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## **FINAL REPORT**

### **Conceptual Model of Ozone Measurements at Palo Duro Canyon**

TCEQ Contract No. 582-15-50415

Work Order No. 582-16-61900-02

Revision 2.0

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**List of Acronyms**

AER – Atmospheric and Environmental Research  
AOD – Aerosol Optical Depth  
CASTNET - Clean Air Status and Trends Network  
DU – Dobson Units  
EPA – Environmental Protection Agency  
GAM – Generalized Additive Model  
HYSPLIT – Hybrid Single Particle Lagrangian Integrated Trajectory Model  
IQR – Inter-Quartile Range  
MDA8 – Maximum Daily 8-hour Average Ozone  
MERRA - Modern-Era Retrospective Analysis for Research and Applications  
NAAQS - National Ambient Air Quality Standards  
NEI – National Emissions Inventory  
NO<sub>x</sub> – Nitrogen Oxides (NO + NO<sub>2</sub>)  
O<sub>3</sub> – Ozone  
PAL190 - Palo Duro Canyon site CASTNET site  
PM<sub>2.5</sub> – Particulate Matter with diameter below 2.5 microns  
PV – Potential Vorticity  
PVU – Potential Vorticity Units  
ppb – parts per billion  
RH – Relative Humidity  
TCEQ – Texas Commission on Environmental Quality  
TPY – Tons Per Year  
UTC – Coordinated Universal Time  
VOC – Volatile Organic Compound

## Executive Summary

In this project, AER developed a conceptual model of ozone causes and formation at the U.S. Environmental Protection Agency (EPA) Clean Air Status and Trends Network (CASTNET) monitoring site located just outside of Palo Duro Canyon State Park in Randall County, Texas. The objectives were to:

- Summarize the ozone air quality levels and trends in the area of Palo Duro Canyon State Park in Randall County, Texas and the temporal and spatial scope of high ozone. Investigate unique, unusual, or important characteristics about the area that may influence air quality levels.
- Describe the ambient monitoring networks used to develop the conceptual model and describe the status and trends of air quality in the area of Palo Duro Canyon.
- Investigate possible relationships between emissions, meteorology, and air quality.

To accomplish these tasks, the CASTNET data was downloaded and evaluated for the Palo Duro Canyon site (PAL190) for the years 2008-2015. In addition to analyzing the 1-hour data provided, the maximum daily 8-hour average (MDA8) ozone concentrations were calculated for the site, as well as the 4<sup>th</sup> highest MDA8 ozone design value for each of the eight years. The number of days that exceeded a MDA8 ozone concentration of 63 ppb amounted to 175 days from 2008-2015, 36 of which exceeded 70 ppb. There is an obvious decrease in the amount of days exceeding 63 ppb from 2012 until 2015, however the year with the fewest days exceeding 63 ppb is 2010. 2011-2013 have the most days exceeding 70 ppb. In general, days with high MDA8 ozone peak between Wednesday and Saturdays. The beginning hour of the MDA8 window generally begins between 10:00 and 13:00 for days with a MDA8 ozone exceeding both 63 and 70 ppb. MDA8 ozone exceeds 63 ppb typically on days with a temperature greater than about 20 °C, when RH is below about 60 %, and wind direction is between 70 and 260 degrees, with little apparent dependence on wind speed.

We then analyzed the Texas emission inventory provided by the TCEQ for TCEQ Region 1. There is a decrease in the total NO<sub>x</sub> source emissions between 2011 and 2014 NEI (-40.6 %). The total NO<sub>x</sub> emissions are dominated by on-road sources in the 2011 NEI inventory, but this switches in the 2014 NEI inventory to a generally equal split between on-road, area, and point sources, with area emissions as the highest, and non-road contributing little to the total emissions. The percent change in NO<sub>x</sub> emissions between 2011 and 2014 for point, area, non-road and on-road emissions are -16.6, -1.7, -19.3, and -72.6 %, respectively. For VOCs, there is a small increase in total emissions between 2011 and 2014 (2.6 %) and the total emissions are dominated by area sources for both years with point, area, non-road and on-road sources changing by -24.0, +2.9, -18.6 and +277.3 %, respectively.

We ran 48-hour HYSPLIT back trajectories for all days exceeding 63 ppb MDA8 ozone which were then used to identify when biomass-burning emissions may be impacting ozone at Palo Duro using NAM12 forecast data. 11 of the 175 days with MDA8 ozone concentrations above 63 ppbv were identified as having been influenced by biomass burning sources within the same 12 km×12 km NAM12 box as the HYSPLIT back trajectories. For the most part, these back trajectories ended east of the Palo Duro CASTNET site except for one (on May 24, 2011) that ended in Mexico. Two other fire-influenced back-trajectories occurred outside of the state of Texas on July 13, 2012, and June 29, 2013. There are also two intersections with fires that occur on the same trajectory (August 26, 2011). The MDA8 ozone concentration for all fire-influenced

days range from 63 ppb to 83 ppb. Increasing the collocation criteria to any biomass burning emissions within a 36 km × 36 km grid box increases the number of fire-influenced days to 40.

We then developed a tool to help identify when stratospheric intrusions may have impacted an air parcel arriving at the Palo Duro CASTNET monitoring site by utilizing the Modern-Era Retrospective Analysis for Research and Applications (MERRA) dataset and the HYSPLIT back trajectories. Of the 25 days with MDA8 ozone above 63 ppbv that were identified as having a back trajectory travel above an altitude of 1500 m, we have identified 9 as possibly influenced by stratospheric intrusions.

In order to examine the formation of ozone on days clearly not influenced by biomass burning or stratospheric intrusions, we excluded these days and the following 1-2 days from our analysis, reducing the number of days from 175 to 125. Re-analyzing the temporal pattern on these days shows a slight shift toward the middle of the week. In addition, the maximum hour of high ozone is no longer 11:00, but now 12:00 for days having a MDA8 ozone greater than 63 ppb, and there is no longer a double peak around 10:00 for days with greater than 70 ppb. After reanalyzing meteorological trends, the reduced number of days do not significantly change the trends already discussed above.

We thus conclude for the Conceptual model at Palo Duro Canyon, TX, based on results from this report, that of the days exceeding a MDA8 ozone concentration of 63 ppb, 40 and 9 days may have been influenced by biomass burning and stratospheric intrusion events, respectively. The majority of days with high O<sub>3</sub> events (~125 out of 175) show no evidence for fire or stratospheric ozone influence and are assumed to be influenced by other sources. On these days, the wind is mostly out of the south/south-west, according to wind direction measurements, with more trajectories out of the southeast according to HYSPLIT back trajectories. The regions south of the Amarillo, TX region that have the highest area emissions include the Midland-Odessa, TX region where there is a large petroleum industry presence. High VOC and NO<sub>x</sub> emissions from the 2011 and 2014 TCEQ emission inventory support the theory that this area may impact ozone formation in the Palo Duro Canyon CASTNET monitoring site.

We recommend that future work focus on:

- The development of datasets in closer proximity to the Palo Duro CASTNET monitoring site in order to evaluate measured species and meteorological parameters. Additionally, measurements of the vertical profile of O<sub>3</sub> at this location would be useful. The addition of these measurements will allow for further validation of air quality impacts on the area, and the relative contribution from regional emissions as well as out of state emissions.
- Continued development of a biomass burning identification tool that contains additional HYSPLIT back trajectories and a more detailed account of chemistry in order to account for biases and variability in meteorology and atmospheric species arriving at the Palo Duro CASTNET measurement site.
- Creating a Generalized Additive Model to relate the Palo Duro MDA8 O<sub>3</sub> to meteorological predictors to further understand O<sub>3</sub> formation in this area.
- Investigating the sources influencing VOCs, NO<sub>x</sub>, and O<sub>3</sub> at this site using TCEQ's 2012 CAMx modeling dataset, as that is the year with the most days exceeding a MDA8 ozone concentration of 63 ppb at Palo Duro.

## 1 Introduction

### 1.1 Project Objectives

AER performed a research project titled “Conceptual Model of Ozone Measurements at Palo Duro Canyon” for the Texas Commission on Environmental Quality (TCEQ). The aim of the conceptual model is to answer the following questions laid out in EPA’s Draft Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, PM<sub>2.5</sub>, and Regional Haze (EPA, 2015):

- What are the pollutants of concern in the area?
- What are the current air quality levels in the area?
- What is the attainment/nonattainment status of the area?
- What is the geographical scope of poor air quality?
- What is the temporal scope of poor air quality?
- What are the air quality trends in the area? Is the problem getting better or worse?
- What are the suspected mechanisms for formation of poor air quality levels?
- What are the sources of emissions that may contribute to poor air quality?
- Are there unique meteorological influences on local air quality levels?

### 1.2 Purpose and Background

For this study, ozone (O<sub>3</sub>) is the pollutant of concern, especially on days when the maximum daily eight-hour average (MDA8) ozone is greater than or equal to 63 ppbv. AER analyzed ambient O<sub>3</sub> measurements at the PAL190 CASTNET monitoring site for the duration of its measurements (2007-2015) to determine the current air quality levels, the temporal scope of days with MDA8 ozone greater than 63 ppb, and to identify days in which biomass burning and/or stratospheric intrusions may have influenced these high ozone days. The schedule for the project is shown in Table 1.

