

Exploratory Analysis of Ozone Dynamics in Grand Junction during Summer 2016

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Ozone has been monitored at Palisade, Colorado, as a representation for the Grand Junction area, and is well below the National Ambient Air Quality Standards. The design value for Palisade has been on the decline, dropping from 68 parts per billion in 2012 to 63 parts per billion in 2016. However, ozone generation, distribution, and transport in the valley is not well understood. The Colorado Department of Public Health and Environment, Air Pollution Control Division, Technical Services Program measured ozone at eight sites in the Grand Junction Valley and obtained data from two sites operated by the United States Forest Service to develop a conceptual model of the generation, distribution, and quenching of ozone in the valley. Human activity, katabatic/anabatic wind flows, and solar heating, combined with a functional geological shelter from synoptic weather patterns result in a build-up of ozone within the valley that persists through stable meteorology and is reduced by turbulent meteorology. Palisade is not the highest concentration site during the study but has representative value for more than ninety three percent of the population in the valley.

Introduction

During April to October of 2016 the Colorado Department of Public Health and Environment (CDPHE) Air Pollution Control Division (APCD) deployed and operated 7 temporary ozone monitoring sites in the Grand Junction Valley of Colorado.

The purpose of this study was to characterize the magnitude and location of ozone in the Grand Junction Valley during the summer months, with a study period of April 5th to October 11th of 2016, and to gain insight into the representativeness of CDPHE's long term ozone site in Palisade. The motivations for this study include a growing population and increasing oil and gas development in and around the Grand Junction Valley.

The topography of Grand Junction is a river valley with mesas and mountains to the north, west, and east. The city of Grand Junction is located near the confluence of the Colorado River and the Gunnison River. An elevation profile of a path along the valley is shown in Figure 1, with the angle in the transect at the Pitkin shelter (a), and an elevation profile roughly transecting the Book Cliffs and Bangs Canyon sites (b). As the Colorado River flows out of the valley to the west, the Grand Junction Valley can be conceptualized as a 3-sided bowl, with the Colorado River entering into the bowl from the northeast and exiting from the southwest, and the Gunnison River entering from the southeast to merge with the Colorado

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River mid-valley. This, in combination with synoptic winds from west to east, plays an important role in how pollutants can build up in the resulting stable air mass in the valley.

Figure 2 shows the Grand Junction Valley with the sites used for the ozone study. There were a total of nine ozone sites deployed for the study, in addition to the long term ozone site at Palisade. Of the 10 sites APCD operated eight and an additional two were operated by the United States Forest Service (USFS). Table 1 summarizes the 10 ozone sites discussed in this report and provides latitude and longitude. The locations of the 7 temporary ozone sites (not including the USFS) were chosen based on experience that suggests higher ozone accumulation likely exits outside of Grand Junction city limits. However, one ozone monitor was deployed within Grand Junction at the Pitkin shelter for completeness.

Site Name	Meteorology	Elevation	Latitude	Longitude
Bangs Canyon	Yes	5621	39.022111	-108.612789
Book Cliffs	Yes	5691	39.222586	-108.511800
Douglas Pass*	No	8271	39.59800	-108.805000
Escalante	Yes	5243	38.894858	-108.401444
Grand Mesa*	No	9730	39.030000	-108.225000
Highline SP	Yes	4750	39.276250	-108.834919
Palisade	Yes	5022	39.130575	-108.313830
Pitkin	Yes	4583	39.064289	-108.561550
Ute Water	Yes	4909	39.148217	-108.556808
Whitewater	No	6309	38.897983	-108.496753

Table 1: Site Description and Location

*USFS Site

Methods

The ozone monitoring equipment used in this study was a combination of Teledyne Air Pollution Instruments (TAPI) and 2B Technologies (2BTech) analyzers. A TAPI model 400 ozone analyzer, as already in use at Palisade, was installed at the additional shelter sites with line power. Pitkin and Whitewater. The autonomous temporary sites, Bangs Canyon, Book Cliffs, Escalante, Highline, and Ute Water, used the 2BTech model 205 ozone analyzer. The 2BTech model 205 is lightweight and low powered and is well suited for long-term monitoring at remote locations. The data generated was stored on a Campbell Scientific data logger, which was routinely polled over a cellular modem. This allows for near real time data collection and data storage on a central computer. For better characterization of the measured ozone, each APCD operated site (except for Whitewater) included meteorological measurements of wind speed, wind direction, and temperature. The autonomous sites were equipped with an Argent



weather station, while the shelter sites (Pitkin and Palisade) are equipped with MetOne and/or R. M. Young weather sensors.

