a hot wire to burn through the string that attaches the sonde to the balloon. The cut-down altitude can either be set before the launch or by selecting the “cut down now” option from the software control panel. This feature was particularly useful for AQUABLUE given the small geographic extent of the launch site and a close proximity to Lake Michigan.

3. Results

3.1. Temperature and Ozone Hourly Correlation

In terms of the hourly correlation “r” between temperature and ozone, there is not a significant relation with Harrington r = 0.02 and Kohler-Andrae r = 0.09 (Table 1). However, there seems to be a threshold temperature around -10 °C as shown in (Figure 1, 2). Below this threshold ozone level, ozone has a relatively low negative correlation with temperature

(Harrington r = -0.15, Kohler-Andrae r = 0.02). Above this threshold, both stations show weak to moderate correlation between temperature and ozone (Harrington r = 0.28, Kohler-Andrae r = 0.43).

3.2. Temperature and Ozone Time Series

Along with an analysis of hourly data, we also looked at the daily mean temperature and ozone time series from March 9 to April 19 at both stations (Figure 3, 4). From the time series plots, ozone and temperature appear to follow similar trends during the first 15 days after our study began. However, there are two major anomalies in the trends proceeding this time period. The first happened 20 days after the study began (March 29) when the ozone concentration at both stations had a significant drop. Another major event happened 30 days after the study began (April 10) when the temperature at both stations experienced a substantial decrease. In the first event, while there was a significant drop in ozone, temperatures remain around 0 °C. The second event involved a major snowstorm, which corresponded with temperatures dropping substantially to down below the -10 °C threshold. In this case, the ozone concentration had peaked during the lowest temperature.

3.3. Temperature and Ozone Diurnal Analysis

A calculation of the mean temperature and ozone at every hour during the entire research period was performed to get an averaged diurnal profile at two stations (Figure 5, 6). Both stations indicated that temperature began to increase in the early morning at approximately 5:00 am and then peaks around 12:00 pm local (Central) time. Diurnal ozone had a strong positive correlation following this temperature trend (Harrington r = 0.93, Kohler-Andrae r = 0.82).

Despite the strong correlation, ozone concentration typically peaks at around 3:00 pm, which is three hours after temperature peak.

3.4. Ozone Relation with Radiation and Relative Humidity

Besides the effects of temperature, we also looked at the relationship between radiation and relative humidity in affecting ozone concentration at Harrington Beach. A time series of radiation (Fig. 7) shows that in the first event, radiation and ozone both drop substantially 16 days after the measurements started. After this, radiation immediately began to increase, while ozone levels were relatively low for another three days before showing an upward trend. During the second snow event, radiation reached a minimum on the 35th day after measurements had begun. Even though there is lack of radiation, the ozone concentration shows a peak at this time without the effect of radiation. Diurnal radiation (Fig. 8) indicates that radiation starts to increase after 10:00 am local time, but ozone starts to increase around 5:00 am. It was found that there was a correlation coefficient of $r = 0.68$ between ozone and radiation. Radiation tends to peak at 4:00 pm, which is one hour after ozone peaks and four hours after temperature peaks.

In terms of relative humidity, a time series plot (Fig 9) shows that during both of the anomalous events, relative humidity was above 90%. Ozone was at a minimum during the first event, but conversely was at a local peak during the second event. In the diurnal plot (Fig 10), relative humidity remains relatively high before 12:00 pm and trends down in the afternoon, while ozone peaks in the afternoon and reaches minimum in the overnight hours. The correlation coefficient (r) between ozone and relative humidity was -0.36.

3.5. Wind Direction vs. Ozone

The influence that wind direction has on ozone concentrations was examined at both Harrington Beach and Kohler-Andrae. At Harrington, it was determined that the wind most often comes from the Southeast and Northeast. These directions are representative of wind coming from Lake Michigan. Ozone is advected in relatively the same magnitude as most other directions when coming from the Northeast with concentrations of around 50-60 parts per billion. Ozone advection has more variability when coming from the Southeast, but still contains a limit of 50-60 parts per billion (Fig. 11).

A similar pattern of wind was observed at Kohler-Andrae in that wind most often comes from the Northeast and the Southeast, but exhibits a few differences when compared to the results from Harrington. At Kohler-Andrae, ozone magnitudes exhibit a greater amount of variability when coming from the Southeast. In contrast, the greatest amounts of ozone come from the Southeast and are between 60 and 70 parts per billion in magnitude, which is around 10 ppb higher than at Harrington (Fig. 12).

3.7. Boundary Layer Soundings

A launch at Harrington Beach was performed during each of our two trips to Sheboygan. Launches were done at Harrington Beach only due to geographic limitations at Kohler-Andrae, as Kohler-Andrae is a smaller park and is highly forested. Harrington Beach provided large extents of prairies and a greater east-west extent, which increased the odds of the Windsond landing in an area of the park in which it could be easily retrieved. The purpose of launching the Windsonds was to determine the height and magnitude of the inversion above the surface layer of the atmosphere. Our hypothesis was that the closer to the surface the inversion was, the greater the concentration of ozone would be.

During both of our Windsond launches, winds at and above ~1 km AGL were westerly, which meant that if our Windsond went above that level, it would land in Lake Michigan once it was cut down. To avoid losing Windsonds in the lake, they were cut down as soon as they reached a level with prevailing westerly winds. Unfortunately, this resulted in neither launch reaching the level of the inversion. In terms of the March 10 launch, the Windsond landed within the park and was retrieved via the GPS locator. However, the data had noticeable glitches around zero degrees Celsius and thus could not be used. This problem was not encountered during the second launch on April 21, and despite not reaching the inversion, the Windsond recorded detailed profiles of temperature (Fig 13a) and Relative Humidity (Figure 13b), as well as pressure, altitude and wind speed/direction data. The Windsond did land in the lake on the second launch, but was later found washed up on shore by a member of the public. Amazingly, the Windsond was still on, collecting data.

Even though the Windsond launches enabled us to obtain detailed vertical profiles of the boundary layer, the launches did not allow us to test our hypothesis as the inversion was never reached. To determine the correlation between ozone and the inversion on a diurnal time scale, soundings from nearby KGRB that were taken on April 21 (the second Windsond launch date) were examined alongside the daily time series in ozone on that same day (Figures 14a-b). There does not appear to be any significant correlation as when the inversion is closest to the surface (the morning), ozone levels are at their lowest daily values.

3.8. Fine Particulates

In order to interpret the data for fine particulates, we plotted the $PM_{2.5}$, wind direction, and frequency data on windrose plots. The direction of the bars shows the direction the wind was coming from. The length of the bars shows the frequency of wind from that direction, and the colors show distribution of $PM_{2.5}$ concentration. The lowest $PM_{2.5}$ values were associated with northeasterly winds (Figure 15) The maximum concentrations of $PM_{2.5}$ came from the southwest, with maximum concentrations of 50-60 $\mu g/m^3$ (Harrington) and 40-50 $\mu g/m^3$ (Kohler-Andrae). Concentrations from the northwest were highly variable at both locations. There was one rogue high (50-60 $\mu g/m^3$) reading from the north at Kohler-Andrae.

4. Discussion

During our analysis of the relationship between ozone and temperature, we noticed that the temperature decrease during the snowstorm did not impact ozone concentration. Possible causes of this could be 1) There is a threshold that when temperature is below -10 °C, ozone concentration will have negative correlation with temperature; 2) Ozone still has positive or no correlation with temperature for all temperature range, but during the second snow event there was some transport of surface level ozone from other polluted areas that brought concentration at Harrington and Kohler-Andrae higher thus misguided the statistical results of correlation coefficient r values in Table 1 to have different behavior below/above -10 °C. Temperature and ozone are strongly correlated when it comes to a diurnal data set, but delayed by a few hours. The offset of the diurnal ozone cycle from the diurnal temperature cycle could be due to Possible reasons for the three-hour delay in ozone could be 1) As temperature started to decrease, there is still radiation that continually forms ozone and then accumulated in the atmosphere; 2) There is another meteorological or chemical mechanism that is further affecting ozone concentration after the temperature peaks. As expected, radiation and ozone are also strongly correlated diurnally. Relative humidity and ozone portray a negative correlation. Overall, there is no easy correlation between ozone and temperature in the wintertime due to the -10 degree celsius differentiation. However, ozone is strongly correlated to both temperature and radiation diurnally.

The significance of our results of the Ozone and Wind Direction relationship indicate that wind most often comes from the lake at both Harrington Beach and Kohler-Andrae. Current research doesn't suggest a wintertime relationship between Ozone and Wind Direction. However, due to the Hadley Cell being most intense during the winter in the Northern Hemisphere (Nguyen et al, 2012), extratropical activity is also more intense. Stratosphere-Troposphere interactions make quite an impact in the winter (Tomassini et al, 2012), so it is possible that ozone could be transported into the troposphere from the stratosphere during this time, and thus influence concentrations of ozone.