Table 1. Schedule for TCEQ Work Order No. 582-16-61900-02

Milestones	Planned Date
<b>Task 1 - Work Plan</b>	
1.1: TCEQ-approved Work Plan	December 31, 2015
1.2: TCEQ-approved QAPP	December 31, 2015
<b>Task 2 – Conceptual Model Development</b>	
2.1: Draft Conceptual Model for the Palo Duro (PAL190) CASTNET Monitoring Site.	June 10, 2016
2.2: Final Conceptual Model for the Palo Duro (PAL190) CASTNET Monitoring Site.	June 30, 2016
2.3: Data Files used in the development of the conceptual model.	June 30, 2016

### 1.3 Report Outline

This Final Report documents the methods and pertinent accomplishments of this project, including comprehensive overviews of each task, a summary of the data collected and analyzed during this work, key findings, shortfalls, limitations and recommended future tasks. It satisfies Deliverable 2.2 of the Work Plan for Work Order No. 582-16-61900-02

**Deliverable 2.2:** Conceptual Model for the Palo Duro (PAL190) CASTNET Monitoring Site.

**Deliverable Due Date:** June 30, 2016

Section 2 and 3 of this report describe the ozone and meteorological trends in Palo Duro, respectively. Section 4 analyzes the TCEQ emissions inventory for 2011 and 2014 and Section 5 summarizes HYSPLIT back trajectory trends for a spatial analysis. Sections 6 and 7 discuss days where the MDA8 O<sub>3</sub> was potentially influenced by biomass burning and stratospheric intrusions, respectively. Section 8 analyzes days that were not influenced by either biomass burning or stratospheric intrusions in an attempt to explain other anthropogenic and non-anthropogenic influences, and our conclusions are discussed in Section 9. Two appendices to this report are supplied as separate PDF files. Appendix A (AppendixA\_HYSPLIT.pdf) contains the plots for all HYSPLIT runs, and Appendix B (AppendixB\_strato.pdf) contains the plots for all days analyzed in the stratospheric intrusion section.

## 2 Trend Analysis of MDA8 Ozone in Palo Duro

The Palo Duro Canyon CASTNET site is one of three CASTNET monitors in Texas. It is located in Randall County, Texas, about 30 miles southeast of Amarillo, Texas, and is surrounded by complex prairie land (Region 1). Figure 1 shows the location of the measurement site and surrounding area

### TCEQ AREAS & REGIONS

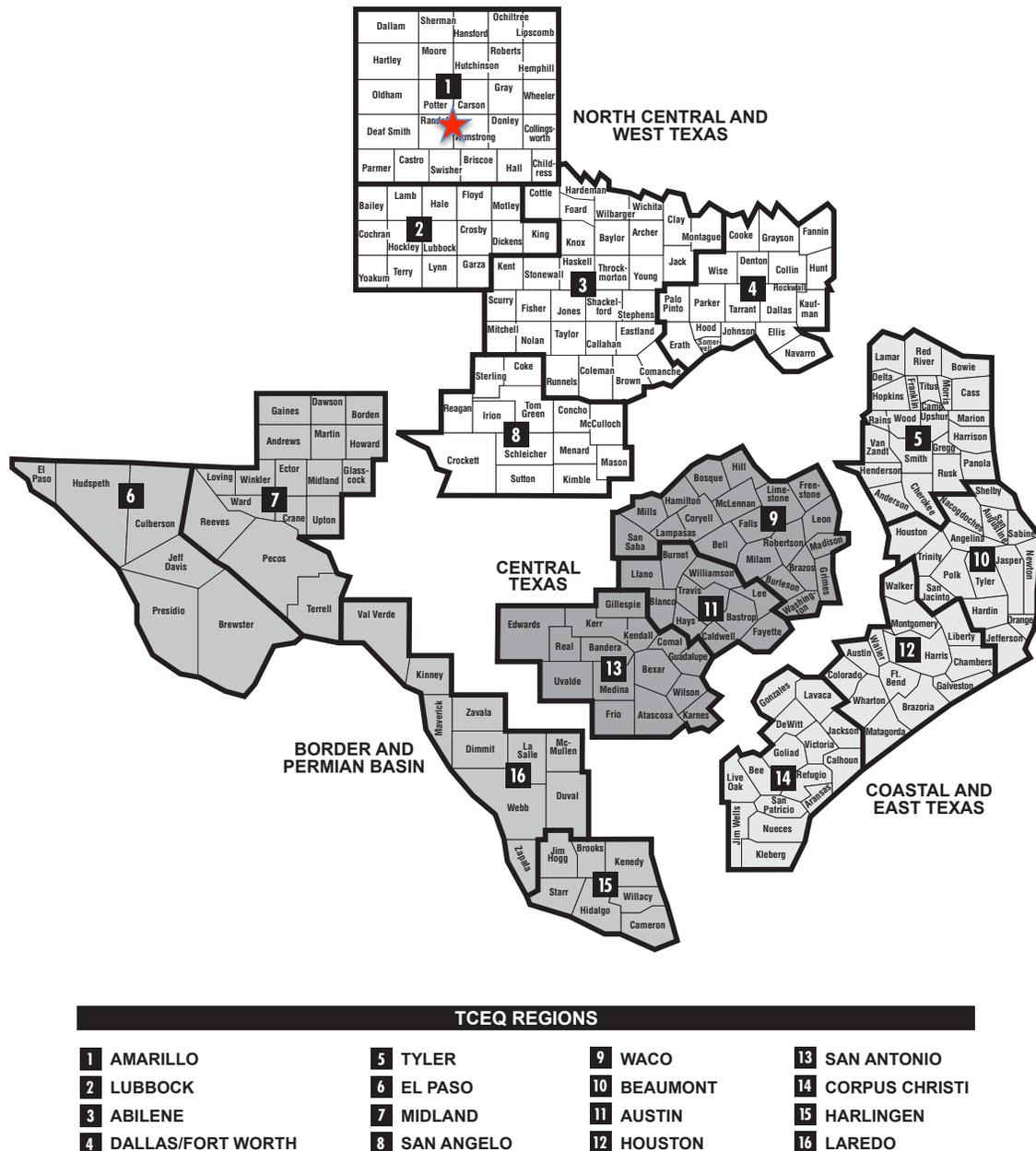


Figure 1. Location of the Palo Duro Canyon CASTNET site (red star) and surrounding areas – acquired from the TCEQ website (<https://www.tceq.texas.gov/gis/>).

The Palo Duro CASTNET dataset contains measurements of hourly ozone, temperature, relative humidity, precipitation amounts, wind speed, and wind direction from April 2007 to present, but here we only analyze years with complete data (2008-2015). Table 2 and 3 contain detailed information about the monitor site and residing county, Randall, TX, respectively.

Table 2. Site information for the Palo Duro CASTNET site (<https://www3.epa.gov/castnet/>)

Site ID	PAL190
Site name	Palo Duro
County	Randall, TX
Latitude (decimal degrees)	34.88061
Longitude (decimal degrees)	-101.664703
Elevation (m)	1053
Operating agency	EPA
Start date	04/24/2007
Primary Land Use	Prairie
Terrain surrounding site	Complex
NADP site code	TX02
Distance to nearest NADP site (km)	144.8
AMoN Site ID	TX43

Table 3. Demographic info for Randall County, TX (available from <http://www.census.gov/>)

Population (estimated July 1, 2015)	130,269
Population per square mile (estimate 2010)	132.4
Median Household income (in 2014 dollars), 2010-2014	\$60,895
Per capita income in past 12 months (in 2014 dollars), 2010-2014	\$30,376
Persons in poverty	9.7 %
Total retail sales, 2012 (\$1000)	1,805,080
Land area	911.54 sq. miles

Figure 2a shows that the average diurnal ozone profile for the Palo Duro CASTNET site peaks around 4:00 pm local time with an average of 47.2 ppb, and a daily minimum around 07:00 am with an average of 27.9 ppb. There is thus a mean difference of about 20 ppb between the minimum and maximum hours. Figure 2b shows the same but for days with a MDA8 ozone that exceeded or equaled 63 ppb. The diurnal maximum peaks around the same time of day with a higher magnitude. Figure 3a shows the monthly average ozone, with the lowest average in December (28 ppb) and the highest average occurring in May (44 ppb) with a difference of 16 ppb between the minimum and maximum months. The maximum daily 8-hour average (MDA8) ozone concentration was then calculated for the Palo Duro ozone dataset. In order to determine

the MDA8, we first calculated each hour's average concentration, determined by the current hour, and following 7 hours. If there were less than 6 hours of consecutive measurements that hour was not included. Next we determined that day's maximum 8-hour average. If a day contained less than 18 hours of data, it was not included in the final dataset (EPA, 1998, 2007). Days with a MDA8 ozone equal to or greater than 63 ppb were selected for further analysis. Figure 3b shows the month in which a MDA8 ozone day exceeded or equaled 63 ppb, with hourly values for that day included. It can be seen that MDA8 ozone days exceeding or equaling 63 ppbv only occurring from March to October. The number of MDA8 ozone concentration days that include and exceed 63 ppb amount to 175 days from 2008-2015 with the number of days per year broken down in Figure 4.