The Pitkin ozone analyzer was incorporated into the existing monitoring site and data streams captured by the onsite data logger. An ozone source was also installed to challenge the analyzer nightly with precise ozone concentrations and zero air. At Whitewater, along with an ozone analyzer, a data logger and cellular modem was installed.

Ozone Analytical Method

The 2B Technologies 205 Dual Beam Ozone Monitor is designed to enable accurate measurements of atmospheric ozone over a wide dynamic range extending from a limit of detection of 1 part-per-billion by volume (ppby) to an upper limit of 100 parts-per-million (ppmv) based on the well-established technique of absorption of ultraviolet light at 254 nm. The 205 Dual Beam Ozone Monitor is light weight and has low power consumption relative to conventional instruments.

Ozone is measured based on the attenuation of light passing through two separate 15-cm long absorption cells fitted with quartz windows. A single low-pressure mercury lamp is located on one side of the absorption cells, and photodiodes are located on the opposite side of the absorption cells. The photodiodes have built-in interference filters centered on 254 nm, the principal wavelength of light emitted by the mercury lamp. An air pump draws sample air into the instrument. A pair of solenoid valves switches in unison so as to alternately send ozonescrubbed air and unscrubbed air through the two absorption cells. Thus, the intensity of light passing through ozone-scrubbed air (Io) is measured in Cell 1 while the intensity of light pass through unscrubbed air (I) is measured in Cell 2. Every 2 seconds, the solenoid valves switch, changing which cell receives ozone-scrubbed air and which cell receives unscrubbed air.

Ozone concentration is calculated for each cell from the measurements of Io and I according to the Beer-Lambert Law. The 2B Technologies instrument uses the same absorption cross section (extinction coefficient) as used in other commercial instruments. A new ozone measurement is made every 2 seconds for both cells, based on updated values of Io and I. These two values are averaged and then digitally output to the data logger (2B Technologies, Incorporated, 2017).

APCD uses only dual cell model 205 ozone analyzers. An older single-cell model is available from 2B Technologies which may have been used by the USFS at Grand Mesa and Douglas Pass. Data presented in this report from USFS have not been subject to quality control outside of the CDPHE and were accepted as presented from the USFS.

The analysis method for the TAPI 400E analyzer is based on the same absorption principle using the well-established Beer-Lambert equation, and a high energy mercury vapor lamp shone behind a bandwidth filter that reduces the light to 254nm (Teledyne API, 2017).

Enclosure

A weather-proof Hammond gray fiberglass enclosure (or similar) contains the analyzer, power system, data logger, modem, and zero-air charcoal container. A CPU style fan near the top and a protected opening below the battery allow for air flow. The fan is actuated if the internal temperature gets warm enough to merit the power consumption. Figure 3 shows the layout of the enclosure. Not shown in the figure is the final modem placement, which is moved to the inside of the enclosure lid, an inch or so above the bottom of the inside of the



enclosure. This is to keep any potential water from getting into the modem. The data logger and battery (though the battery is sealed) are also above the bottom of the enclosure.

The measurement platform is based on a 12 volt system including a solar panel, a voltage regulator, and a lead acid storage battery. Under normal summer conditions the system shown is sufficient to run all equipment therein including modems that have limited connectivity, thereby increasing their common draw.

Figure 3 also shows the external station set up, where the enclosure is affixed to two T-posts, with the solar panel mounted above. Mounting the enclosure below the solar panel provides shade to the enclosure. A PVC mast houses the sample train and ensures the sample inlet, consisting of quarter inch Teflon tubing and Teflon particle filter, is approximately 2m above ground. The weather station is mounted on top of the PVC mast and supported by parachord attached to earth anchors.

Routine Monitoring Operations

During the first week of April 2016, APCD deployed all the additional APCD ozone monitors. Upon installation, the monitors were calibrated with a certified ozone source. To ensure quality data capture the sites were visited monthly to change filters, fix any issues identified, and check the calibration of the analyzer. Since data is available in near real time, daily review of measured parameters was performed to assess the health of the system. This review also allowed for identification of issues to be resolved to mitigate loss of data. In addition, the APCD Quality Assurance unit performed audits of the ozone monitors prior to decommissioning of the site in October 2016.