Ozone Advection Event

Another mechanism to be considered for ozone spikes is the advection of ozone, from either surrounding counties or even stratospheric intrusion. Thus far, this paper has made mention mostly to transport of precursors as being a dominant driver in ozone spikes. On 6 April there is an anomalous plume of ozone at the Harrington Beach site. At 0600 UTC 6 April (1 am local time) ozone is at 28 ppb. By 1000 UTC 6 April ozone spikes all the way up to 51 ppb. There is clearly no correlation to ozone and available shortwave radiation in this event (Figure 17). The mechanism behind generation of ozone from precursors is heavily dependent on available radiation as previously brought up in the paper. It follows, this event is the result of ozone advection.

To discover the source of this ozone advection the hybrid single-particle lagrangian integrated trajectory model (HYSPLIT) model was run. This model used an ensemble of mesoscale weather model High Resolution Rapid Refresh (HRRR). This trajectory analysis took a parcel of air from 10 m AGL above the ground at the Harrington Beach site and back-tracked it for 24 hours. The ensemble showed two possible trajectories (Figure 18). One trajectory came from central Illinois and the other came from northern Wisconsin. DNR air quality data was then compared to see the likely contributor. On 5 April the northern part of Wisconsin had beyond moderate values for ozone across a very wide swath (Figure 19). In consideration of all that the spike at Harrington Beach on 6 April was likely due to high ozone air coming from northern Wisconsin. The exact cause of the spike on 5 April in northern Wisconsin was likely not anthropogenic because of lack of industry or urban expanse and just the nature of how wide the spike was. One such explanation could be the tropopause folding suggested previously, that would act to advect ozone rich stratospheric air to the troposphere. This dynamic analysis is beyond the scope of our study but would be worth further discussion.

Windsond

Although our hypothesis was not entirely correct and the Windsonds did not reach the boundary layer, the AQUABLUE experiment was a good way to test out these instruments in their early stages to determine their capabilities and uncover any glitches, such as the zero degree issue. In part to our launches, the Windsond manufacturers were able to determine the cause of the zero degree issue and fix it. The Windsond landing in the lake and still working after several hours in the water is a testament to the durability of the instruments, which another useful finding to future studies.

To make these Windsonds useful in future air quality experiments, it might be useful to do multiple launches per day over several days to test ozone vs. inversion correlations in day-to-day comparisons. This was not possible in AQUABLUE due to time constraints. It would also be useful to have a sensor on the Windsond that would allow it to take ozone measurements in the boundary layer. Lastly, if retrieving the Windsonds was not a high priority, it would be interesting to let the Windsond go out over the lake t measure the marine boundary layer. Inversions over the lake tend to last much longer over open water due to less heating of the surface versus land during the day, and thus a ozone-inversion correlation might be more obvious over water. Launches from a boat or ferry would be a useful way to attain such a marine boundary layer sounding.

Fine Particulate Analysis

We had some interesting results with this study. We were correct about the direction the lowest concentrations came from, as $PM_{2.5}$ rarely exceeded $10ug/m^3$ with northeasterly winds. However, while we did get somewhat elevated concentrations from the southeast, the maximum concentrations actually came from the southwest. Upon further investigation, Interstate 43 runs north/south just one and two miles to the west of Harrington Beach State Park and Kohler-Andrae State Park, respectively (Figure 16). This close proximity to a major highway could be the cause of the elevated levels of fine particulates from that direction. Meanwhile, air temperatures were below freezing on virtually all but the last few days of our study. A lack of daytime heating and subsequent boundary layer mixing may have hindered aerosols from becoming airborne enough to reach our sites from Milwaukee and Chicago.

5. Conclusion

Our results suggested that in winter months the formation of ozone is not as strongly associated with the lake transporting southern precursors, a mechanism which the Lake Michigan

Ozone Study identified in the summer. Prior work has suggested that precursor formation in winter is less associated with ozone distribution, as Lake Michigan's proximity to precursor hotspots such as Chicago and Gary do no lead to particularly high levels of ozone in winter and spring, though the lake is a local maxima in summer and fall (Spak and Holloway 2009). As for $PM_{2.5}$, the DustTrak that was closer to I-43 measured higher amounts from that direction, suggesting a link between the highway and fine particulates. More research would need to be done to confirm this. Regardless of the findings, the incorporation of various meteorological instrumentation provided useful experience with the assemblage, data retrieval, and overall incorporation of field instrumentation into a thorough and detailed research experiment.

6. References

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Table 1. Correlation coefficient R between temperature and ozone for temperature below -10 °C, greater -10 °C and overall correlation at Harrington and Kohler-Andrae.

	<= -10 °C	> -10 °C	Overall
Harrington	-0.15	0.28	0.02
Kohler-Andrae	0.02	0.43	0.09

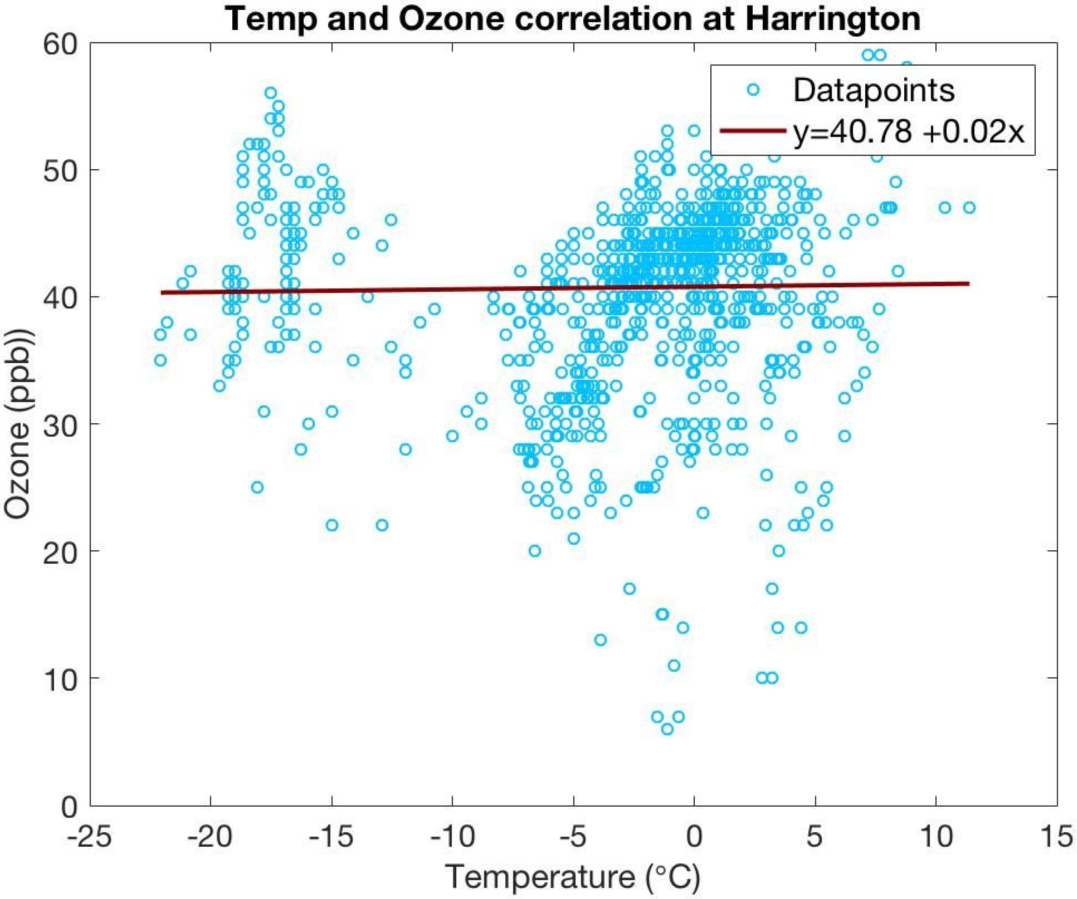

Figure 1. Temperature and ozone correlation at Harrington.