There is an obvious decrease in the number of days that have a MDA8 ozone exceeding 63 ppb and 70 ppb from 2012 until 2015, however the year with the fewest high ozone days is 2010. 2011, 2012, and 2013 have the most days exceeding 70 ppb, as seen in Figure 4. Figure 5 shows the 4<sup>th</sup> highest MDA8 ozone day for each year, with a similar pattern to Figure 4, where there is a decreasing trend between 2011 and 2015, but 2010 has the lowest value.

Figure 6 shows the monthly maximum MDA8 ozone for the study period, with a similar story to that of Figure 4 as well, in that since 2011 there seems to be a decrease in the monthly maximum MDA8 ozone concentrations, with a minimum in 2010.

When looking at MDA8 ozone versus day of the week (Figure 7), we see in general there is a peak between Wednesday and Saturdays for days exceeding both 63, but more obvious in days exceeding 70 ppb. When looking at starting hour for the MDA8 ozone window for each day, it can be seen in Figure 8 that in general there is a peak between 10:00 (CST) and 13:00, for days with MDA8 ozone exceeding both 63 ppb, and for days exceeding 70 ppb there is a double peak at 10:00 and a maximum at 12:00. This trend in the MDA8 window tends to peak later than areas in Houston and Dallas, perhaps suggesting ozone sources arriving later in the day due to a longer transport distance.

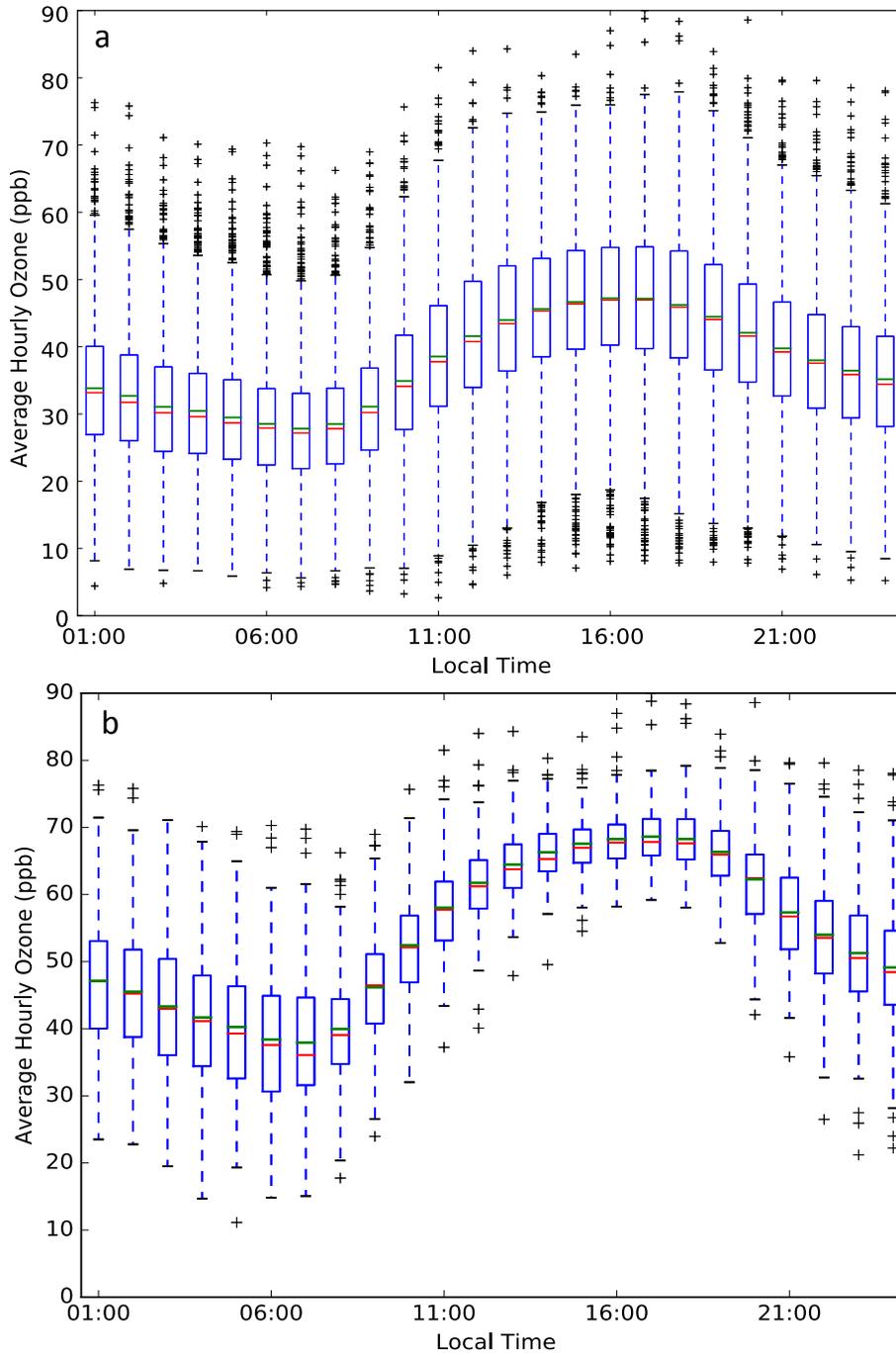


Figure 2. Average ozone concentration per hour where box plots show the mean (green), median (red), interquartile range (IQR, blue box), whiskers at 1.5 IQR and outliers beyond that. Top plot (a) shows all days at the Palo Duro CASTNET site (2008-2015) and (b) shows the MDA8 ozone days above 63 ppb.

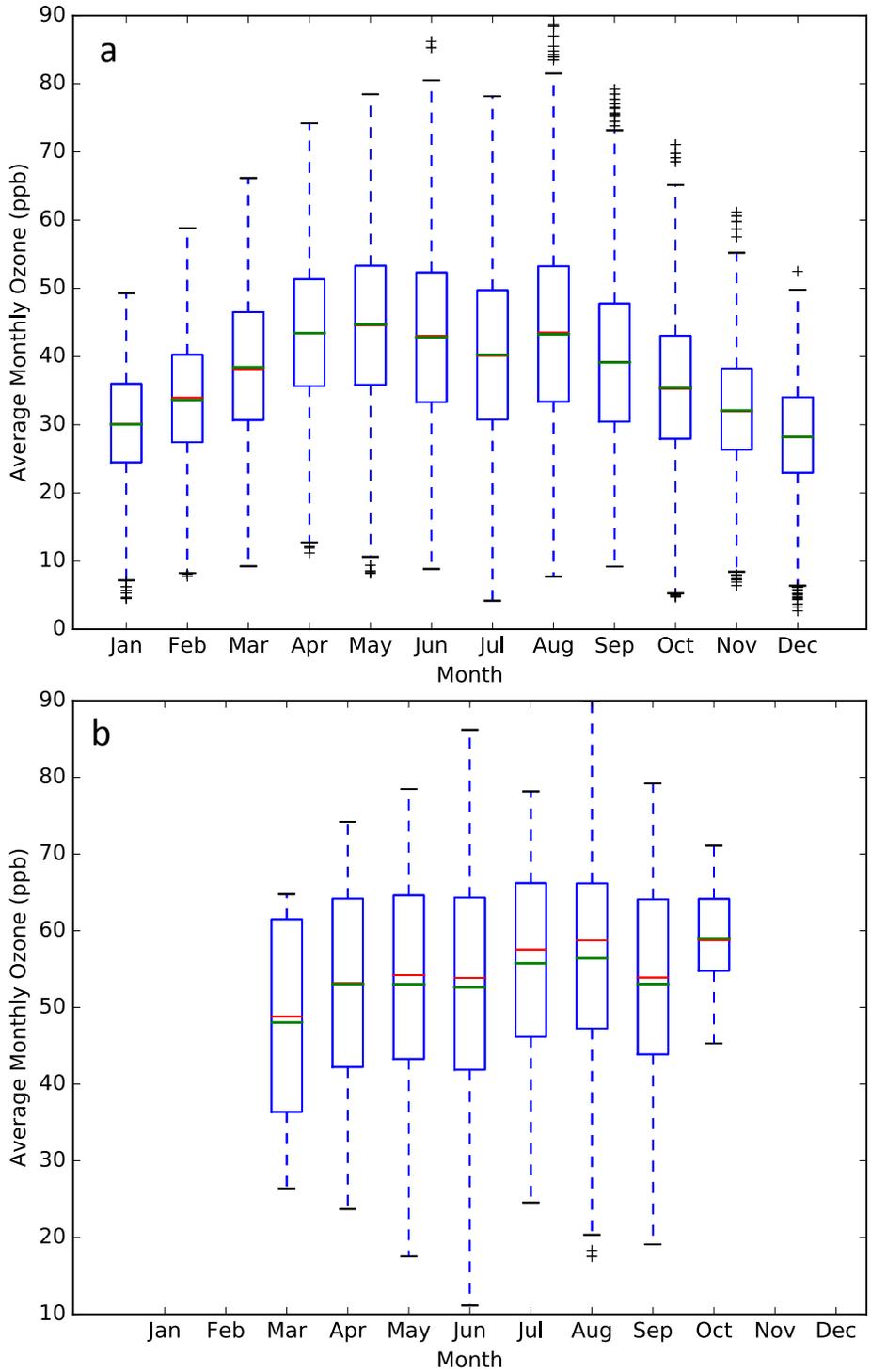


Figure 3. Same as Figure 2 but for average ozone concentration per month.