The 2BTech ozone monitor is equipped with a solenoid in the sample stream that can be switched to a zero-path with a charcoal scrubber. As a check, nightly zeros were performed at midnight for a duration of 15 minutes. Thus the data logger activates the solenoid and the sample stream is switched to the charcoal scrubber so that both cells sample air that is devoid of ozone. This constitutes measurement for zero drift of the analyzer.

APCD did not visit the two USFS sites, Grand Mesa and Douglas Pass, for routine maintenance. This was left to the USFS to conduct.

Results

Meteorology

The two major meteorological factors that contribute to the buildup of ozone are the winds and atmospheric stability (as well as sunlight). The winds determine where the ozone plume will be directed and the atmospheric stability determines whether the ozone will diffuse upwards or remain trapped near the surface. If the atmosphere is stable, which typically occurs when the surface temperature is cooler than the air aloft, a low mixing height forms and inhibits upward flow. This cap then can allow for the increase in ozone concentrations by trapping ozone near the surface.

The conceptual model of the wind patterns in the Grand Junction Valley is that of thermally induced mountain-valley winds (katabatic and anabatic flow). Under clear skies and light synoptic winds the thermally induced winds flow up and down both in the mountain valley and the valley walls. During the daytime the winds would be up valley and upslope, while during the night the winds would switch to down valley and downslope. However, these wind



patterns can be altered via upper air pressure disturbances, frontal passages, and thunderstorm outflows. Figure 4 shows the wind roses for the sites that collected meteorological data for the entire study period. The spokes represent which direction the wind is coming from and are colored by the wind speed. The rings indicate the percentage of time the wind was blowing at that speed and direction. Taken individually, there is some pattern of up/downslope winds during the respective day and night times. This bimodal signal is somewhat masked by the passage of fronts, changes to synoptic weather patterns, and thunderstorm outflows that occurred during the study period. For instance the Palisade wind direction is bimodal with a high percentage of the time the winds being downslope, and a small percentage of the time upslope. This suggests that the complex terrain and other meteorological factors are having an influence on the local wind directions and speeds.

When viewed on average per hour of the day, wind flows at all stations follow a pattern of cooler air coming from the direction of higher elevation at night, a period of turbulence in the morning and evening, and warm air coming from the direction of lower elevations during the day. Figure 5 shows such a pattern seen at the Book Cliffs site. There, winds come from the north and northeast, effectively a down sloping wind, between 21 and 7. Winds are bimodal and variant at hours 8 and 18. Winds from the south and southwest between hours 9 and 17, are upslope. This represents a typical katabatic and anabatic diurnal wind pattern.

Ozone

The entire data set for the collected ozone observations for the study can be found in graphical representation in Figure 12, Figure 13, Figure 14, and Figure 15.

Ozone sites during this study fell into two main categories upon analyzing their data, referred to here as background and urban-influenced. The background sites consist of the two United States Forest Service sites, Grand Mesa and Douglas Pass, and had little diurnal signal due to neither NOx nor VOC quenching at night or surplus ozone from urban activity during the day. The urban-influenced sites showed both of these characteristics.

Estimates for background ozone range from 40 to 60 parts per billion for the inter-mountain west, and normal concentrations at Mines Peak and Storm Peak range between 45 and 55 parts per billion. The Douglas Pass and Grand Mesa sites showed similar flat diurnal patterns with concentrations ranging from 22 to 73 parts per billion with outliers likely due to in-flow from wild fires to the southwest and other naturally occurring events. Calculating a per-hourof-day average across the sampling period as a baseline to highlight urban-influenced ozone was considered but slight fluctuations in the diurnal cycle in both background sites caused this approach to be abandoned. A background mean concentration considering the entire sampling period was determined to be 48.3 parts per billion between the two sites, and is used here only as a reference point.