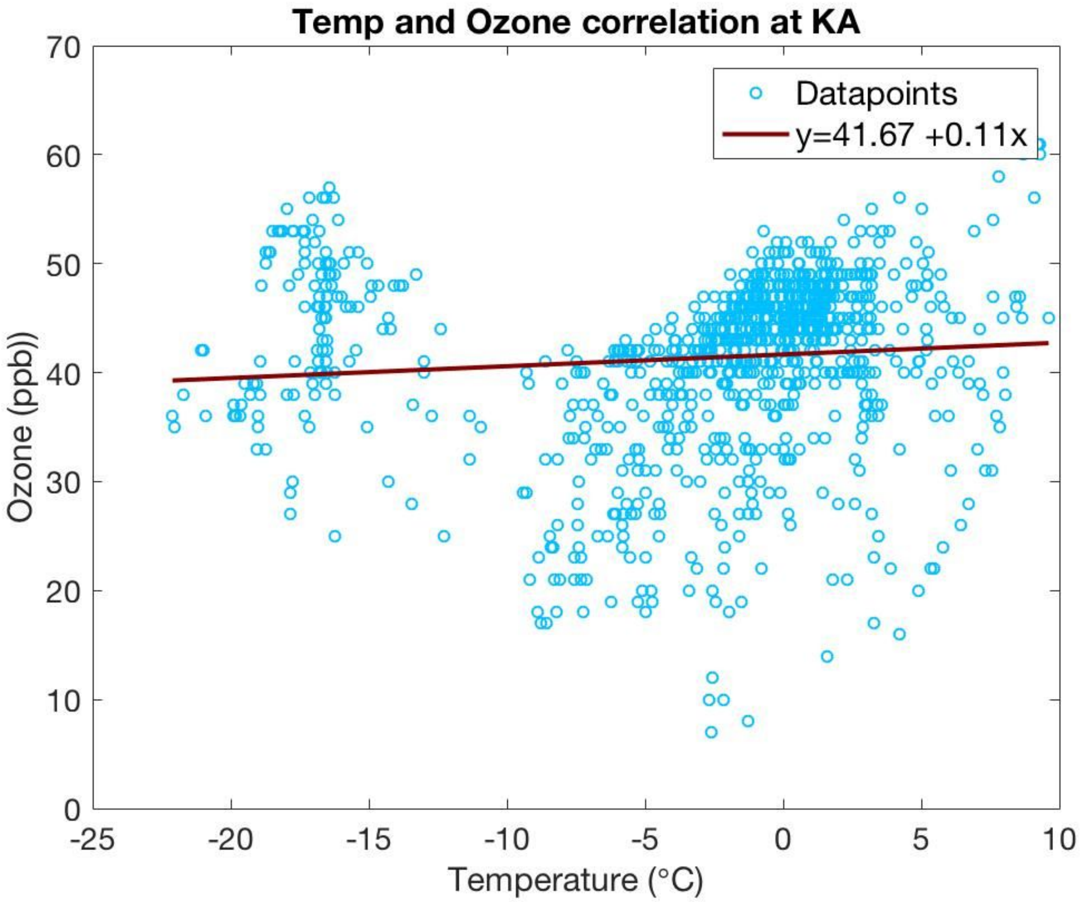

Figure 2. Temperature and ozone correlation at Kohler-Andrae.

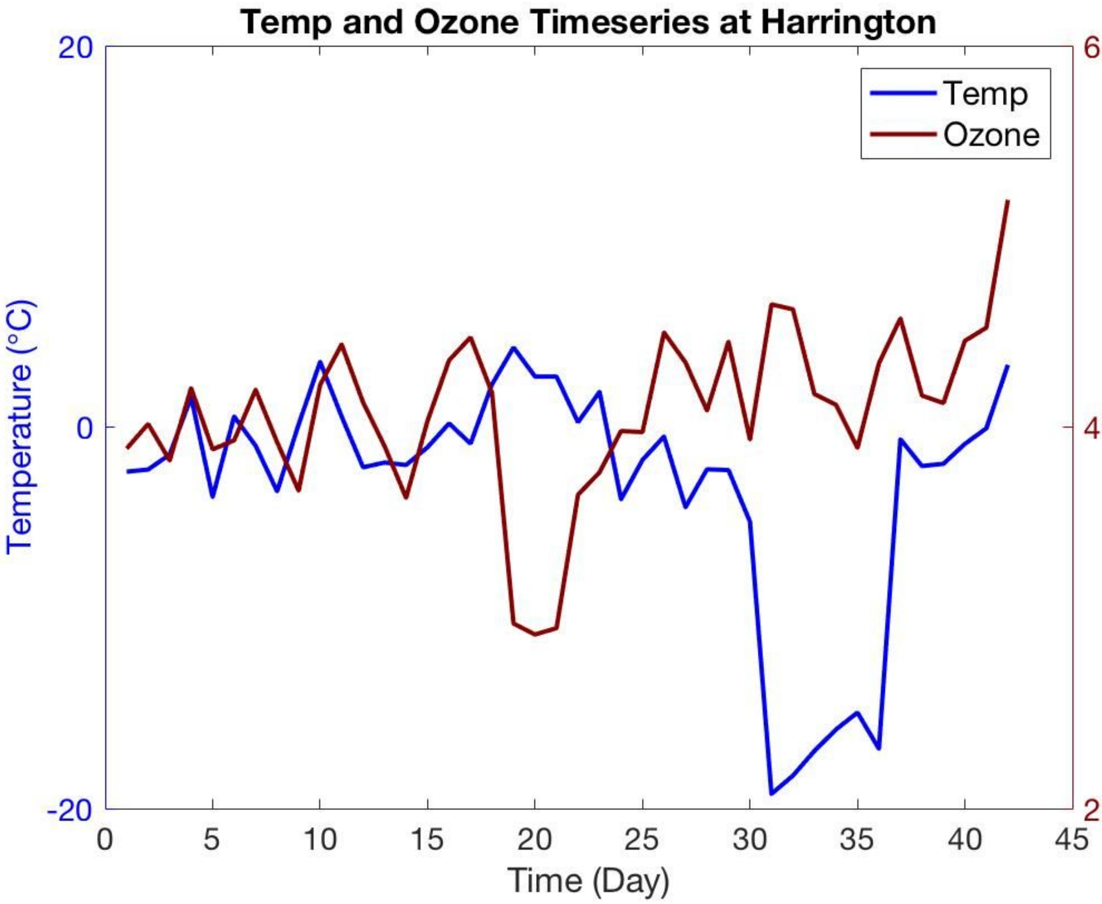

Figure 3. Temperature and ozone time series Harrington.

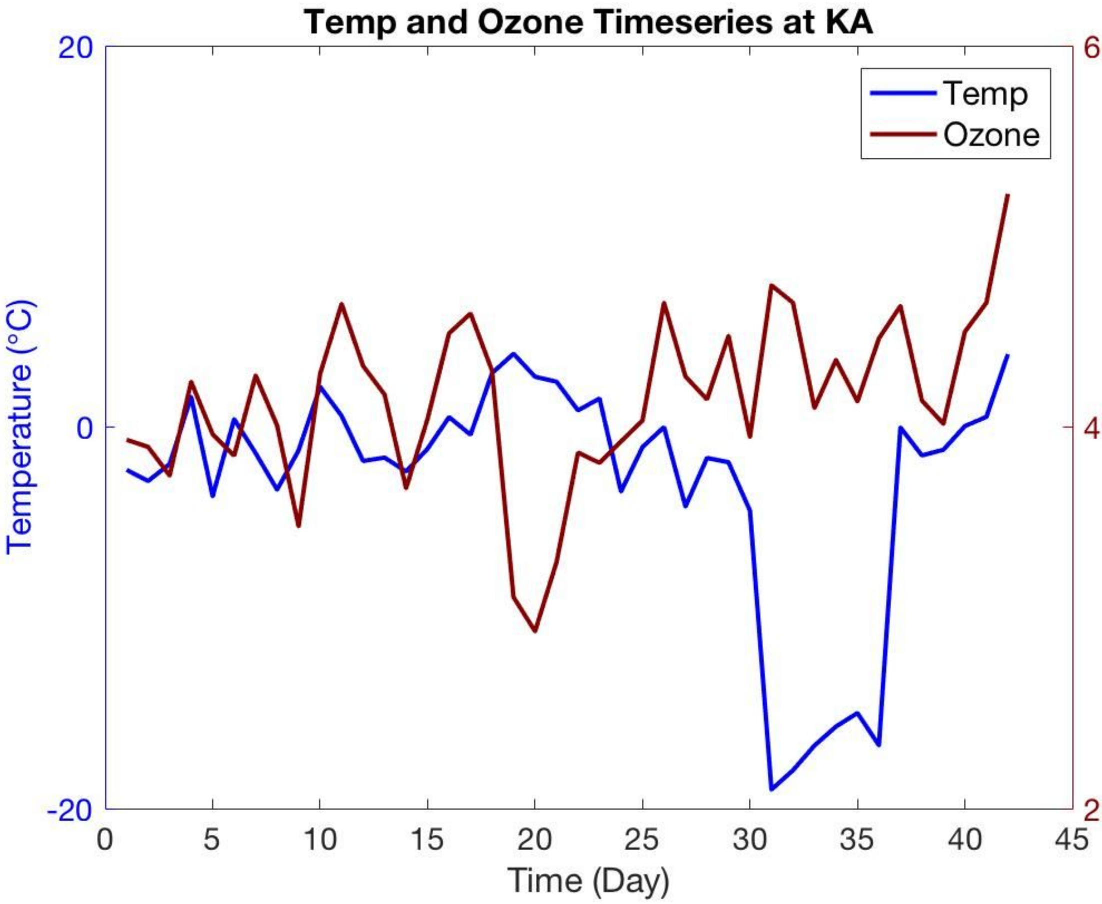

Figure 4. Temperature and ozone time series at Kohler-Andrae.