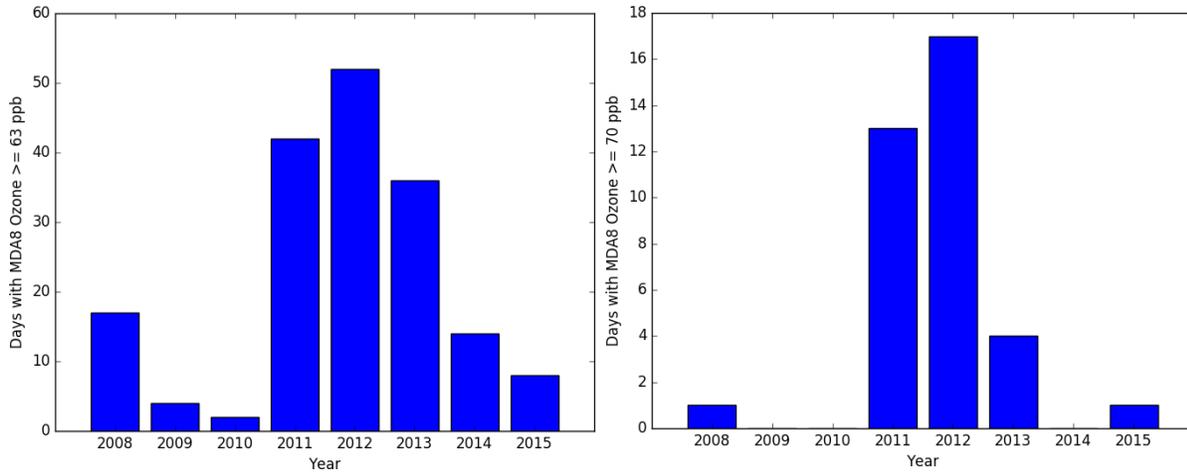


Figure 4. A bar chart showing the number of MDA8 ozone days greater than or equal to 63 ppb (left) and greater than or equal to 70 ppb (right) at the Palo Duro Canyon CASTNET site. Note the y-axis scale is different in the two plots.

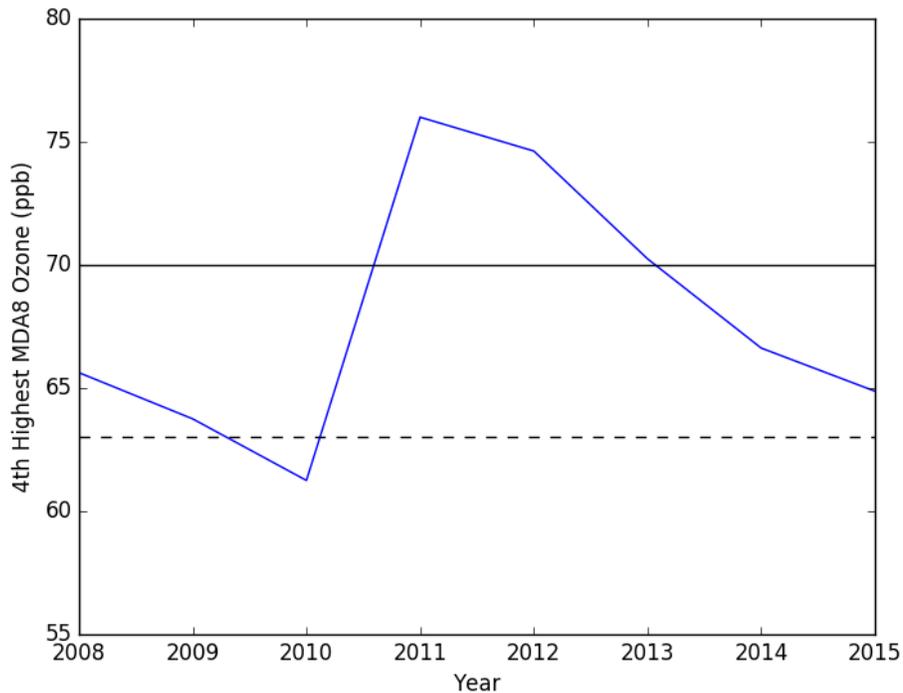


Figure 5. The 4<sup>th</sup> highest MDA8 ozone for each given year where the solid line is the current NAAQS for ozone at 70ppb, and the dashed line is 63 ppb.

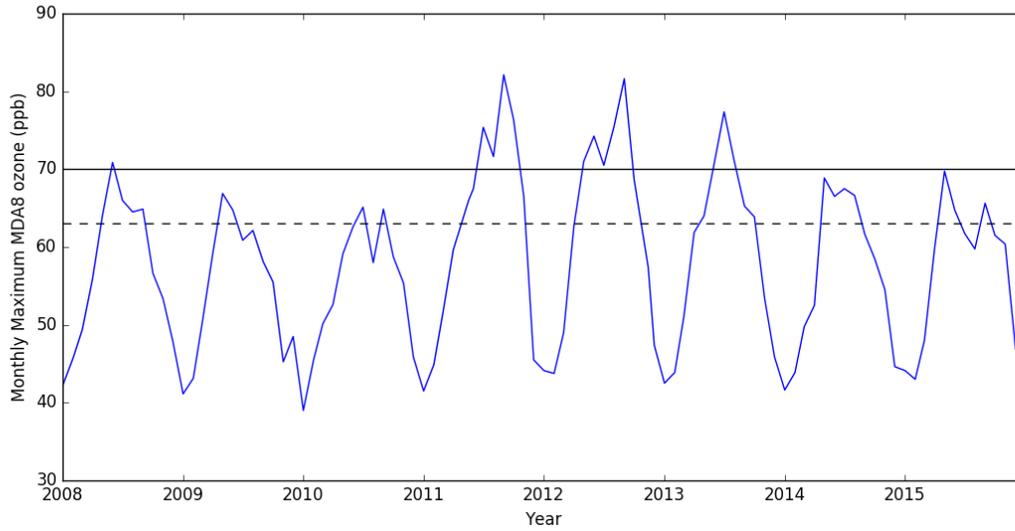


Figure 6. The monthly maximum MDA8 ozone for the Palo Duro Canyon CASNET site.

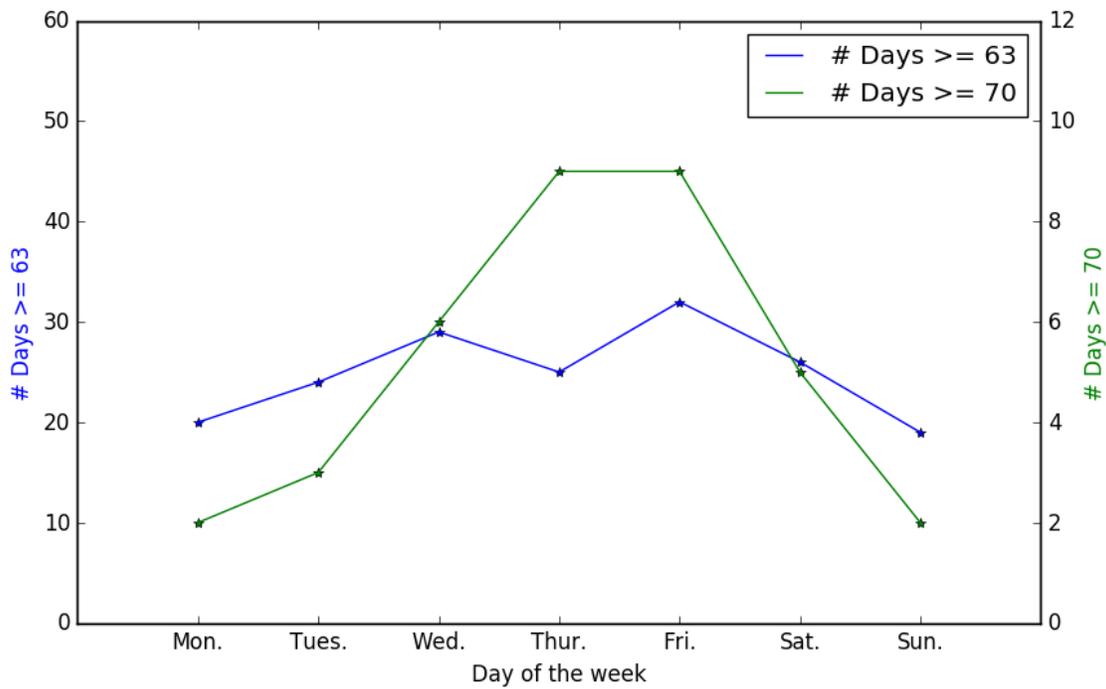


Figure 7. The number of days exceeding MDA8 ozone of 63 ppb (blue) and 70 ppb (green) for the days of the week at the Palo Duro Canyon CASNET site.