The remaining eight sites were compared with the background ozone estimate. As expected, Pitkin showed lowest concentrations, ranging from 25 to two parts per billion below background due to quenching overnight and nearness to ozone precursor sources during the day. Whitewater showed some overnight quenching but was in general much closer to background concentrations than the other non-background sites. Bangs Canyon showed the highest overall concentrations against background, with some early morning quenching and mid-day concentrations eight parts per billion above background. Escalante is the next highest site, showing a slower rate of increase in the morning, aligning with Bangs Canyon at hour 16. Figure 6 shows the hour-of-day average for the sampling period for the eight nonbackground sites.



Highline state park shows average deviations from background that were unexpected. Overnight quenching drew ozone concentrations to -17 parts per billion and daytime concentrations were third or fourth highest tying with Book Cliffs and Ute Water respectively depending on the hour of the day. Given that this site is lower elevation, well outside the city limits, and surrounded by vegetation, the TSP suspected Highline would be more closely aligned with background than urban-influenced sites. As described in the discussion below, this may be representative of the fourth side of the valley bowl.

Multiple Day Ozone Concentration Increases

During certain time periods, ozone observations can be seen to increase day after day, both in the minimum and maximum. The upward movement of the mean ozone concentrations is partly explained by the conceptual model discussion in Updates to the Conceptual Model below. Effectively, not all ozone is quenched, destructed, or vacated during the katabatic and anabatic flow pattern, especially during periods with a low mixing height, and some ozone and other contaminants remain in the air shed. This remnant pollution contributes to the mean concentration the following day, and even for several days, until the synoptic weather pattern introduces enough turbulence to remove the build-up, lowering the mean ozone concentrations at approximately 60 parts per billion, building up to about July 16, where the maximum was approximately 70 parts per billion. On July 18, a weather front moved through the area and the ozone observations reduced to below 50 parts per billion (only to start building again).

Naturally Occurring High Ozone Events

On two occasions, ozone was observed at concentrations well above background and significantly above concentrations on days just before and after each event. First, on April 23, Figure 12, before the United States Forest Service analyzers were operational, analyzers reported one-hour average concentrations up to 88 parts per billion at both Bangs Canyon and Escalante. Ozone was elevated across all analyzers operating at the time. Second, on June 25, Figure 13, analyzers reported one-hour concentrations up to 74 parts per billion, at Bangs Canyon and Book Cliffs. As with the April 23 event, concentrations were elevated at every operating ozone monitor in the study.

MOZART-4 models for both of these events indicate an increase of approximately 20 parts per billion of ozone to the free troposphere. This increase is indicative of a downward fold in the tropopause resulting in a downward mixing from the stratosphere, shown in Figure 7. This kind of event, a stratospheric intrusion, is well documented across the inter-mountain west. If the analyzers in this study were originally assembled and deployed with the intent of meeting the full Environmental Protection Agency regulatory requirements to determine attainment with National Ambient Air Quality Standards, these events could have been categorized as Exceptional Events since the stratospheric intrusion mechanism is fairly well understood. Meteorologists with the Air Pollution Control Division consider ample evidence to exist between the MOZART-4 model and other data products to attribute the elevated ozone observations on those days to the stratospheric intrusion.



Discussion

Updates to the Conceptual Model

On a cool morning in the Grand Junction Valley, the air is calm (or has just finished sinking, see below). As the sun rises, the canyon walls at the top of the Valley get warmed by the sun. They in turn warm the air next to them, which becomes less dense and starts to rise. The rising air draws the cooler air from beneath it upward, and the canyon walls start heating that air. As the sun continues to rise, more of the canyon wall gets warm, and more air rises. Since the sun is in the southern sky at this latitude, the face of the Book Cliffs to the north may warm somewhat more than those at Colorado National Monument or toward Whitewater. The draw of the rising air pulls air up from the valley, and in turn from the valley floor. Eventually air from down the Colorado River basin is drawn into the system.

While this is happening, anthropogenic activity rises in the valley which causes an increase in electrical consumption and the added burden of hydrocarbon-based commuting to the atmosphere. The emissions from these activities and others are carried up in the anabatic winds the sides of the Valley are now producing. As the sun angle increases during daylight hours, this mixture of volatile organic compounds and oxides of nitrogen have the solar power and time needed to form ozone. During the afternoon hours, photochemical processes increase with continued anthropogenic emissions, which in turn increase ozone concentrations. Put another way, the higher the air, the more time it's had to go through the photochemistry processes, and the more ozone there is.