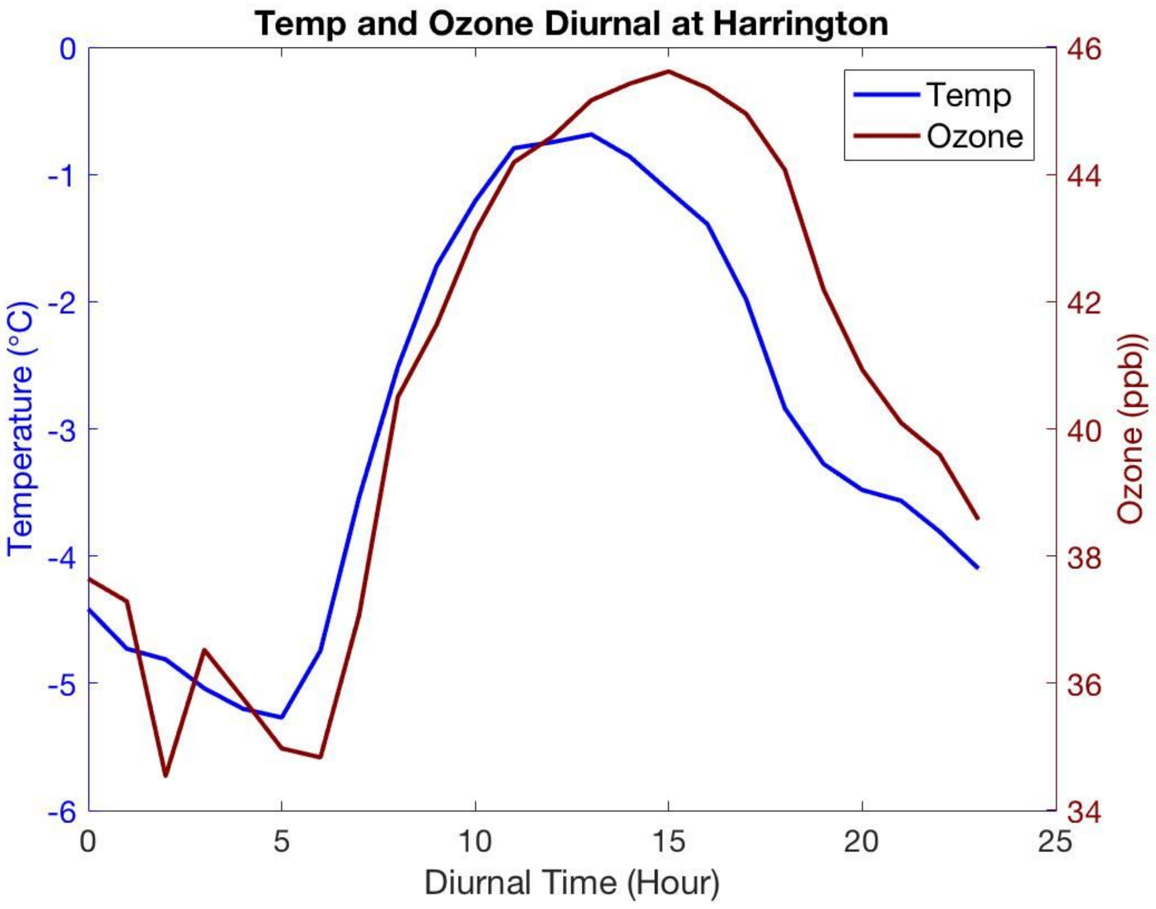

Figure 5. Diurnal temperature and ozone at Harrington.

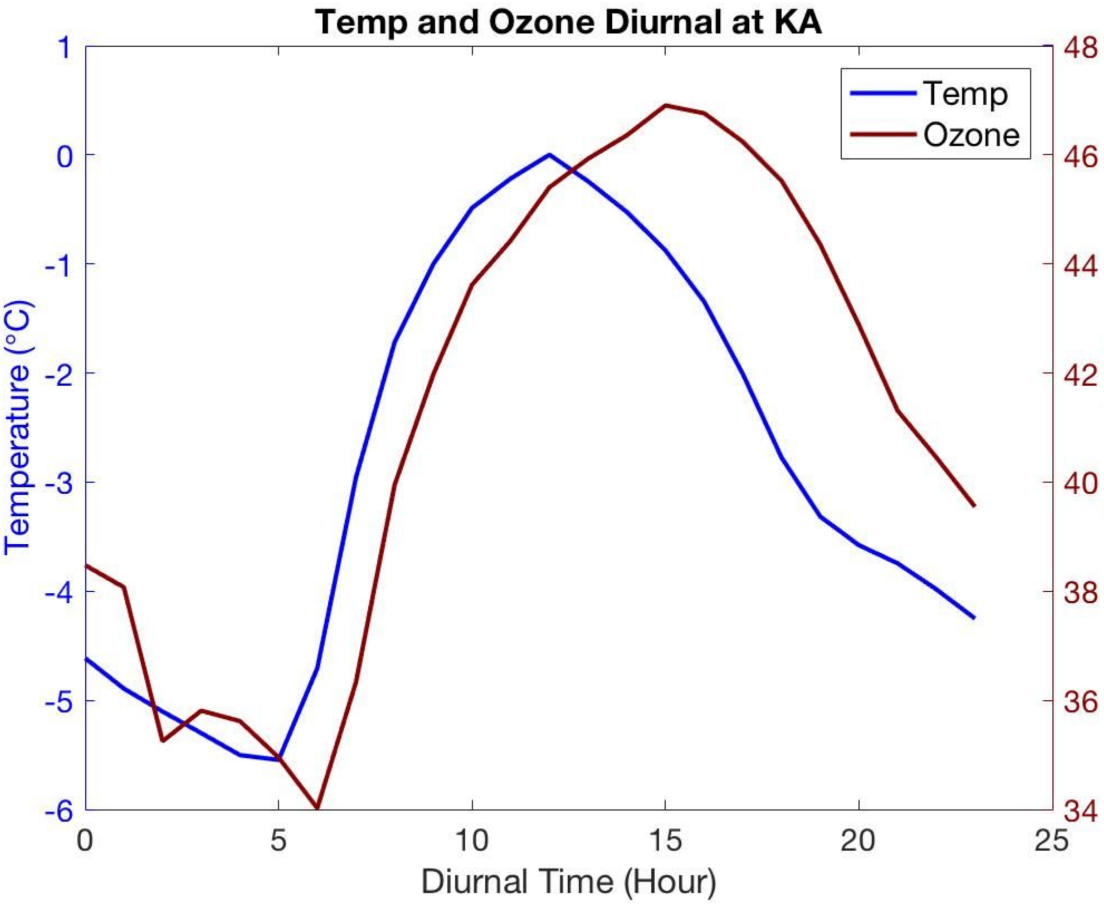

Figure 6. Diurnal temperature and ozone at Kohler-Andrae.