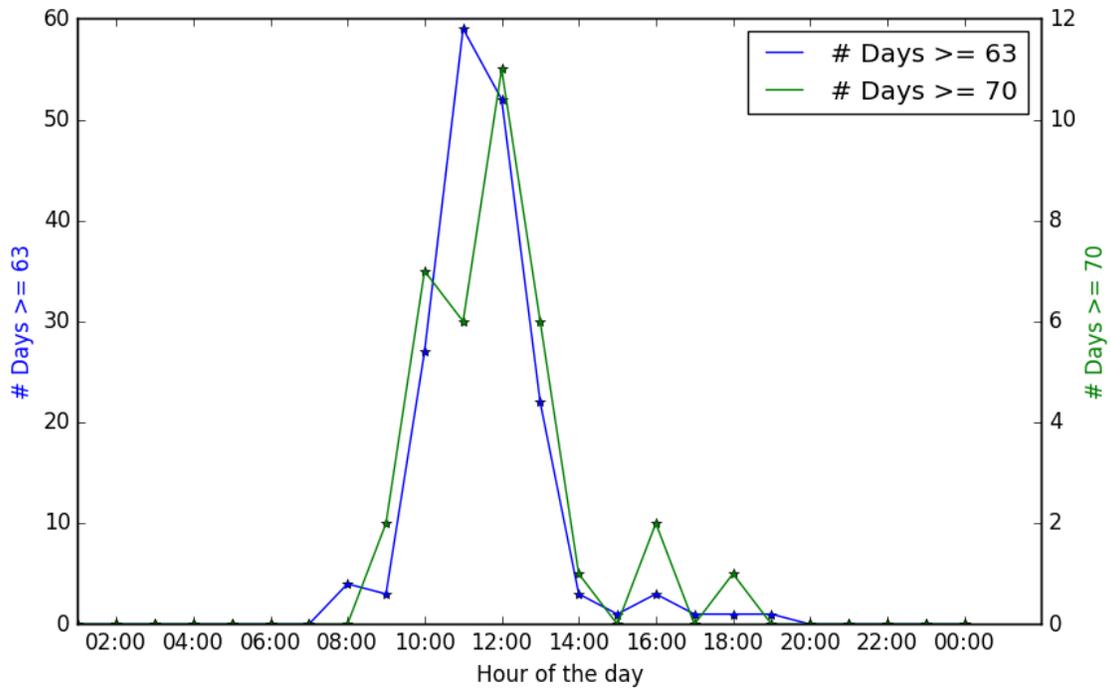


Figure 8. The number of days exceeding MDA8 ozone of 63 ppb (blue) and 70 ppb (green) versus the starting hour of the MBA8 window at the Palo Duro Canyon CASNET site.

### 3 Trend Analysis of CASTNET Meteorological data

The plots below show the MDA8 ozone concentrations for all days between 2008-2015 at the Palo Duro site compared to the available meteorological measurements at the site; daily maximum temperature, daily average relative humidity (RH), daily average wind direction, and daily average wind speed. MDA8 ozone exceeds 63 ppb typically on days with a temperature greater than about 20 °C, when RH is below about 60 %, and wind direction is between 70 and 260 degrees. However, there is little apparent dependence on wind speed. For days that exceed 70 ppb MDA8 O<sub>3</sub>, the temperature is never below 25 °C (Figure 9), RH is never above 55 % (Figure 10) and wind direction is between 100 and 230 degrees. Looking at both wind direction and wind speed together, for days exceeding 63 ppb we can see that no days have winds coming from the northern direction, and that winds are usually between 2-12 m/s, with most days having winds out of the south. The wind direction on days exceeding a MDA8 O<sub>3</sub> concentration of 63 ppb is consistent with transport of pollution from south of the Amarillo Region. This is further discussed in Section 4.

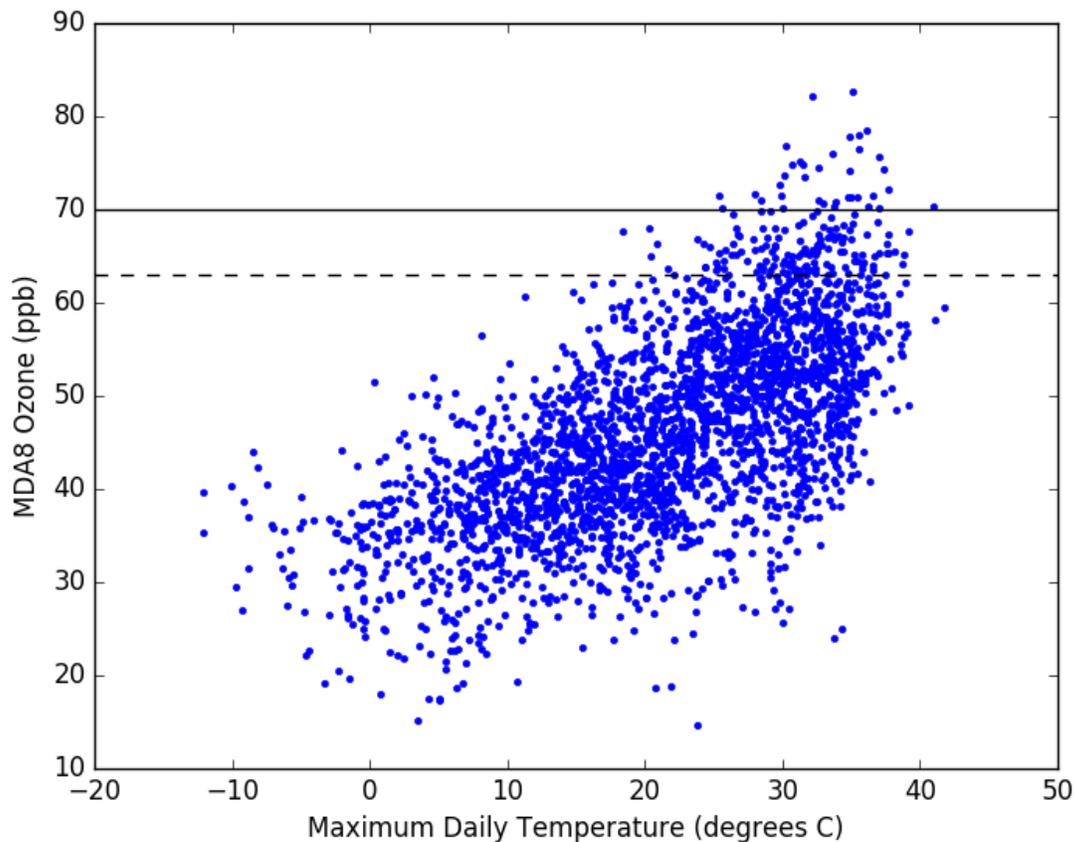


Figure 9. MDA8 Ozone for the Palo Duro Canyon CASTNET site plotted against the station measured maximum daily temperature, where the dashed line marks 63 ppb, and the solid line marks the current NAAQS ozone standard of 70 ppb.

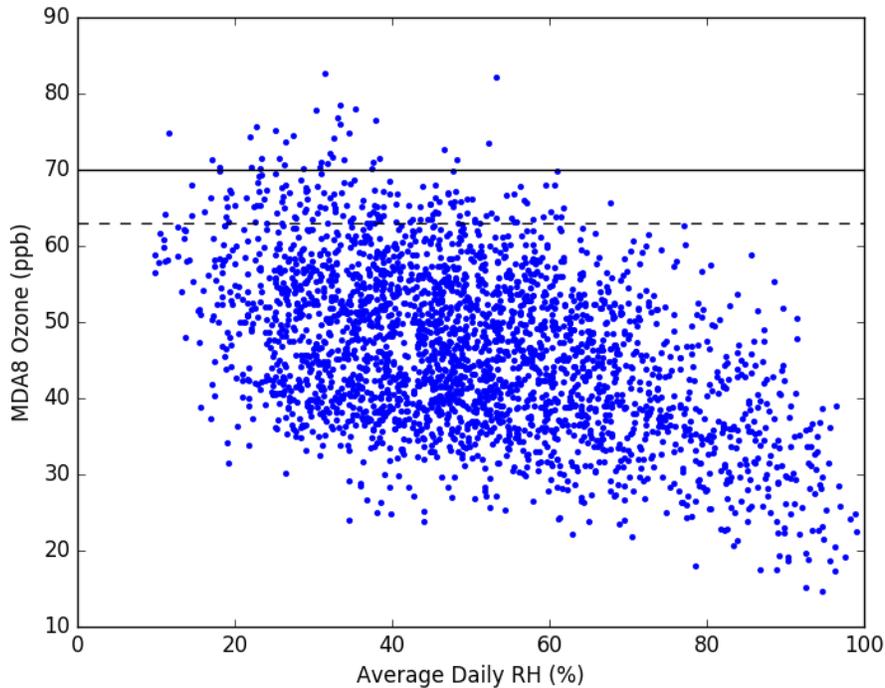


Figure 10. MDA8 Ozone for the Palo Duro Canyon CASTNET site versus the station measured average daily relative humidity where the dashed line marks 63 ppb, and the solid line marks the current NAAQS ozone standard of 70 ppb.