Late in the afternoon, the sun angle is lower, and the canyon walls start to cool faster than the air around them. As they do, the air around them cools too, gets more dense, and starts to sink. This pushes the air under them, which is also cooling, all the way back down to the Valley floor, and down the Colorado River to the west. As it does so, anthropogenic activities continue to cause emissions. Without the sun to drive the photochemistry to create ozone, the oxides of nitrogen react with the ozone and cause concentrations of ozone to fall.

This cycle starts again every day. Some of the oxides of nitrogen, volatile organic compounds, and even ozone may stay in the air that's moving up and down the valley walls and contribute to higher still ozone potential the following day. Under especially stable larger weather patterns, concentrations can continue to rise day after day until a weather front moves through, blows out much of the urban air with cleaner air, allowing the larger cycle to start over. The functional air shed of the Grand Junction Valley may even be capped by a synoptic weather pattern just above the cliff walls that does not mix well with the air inside the valley. The larger build-up cycle can be seen in the first week of May, and through late July in Figure 12 and Figure 13.

This is the broad conceptual model the Air Pollution Control Division have developed with both the meteorological and ozone measurements collected during this study. Evidence for this hypothesis is shown in Figure 8. In subfigure a, ozone concentrations at Book Cliffs, on the north side of the valley, have down sloping overnight winds, and upsloping winds (from the direction of Grand Junction) during daylight hours. Largely because the sun is not providing the engine for photochemistry, concentrations at night are generally lower. Subfigure b shows the same pattern at Palisade, where overnight winds are downslope and daytime winds are upslope, and again, concentrations during the day are higher. Please note the scale differences between subfigures a and b. Palisade was originally sited with the katabatic model in mind (the specifics of siting an air monitoring shelter is a mixture of science and pragmatism, and the full suite of original reasons for Palisade's location are



outside of this study). One fairly large update to the conceptual model is that, while Palisade would capture air from down-valley as it traveled up the I-70 corridor, some of the urbaninfluenced air may follow US 50 and the Gunnison River. Specifically, Escalante is higher in concentration on average than Palisade.

Elevation and Concentration

The conceptual model hypothesized above uses air density, time, and sunlight to conclude that higher elevation results in higher ozone concentrations. On average, the data agree with this with some micrositing differences. Pitkin is not only the lowest site in elevation, but the closest to the urban core, and more subject to guenching from reactive compounds reducing the average ozone concentration. Palisade, Ute, and Highline are clustered together both in elevation and concentration, as are Book Cliffs, Bangs Canyon, and Escalante though to a lesser extent. Whitewater is a clear outlier, at both the highest elevation and lowest concentration. This doesn't necessarily disagree with the conceptual model, however, since Whitewater may have been above the effective air shed, and commonly analyzed concentrations closer to the background sites operated by the United States Forest Service. Those two sites, Grand Mesa and Douglas Pass, are not included in Figure 9, which displays the fourth maximum eight hour ozone concentration at each site relative to their elevation in meters above mean sea level.

The background sites are at such high elevations that they exist above the boundary mixing layer and are presumed to experience free tropospheric air most of the time. Ozone concentrations in the free tropospheric air are more constant and are more representative of regional background concentrations. Daytime hourly maximum concentrations at these sites are almost always lower than maximum concentration lower elevation urban influenced sites. Because this air does not experience the diurnal swings in ozone concentrations as observed in urban influence air, annual average concentrations at these site can be equal to or exceed those of urban influenced sites.

Consideration on Palisade's Representativeness

The Air Pollution Control Division often discusses exceedances as a resultant average that, if held equal for the entire evaluation period, would violate the standard, despite not having enough data to meet the standard's requirements (United States Environmental Protection Agency, 2017). In this case we can consider an exceedance as any maximum eight hour average ozone concentration of the existing data set that exceeds the standard of 70 parts per billion, whereas a violation of the standard would need a three year average of the annual fourth maximum eight hour average to exceed the standard of 70 parts per billion. None of the sites except for Palisade were in operation long enough to derive a three year average to resolve a fourth maximum from, so evaluation here is based only with the data at hand.