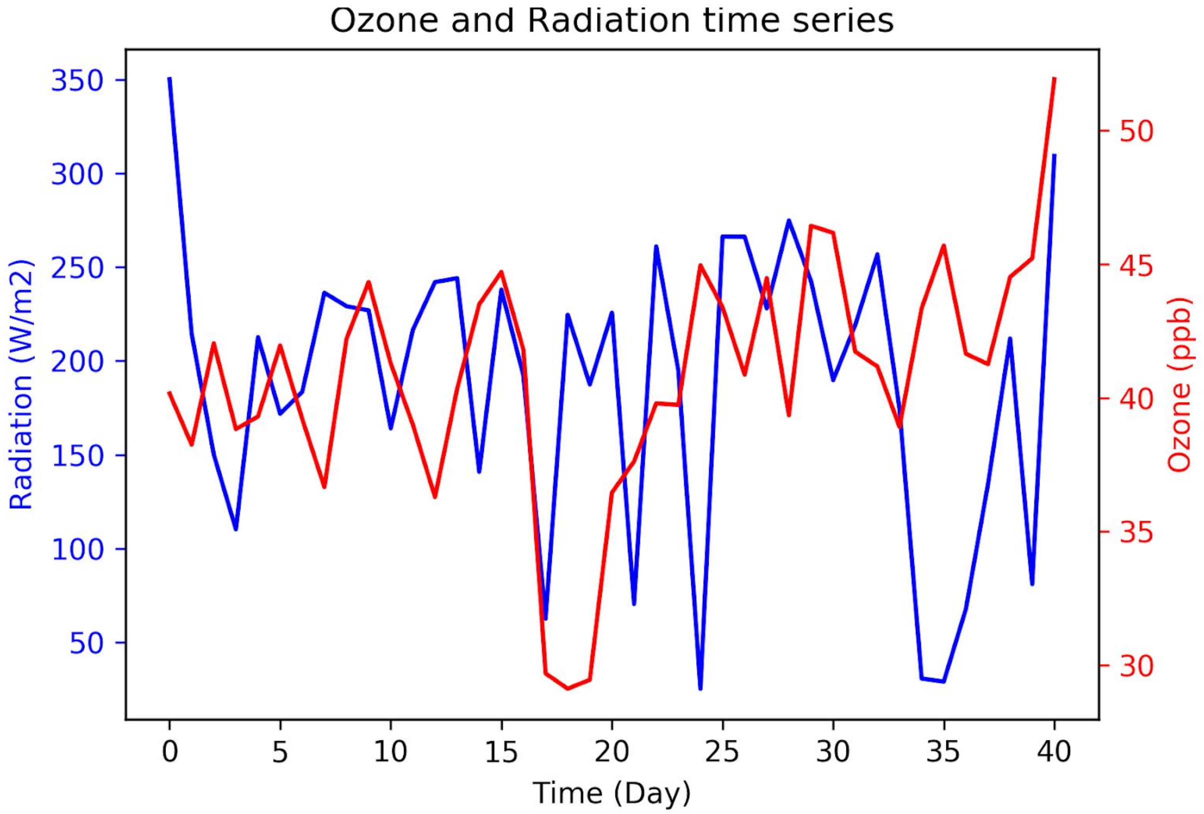

Figure 7. Radiation and ozone time series at Harrington.

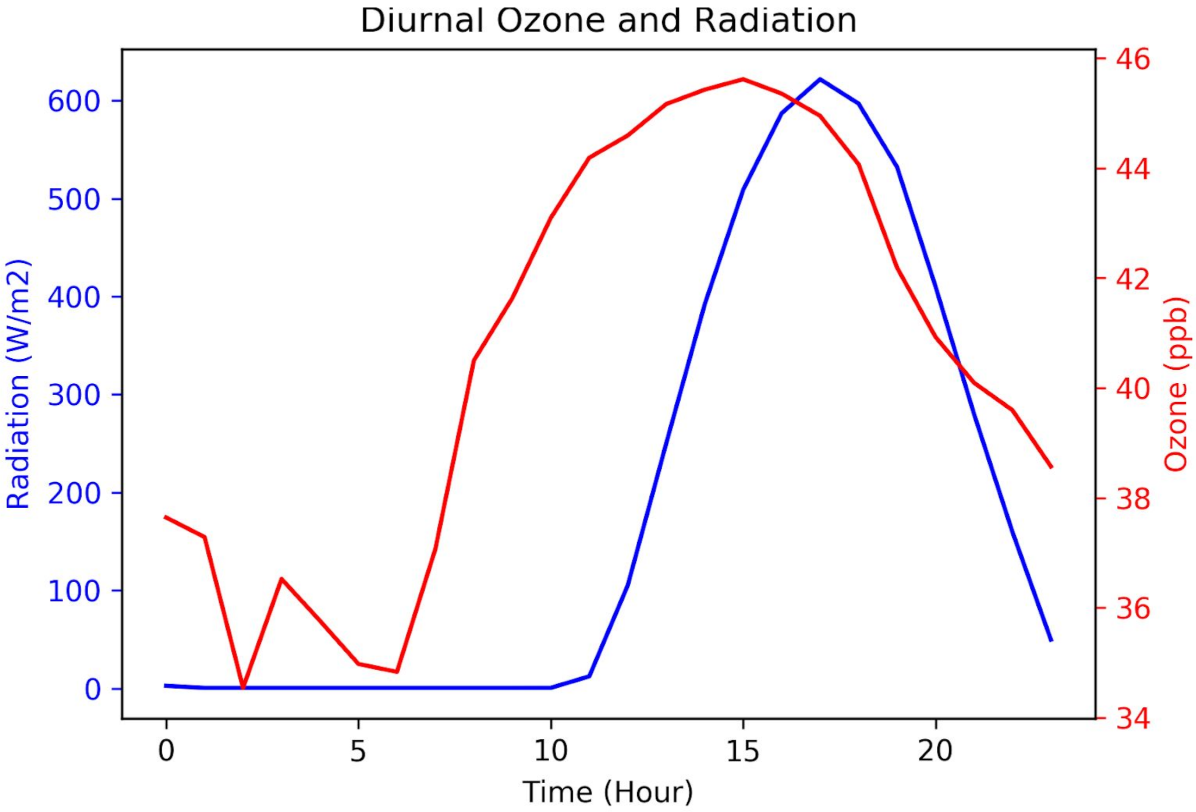

Figure 8. Diurnal radiation and ozone at Harrington.

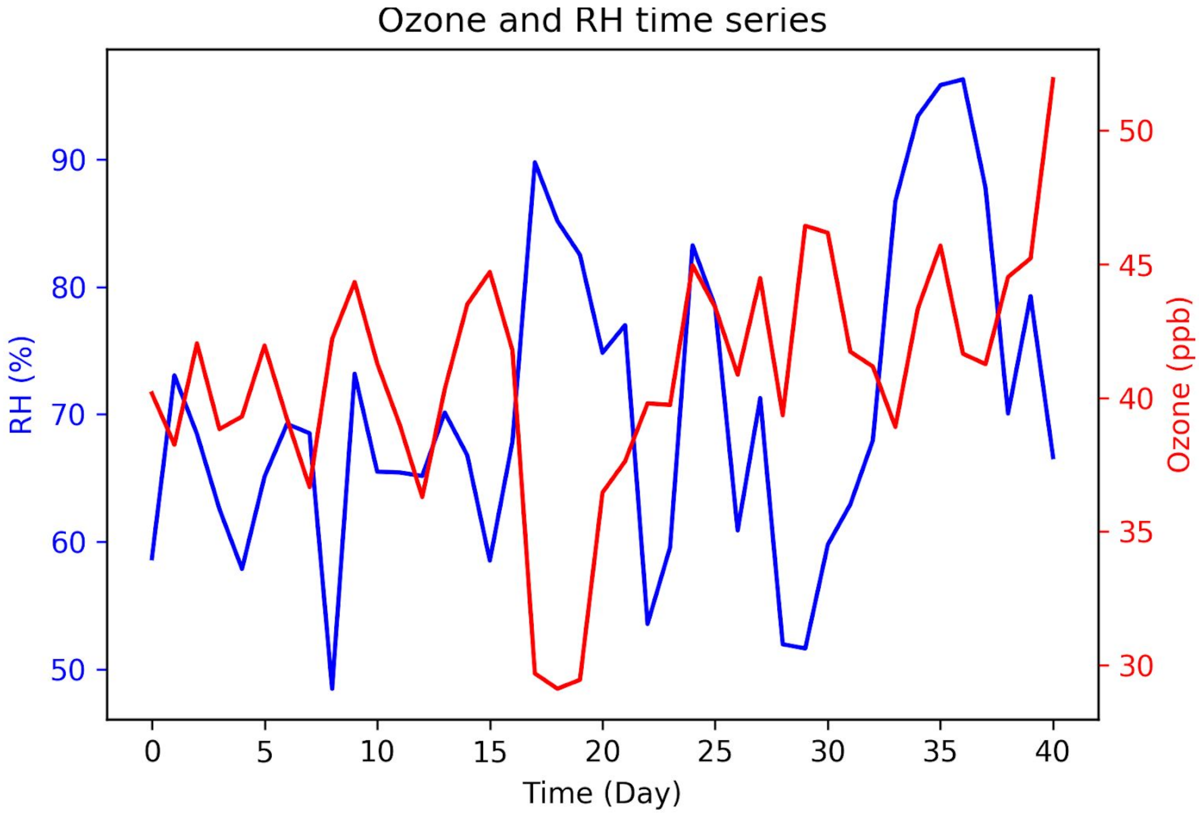

Figure 9. Relative humidity and ozone time series at Harrington.