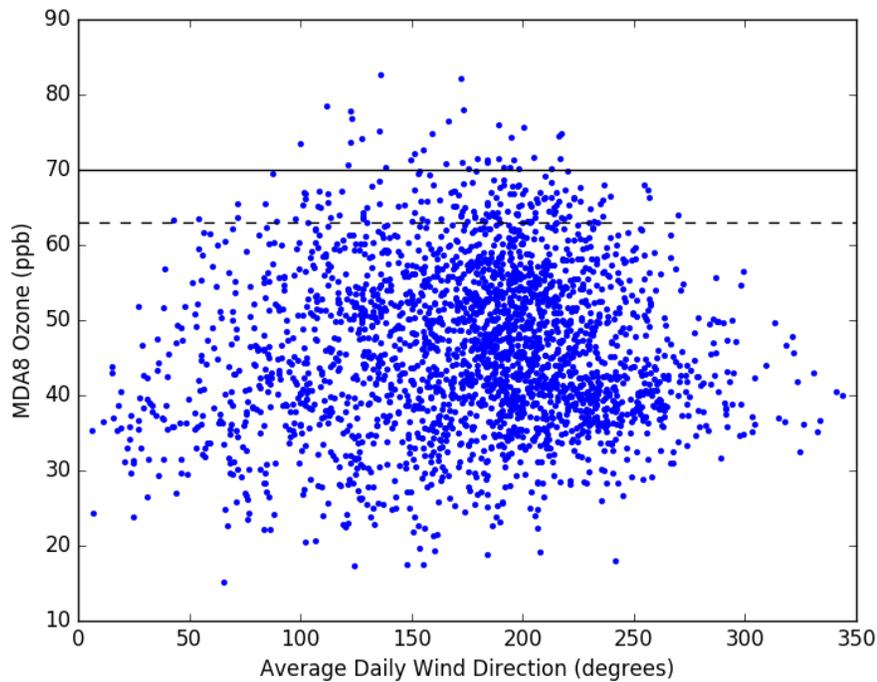


Figure 11. MDA8 Ozone for the Palo Duro Canyon CASTNET site plotted against the station measured average daily wind direction where the dashed line marks 63 ppb, and the solid line marks the current NAAQS ozone standard of 70 ppb.

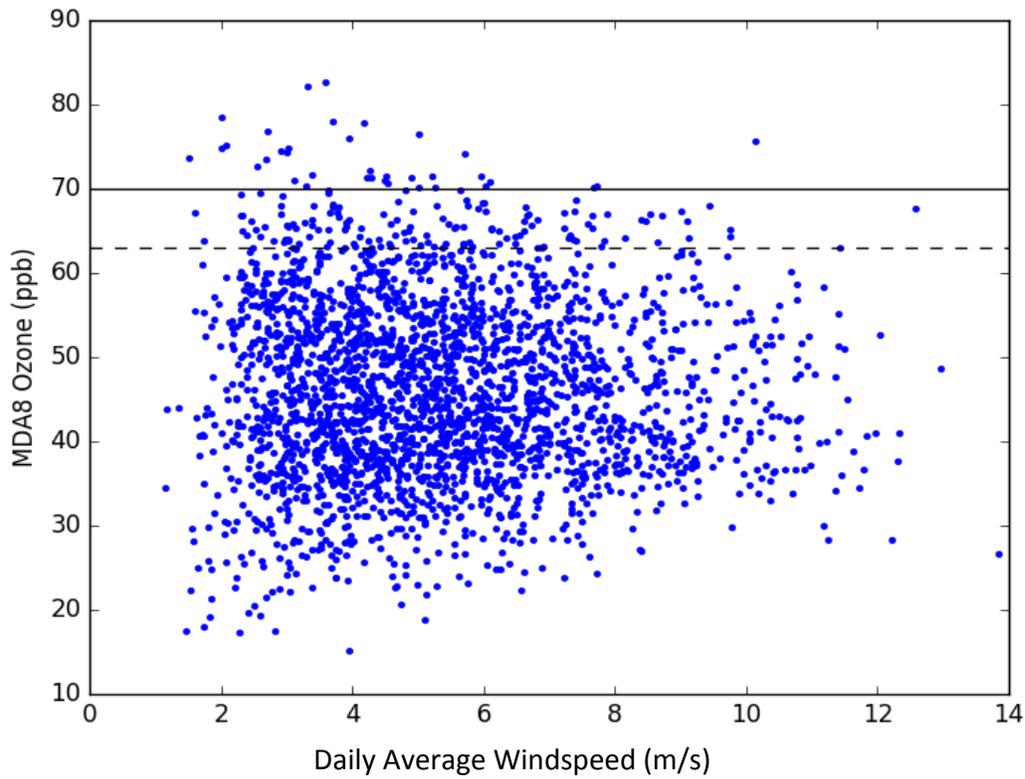


Figure 12. MDA8 Ozone for the Palo Duro Canyon CASTNET plotted against the station measured average daily wind speed where the dashed line marks 63 ppb, and the solid line marks the current NAAQS ozone standard of 70 ppb.

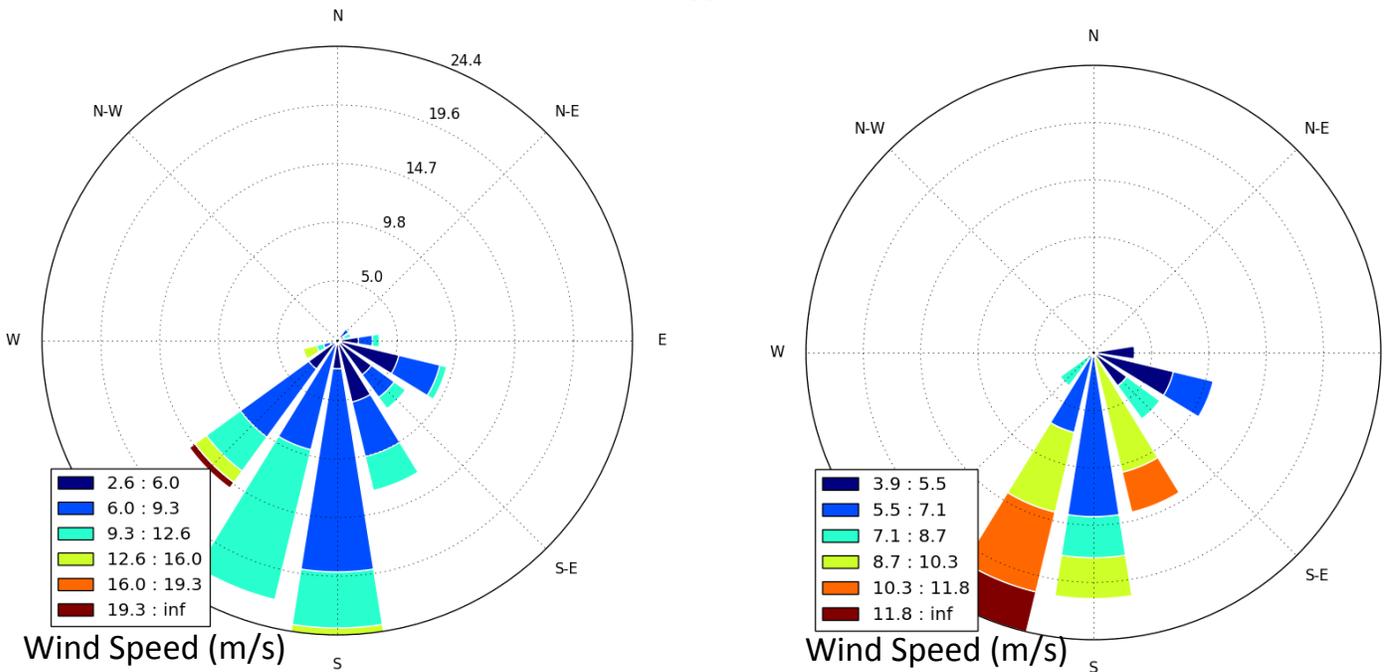


Figure 13. Wind rose diagram for days exceeding a MDA8 ozone of 63 ppb (left) and days exceeding 70 ppb (right).