None of the ozone monitors gathering data during this study resulted in values that exceeded the 2008 Environmental Protection Agency's ozone standard of 75 parts per billion over eight hours. One site, Escalante, exceeded the 2015 Environmental Protection Agency's ozone standard of 70 parts per billion over eight hours. Another site, Bangs Canvon, equaled this standard but did not exceed it. Figure 10 shows the minimum, first quartile, median, third quartile, and maximum for each shelter for the study period.



Against this it would seem appropriate to move the long-standing ozone analysis site to the Escalante area, or perhaps another location at approximately the same elevation. However the determination of a site's location is balanced with population exposure, and such a move would not dramatically increase the number of people in the valley represented by the site. The Bureau of Land Management Grand Junction Field Office has looked briefly for a suitable location with no possibilities as of this writing, though they continue to keep this kind of move under consideration. The goal of the Air Pollution Control Division is still being met by Palisade for two reasons.

First, using the conceptual model hypothesized above, Palisade should represent a maximum ozone concentration for anyone living at or below Palisade's elevation. An analysis using 2010 US Census data projected to 2016 is shown in Figure 11. Given that the population density of Mesa County is centered around the city of Grand Junction, an estimated 93.2 percent of the population in Mesa County lives at or below Palisade's elevation. While higher concentrations may be found above Palisade, the vast majority of people don't live or spend substantial amounts of time there.

Second, using the conceptual model, forecasters now have a more developed understanding of the impact of elevation in the Grand Junction Valley and can use this in their forecasts for areas higher in elevation than Palisade.

Further Study

Highline reservoir was originally picked as a background location, with the suspicion that clean air from the west of the Grand Junction Valley would provide a background of ozone coming into the area. This idea involved predominant wind directions in the area being from west to east, and the low population density and lack of industry or natural resource extraction in the upwind direction.

As seen in Figure 6, however, concentrations at Highline closely mirrored those at Book Cliffs and Ute Water to the north of the city, averaging about seven parts per billion above background. Several ideas have been internally posited about the cause of the increased concentrations at Highline. Perhaps the site is far enough north of I-70 that fresh reactive emissions from vehicle traffic have had time to be converted into ozone by the sun. Agricultural emissions could play a role. Or there may be a source of reactive air emissions not currently known to the west of Highline. There is substantial natural gas exploitation in the Uintah Basin to the northwest of Highline but it lies on the other side of a high mountain range, and the Basin has an outflow along the Green River directly to the south, making it an unlikely source candidate. The higher than expected concentrations could indicate that the functional air shed of the Grand Junction Valley has a lid that is sloped downward in elevation toward the west, such that it is capped at elevations around Land's End to the east and out toward Mack to the west.

These are just ideas, however, and further monitoring would be required to better understand these elevated concentrations.

Conclusion

The Grand Junction Valley is in compliance with National Ambient Air Quality Standards, and the declining design value at Palisade suggests this won't change in the near future. Monitoring around the Grand Junction Valley has led to a better understanding of how the air shed moves, and how ozone is generated and quenched. Palisade represents the maximum



exposure for ozone for the vast majority of the people living in the Grand Junction Valley, and its long standing record helps to create reliable models for future forecasting, which can be influenced by this study. Ozone mechanisms to the west of town are surprising, and remain poorly understood.

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Figure 1: Elevation profile in the Grand Junction Valley



Figure 2: Site Locations - Autonomous APCD sites in blue, long term APCD shelters as sunny thermometers, and USFS sites in pink





(a)



Figure 3: Autonomous Sampling System





Grand Junction Valley Winds

Frequency of counts by wind direction (%)

Figure 4: Wind roses for the entire study period





Figure 5: Wind roses for hours of the day at Book Cliffs



Figure 6: Ozone deviation from USFS background concentration



Figure 7: MOZART-4 Model Imagery for Stratospheric Inversion Events





(b) Palisade Figure 8: Average Hourly Pollution Roses





Figure 9: Fourth maximum eight hour ozone concentration against elevation above sea level



Figure 10: Box and Whisker plot for eight hour ozone concentrations



Figure 11: Elevation at Palisade implied on the rest of the Grand Junction Valley





Figure 12: Rolling 8-hour ozone concentrations for April and May, 2016

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Figure 13: Rolling 8-hour ozone concentrations for June and July, 2016

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Figure 14: Rolling 8-hour ozone concentrations for August and September, 2016

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Figure 15: Rolling 8-hour ozone concentrations for October 2016