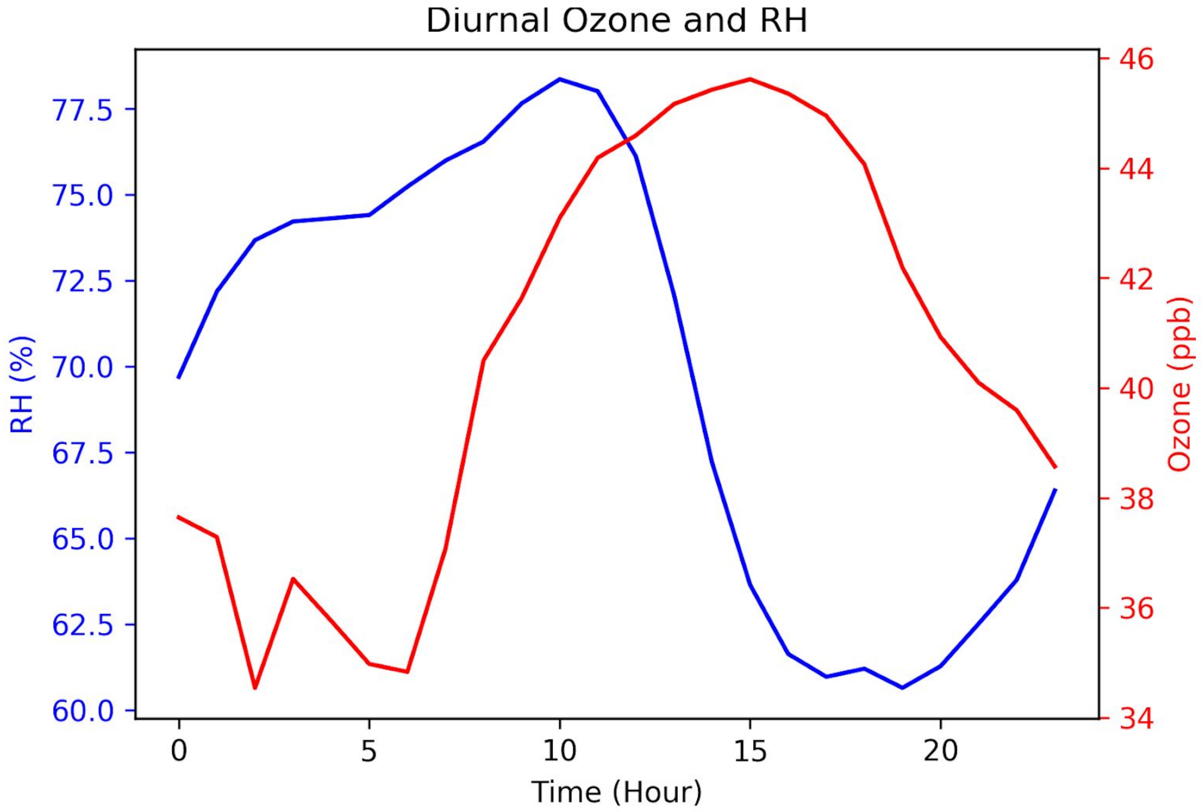

Figure 10. Diurnal relative humidity and ozone at Harrington.

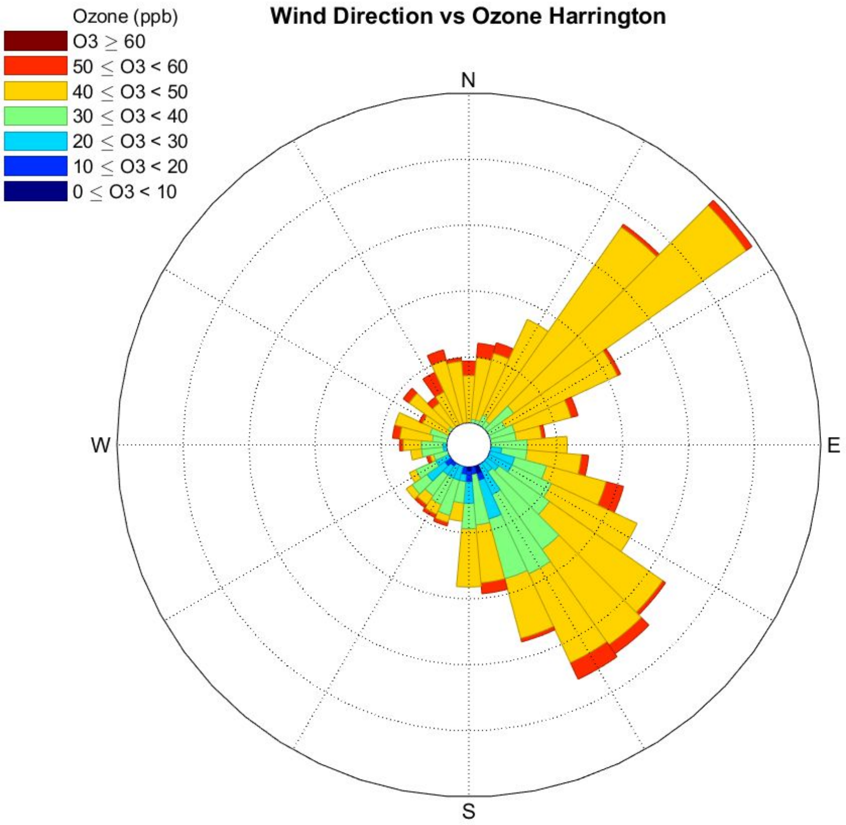

Figure 11. Wind direction vs Ozone at Harrington Beach State Park. Length of arm represents the amount of times ozone comes from that direction. Colors represent concentration of Ozone.

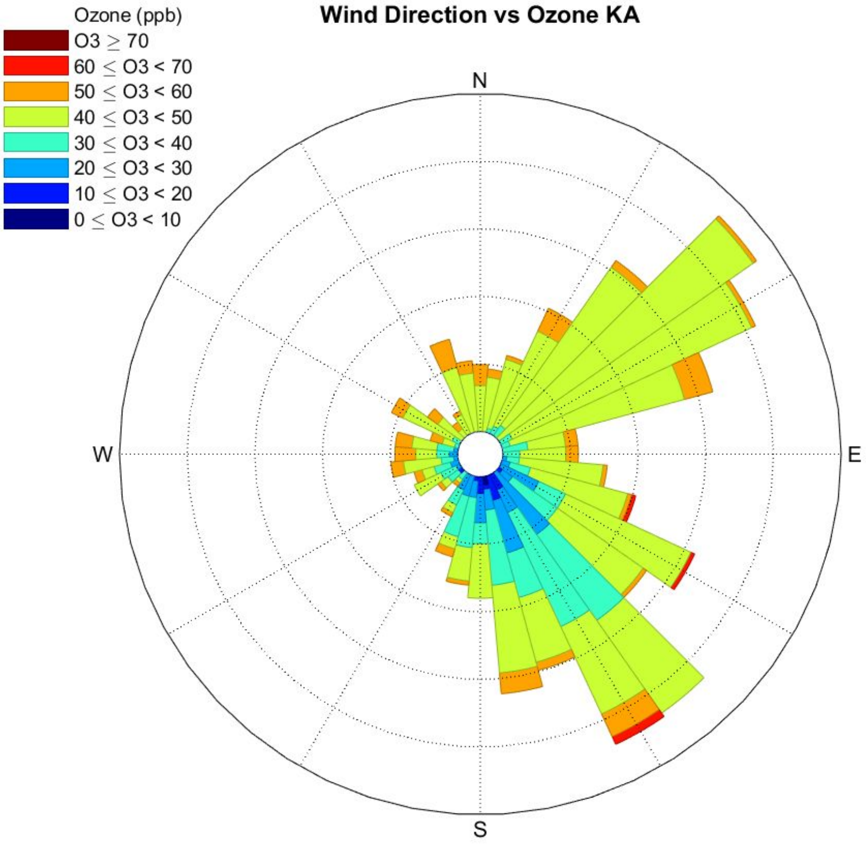

Figure 12. Wind direction vs Ozone at Kohler-Andrae. Length of arm represents the amount of times ozone came from that direction. Color represents concentration of ozone.