#### 4 Emissions Inventory Analysis for Amarillo, Texas (Region 1)

AER received emissions estimates for the state of Texas and TCEQ Region 1, Amarillo, TX, for the years 2011 and 2014. Table 4 shows the break down of NO<sub>x</sub> and VOC emissions by source sector for both years for Region 1. Source sectors discussed here include point, area, on-road mobile, and non-road mobile sources. The sums presented are the total Tons Per Year (TPY) for all counties in Region 1 that reported values. NO<sub>x</sub> emissions from all sectors decrease between 2011 and 2014 NEI, with the largest decrease occurring in on-road emissions. As for VOCs, there is a small increase in total emissions between 2011 and 2014 due primarily to a similar small increase in the dominant area source sector that overwhelms the decreases in VOC emissions from point and non-road sources. Percent change in Table 4 and Figures 16-17 is calculated as the difference in emissions between years (2014-2011) divided by the emissions in 2011 multiplied by 100 %.

Table 4. The total Tons Per Year (TPY) as reported in the 2011 and 2014 emissions inventory for each emissions type and NO<sub>x</sub> and VOC species for the Region 1 area, Amarillo, TX.

Source Type	NO <sub>x</sub> (TPY)			VOC (TPY)		
	2011	2014	% change	2011	2014	% change
Point	28642.32	23876.20	-16.6	7397.79	5620.89	-24.0
Area	20803.19	20453.19	-1.7	72176.36	74256.82	+2.88
On-road	53450.53	14634.79	-72.6	994.88	3256.25	+277.30
Non-road	10024.88	8088.12	-19.3	2351.63	1913.55	-18.63
<b>Total</b>	<b>112920.92</b>	<b>67052.30</b>	<b>-40.6</b>	<b>82920.66</b>	<b>85047</b>	<b>+2.56</b>

In Figures 14 and 15 below the percentage contribution of each source sector to the total emissions in Region 1 is shown. For VOCs, the total sources are dominated by area sources, and this does not change between inventory years. As for NO<sub>x</sub>, the total contribution is dominated by on-road sources in the 2011 NEI inventory, but the dramatic reduction in on-road NO<sub>x</sub> emission in the 2014 NEI inventory leads to a generally equal split between on-road, area, and point sources, with area sources having the highest contribution, and non-road the lowest. Additionally, of the total NO<sub>x</sub> emissions in 2011 (112,921 TPY) agricultural emissions contributed 0.7 %, and the Oil and Gas sector emissions contributed 19.4 %. For 2014 this percentage contribution increased to 1.3 % Agricultural, and 29.5 % Oil and Gas. For total VOC emissions in 2011 (82,921 TPY), agricultural emissions contributed 1.6 %, and the Oil and Gas sector emissions contributed 68.0 %. For 2014 this percentage contribution remained the same for agricultural emissions, and increased to 72.9 % contribution from oil and gas emissions. The small change in the agricultural section may be due to an extrapolation between inventories due to lack of recorded measurements in 2014, but this requires further investigation.

In summary, Region 1 emissions of VOCs increased by 2.56 % and emissions of NO<sub>x</sub> decreased by -40.6 % between 2011 and 2014. A majority of the total VOC emissions are from Oil and Gas sources, with area sources overall dominating the total VOC emissions. NO<sub>x</sub> sources

go from on-road dominated to area/point source dominated, with a large (29.5%) contribution from Oil and Gas emissions.

However, the meteorological analysis in Section 3 suggests that sources to the south and southeast of Palo Duro are generally more important to O<sub>3</sub> formation at the site. A map of emissions by county in the state of Texas is shown in Figure 16 and 17. Figure 16 shows the area VOC and NO<sub>x</sub> emissions per county for 2011 (top) and 2014 (middle), with the percent change between years at the bottom. Figure 17 shows NO<sub>x</sub> on-road (left) and point sources (right) for counties reporting emissions. It can be seen that for NO<sub>x</sub> area emissions and VOC area emissions (which dominate the VOC inventory) there is a large region south of Palo Duro around Region 7 (Midland) with very high emissions. For VOCs these emissions increase in 2014 in Region 7, except for Pecos and Terrell County. For NO<sub>x</sub> area emissions this increase is similar in 2014 in Region 7, with the further exclusion of Winkler and Crane Counties. The same is true for NO<sub>x</sub> point sources (Figure 17 right), which, combined with area sources, dominate the NO<sub>x</sub> inventory. The emissions in this region may play an important role in Palo Duro ozone formation, since most high O<sub>3</sub> measurements at Palo Duro occur when the winds are from the south/south-west, as indicated in the wind rose in Figure 13.

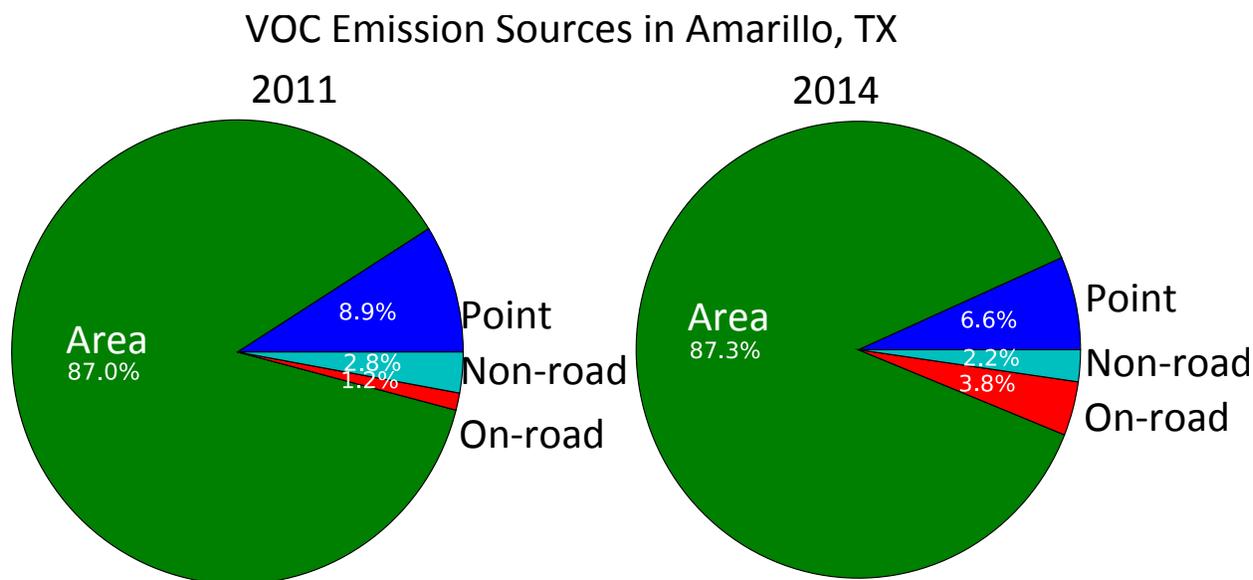


Figure 14. A pie chart showing the contribution of source sectors to total VOC emissions in the 2011 (left) and 2014 (right) NEI in Region 1 in Texas.

### NO<sub>x</sub> Emission Sources in Amarillo, TX

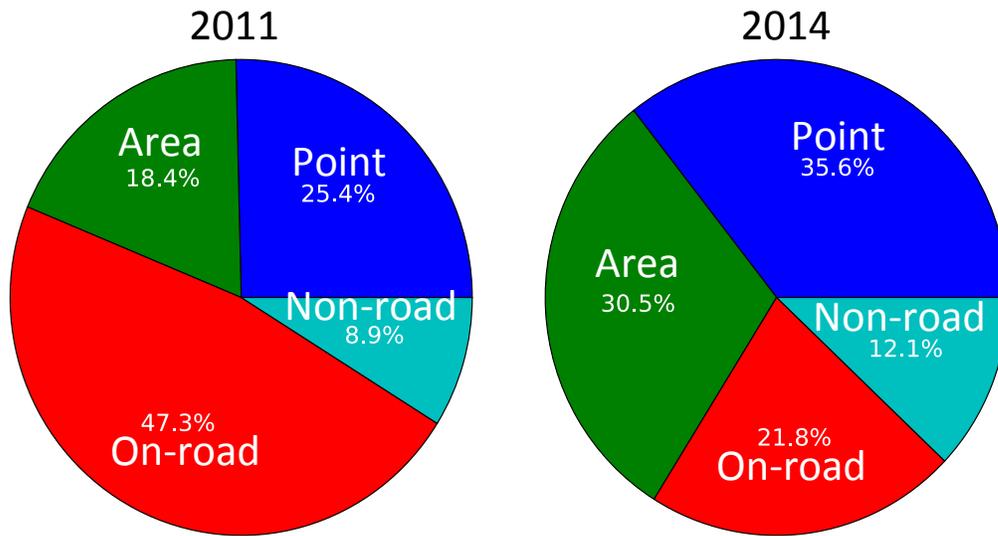


Figure 15. A pie chart showing the contribution of source sectors to total NO<sub>x</sub> emissions in the 2011 (left) and 2014 (right) NEI in Region 1 in Texas.