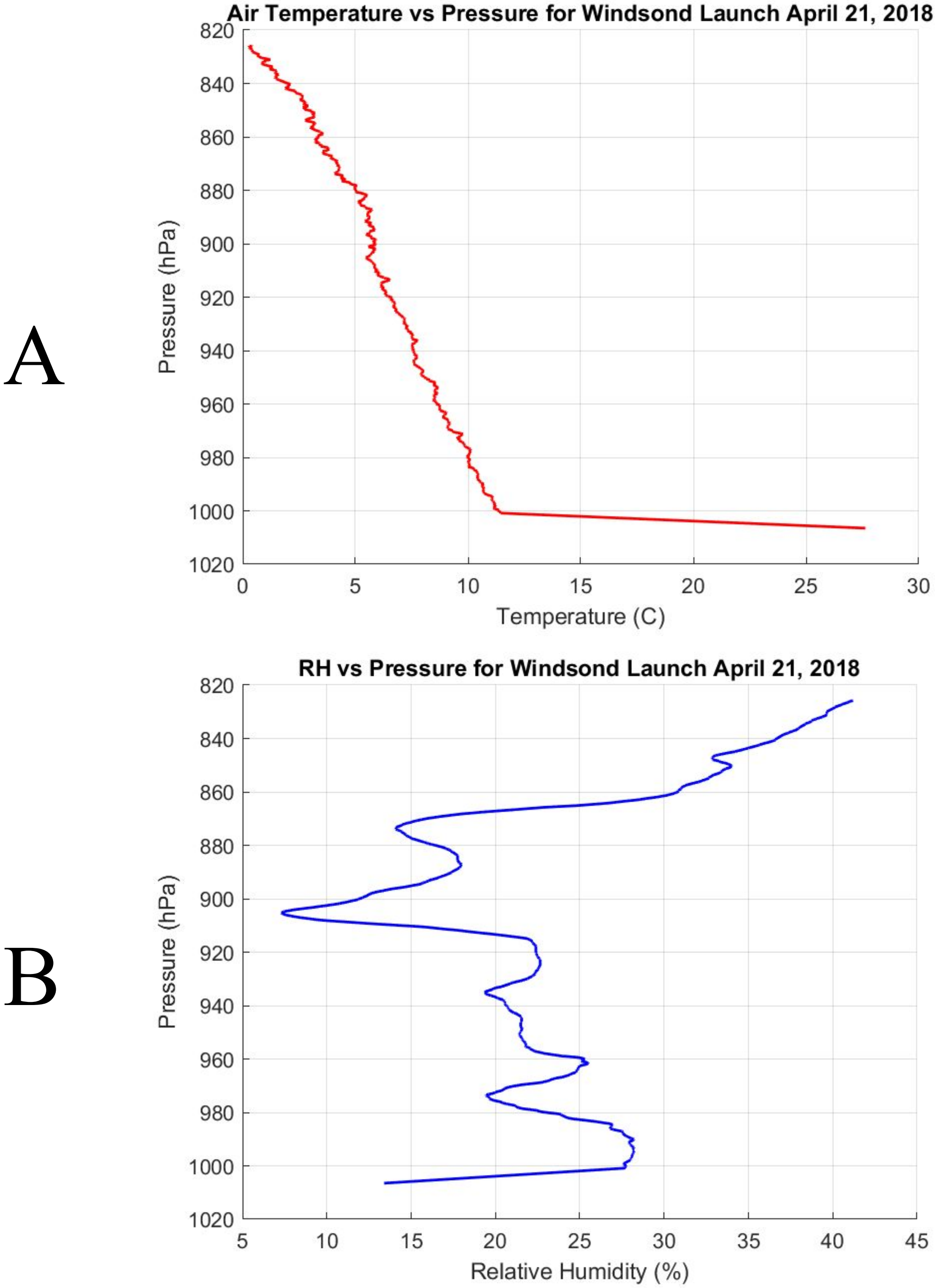

Figure 13: Soundings for the April 21 Windsond Launch at Harrington Beach - Temperature (A), Relative Humidity (B)

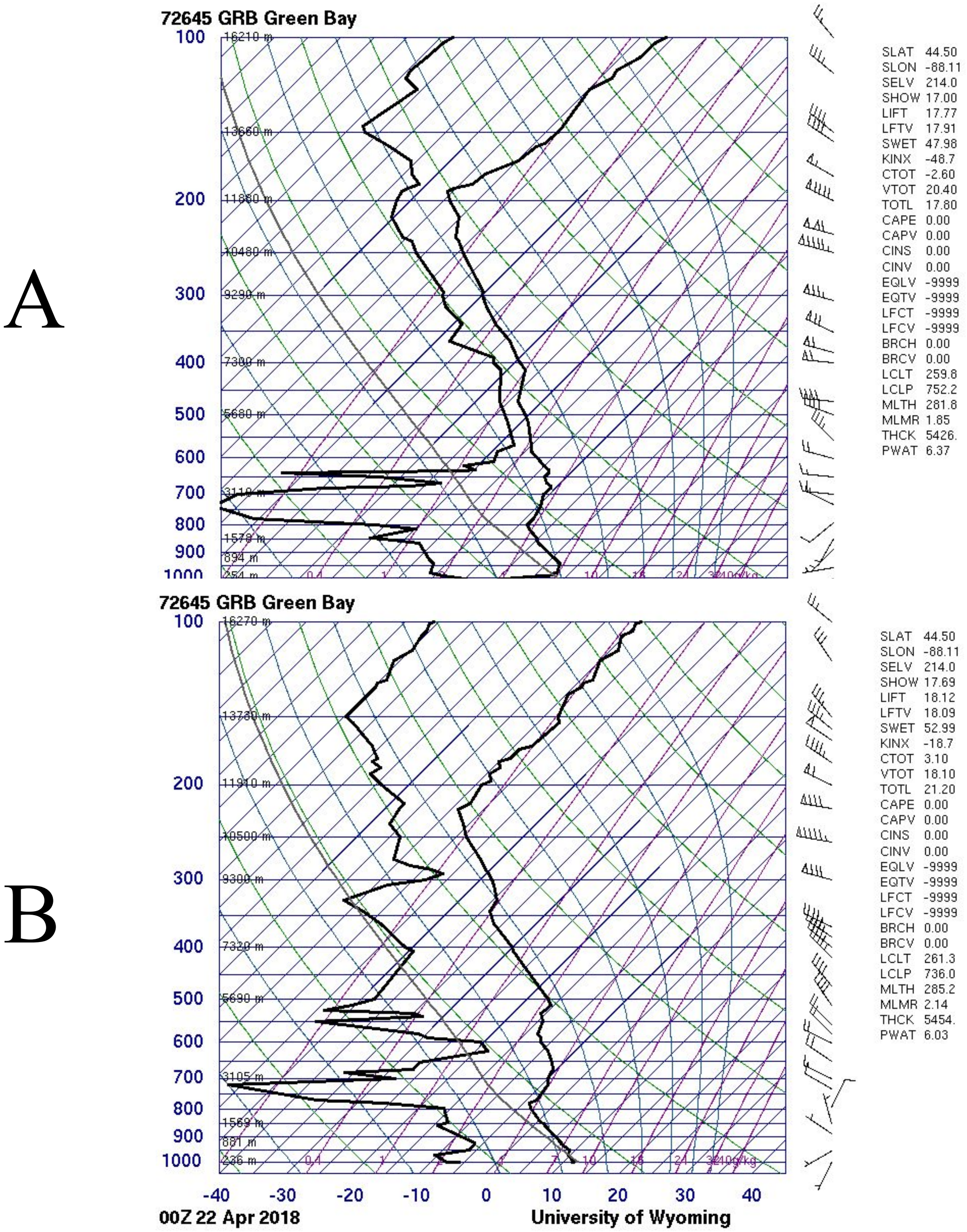

Figure 14: Soundings taken from the Green Bay, WI National Weather Service office - 12Z 21 April 2018 (A), 00Z 22 April 2018 (B)

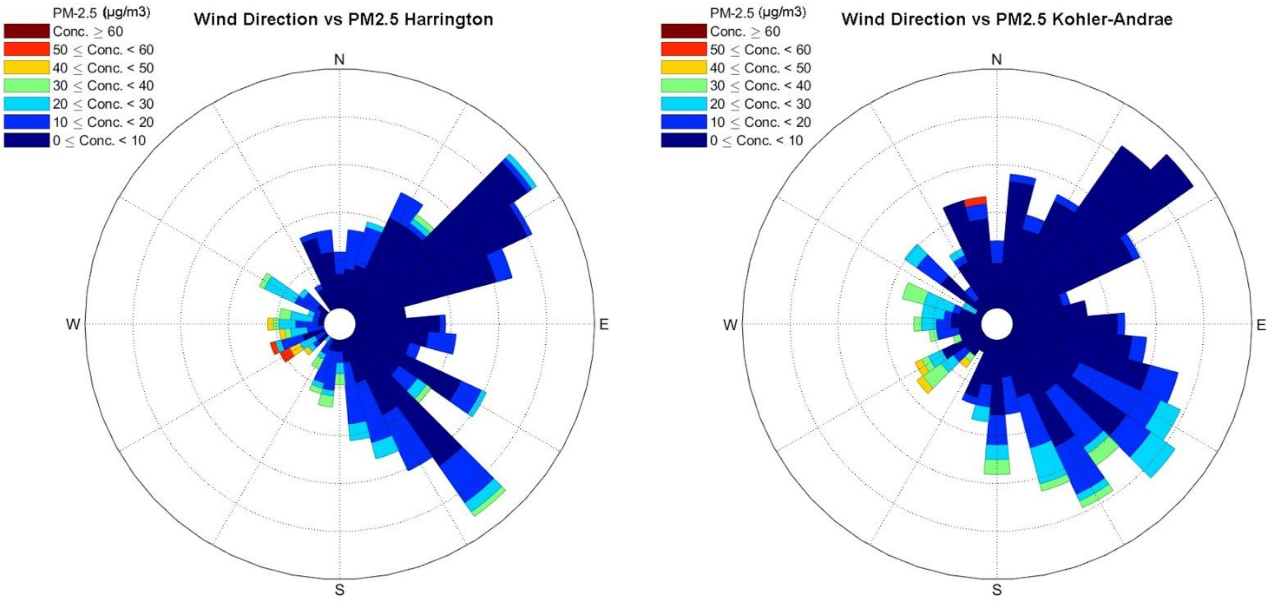

Figure 15: PM$_{2.5}$ concentration, wind direction, and frequency

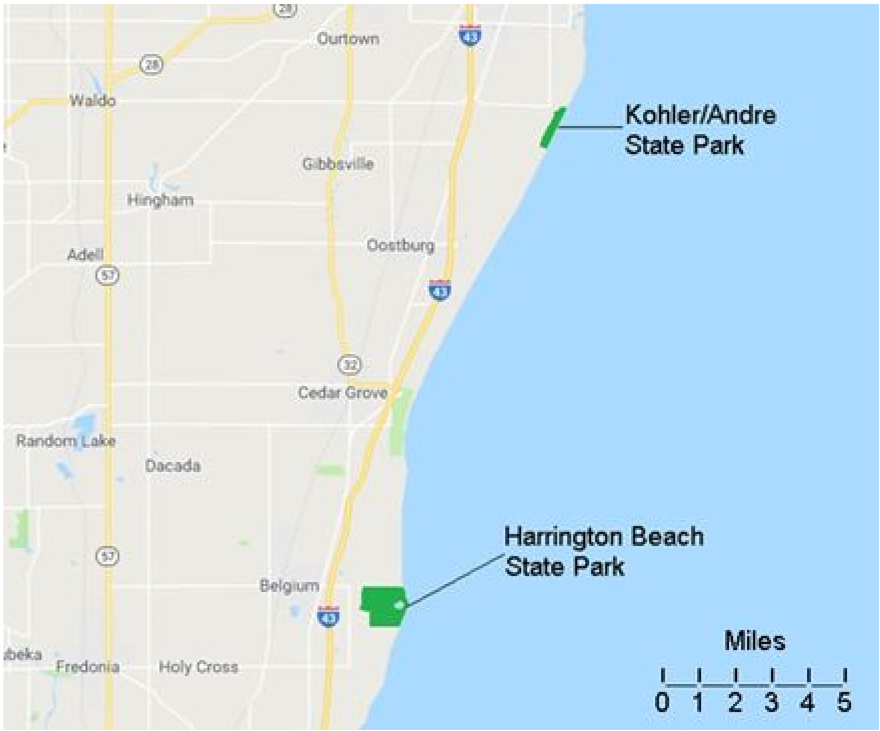

Figure 16: Map of both deployment locations and Interstate 43

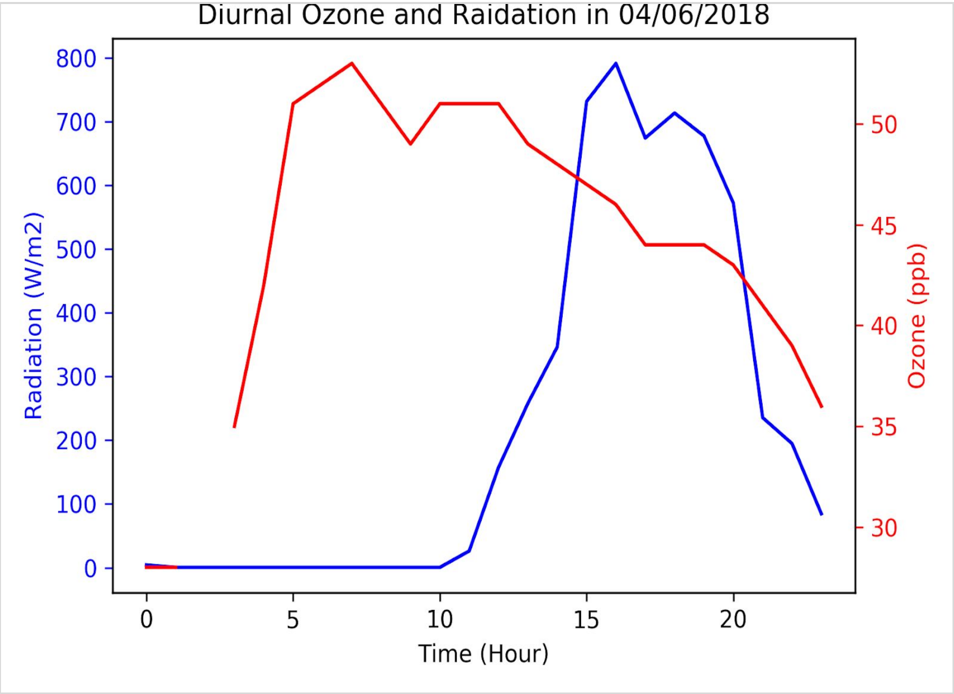

Figure 17: Time series of Ozone concentration (ppb) and incoming solar radiation (w/m2) on 6 April 2018. Time is in CST.

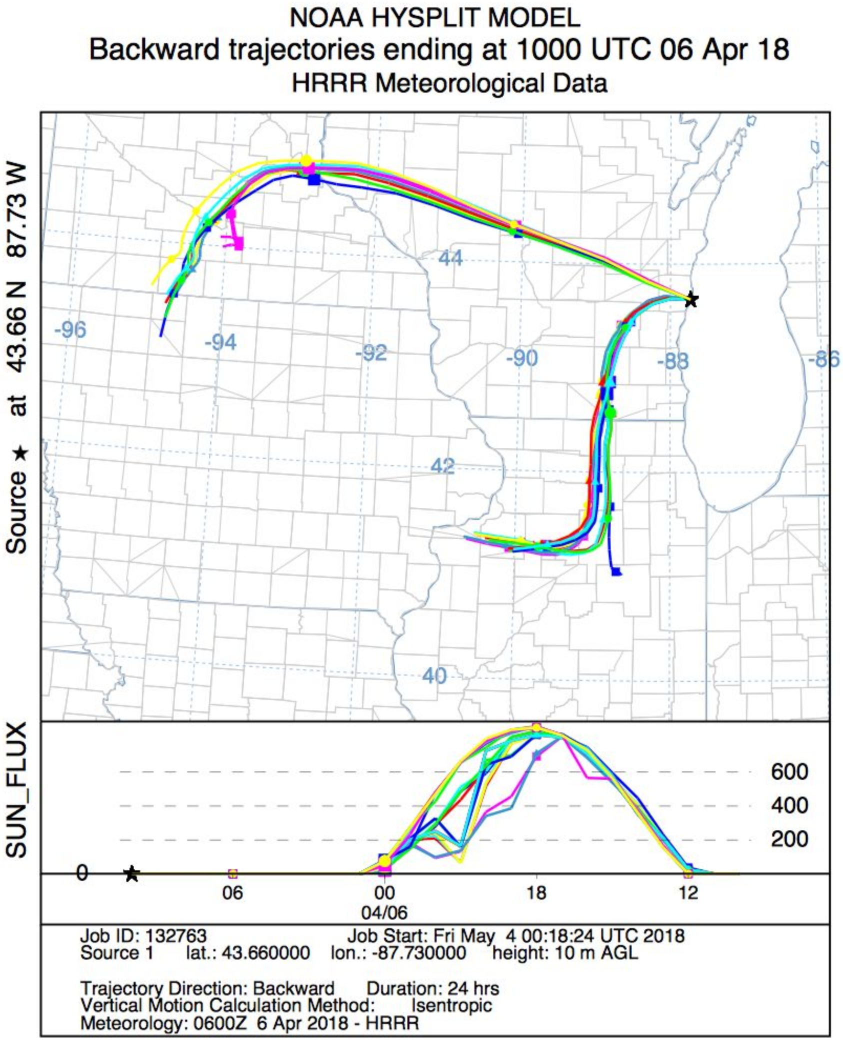

Figure 18: HYSPLIT model initiated at 1000 UTC 6 April 2018 . Shows trajectory and incoming solar radiation in (w/m2)

Figure 19: DNR air quality index 5 April 2018 for Wisconsin and Minnesota. Plotted in yellow is daily averaged ozone levels between 50-100 ppb