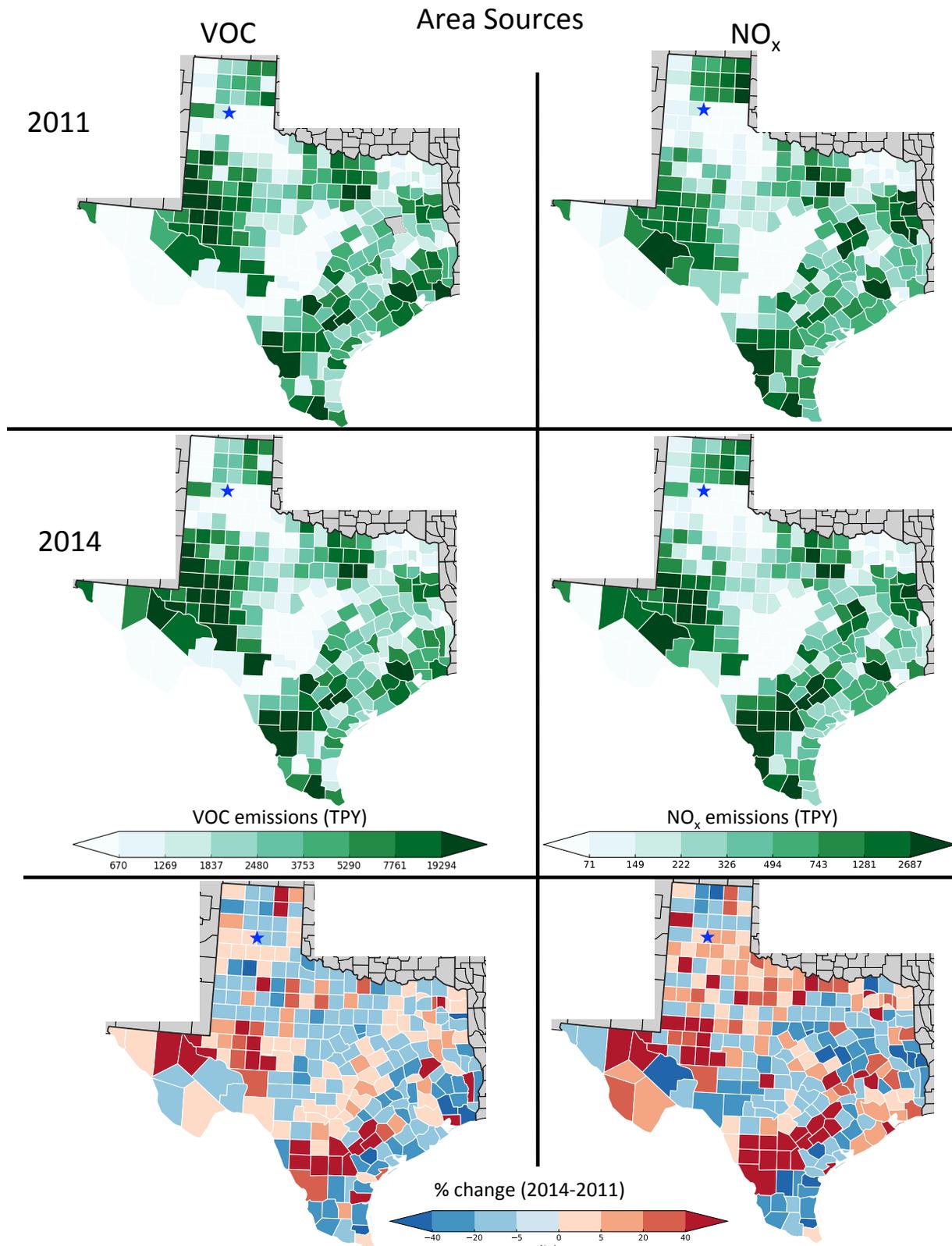


Figure 16. Map of area emissions per county for VOCs (left) and NO<sub>x</sub> (right) in tons per year. Top row is 2011, middle row is 2014, bottom row is the % change =  $100\% \cdot (2014-2011) / 2011$

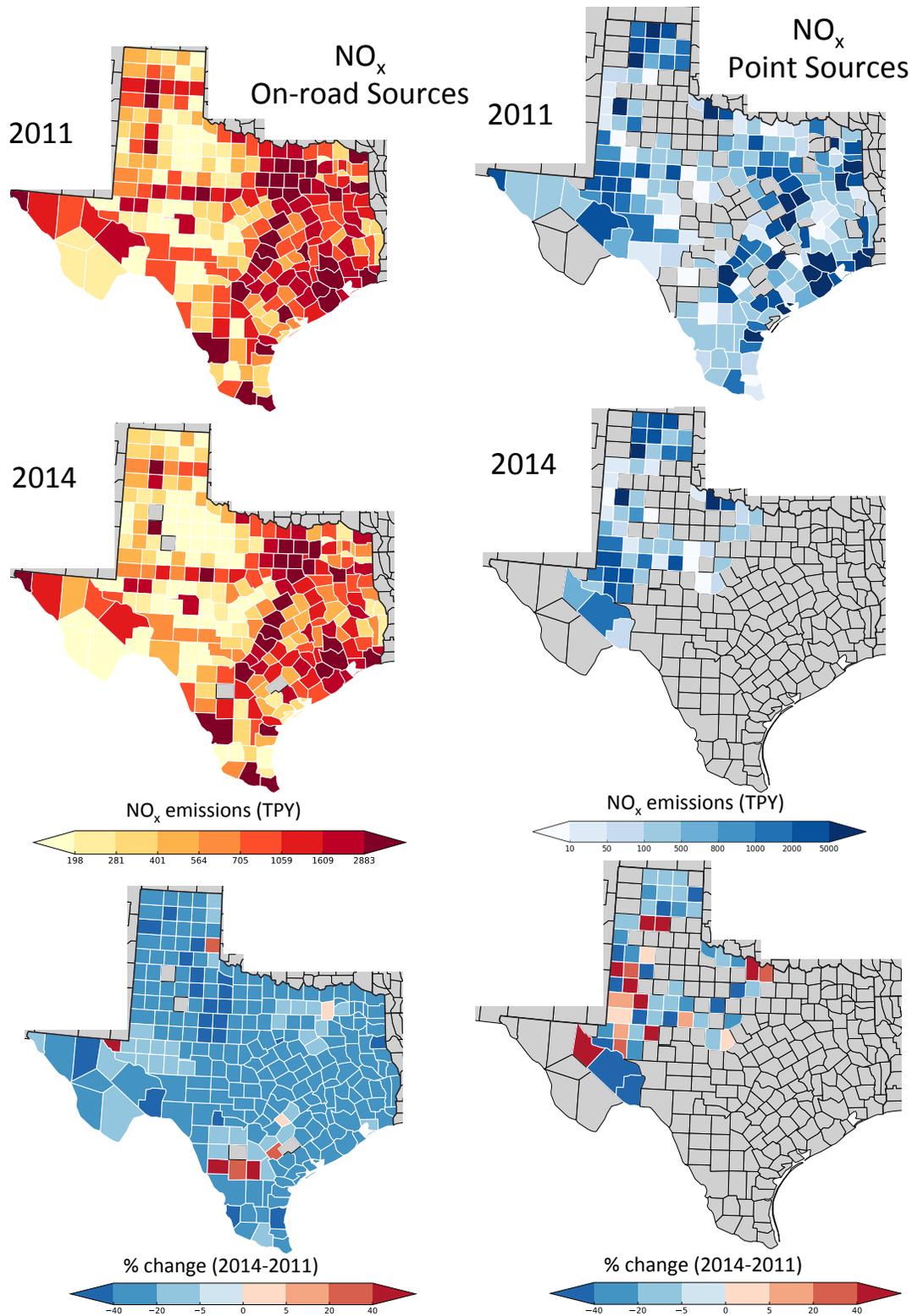


Figure 17. Map of on-road (left) and point source (right) emissions per county for NO<sub>x</sub> in tons per year. Top row is 2011, middle row is 2014, bottom row is the % change = 100%\*(2014-2011)/2011

\*grey indicates counties with missing data.

## 5 HYSPLIT Back Trajectory Analysis

We performed 48 hour HYSPLIT back trajectories from the first hour of the MDA8 ozone window exceeding 63 ppb from the Palo Duro CASTNET site. We used Version 4 of the HYSPLIT model using meteorology from the NAM12 (12 km domain) reanalysis (Draxler and Hess, 1998), with runs starting at 100 m above the ground starting from Palo Duro (blue star, Figure 18). It can be seen in the figure below that most trajectories seem to originate from the southeast, with much fewer points originating from the north/northwest. We assume that these western back-trajectories are more likely to have encountered stratospheric ozone or biomass burning influences, and thus these points were further analyzed with our biomass burning emissions and stratospheric intrusion identifier tool described in Sections 6 and 7, respectively. Appendix A contains plots for all HYSPLIT back trajectories performed in this study. After analyzing the total transport distance, speed, and bearing of the each trajectory against the average meteorological measurements at the CASTNET site (Figures 9-13), and against the MDA8 ozone for that day, no correlation was seen.

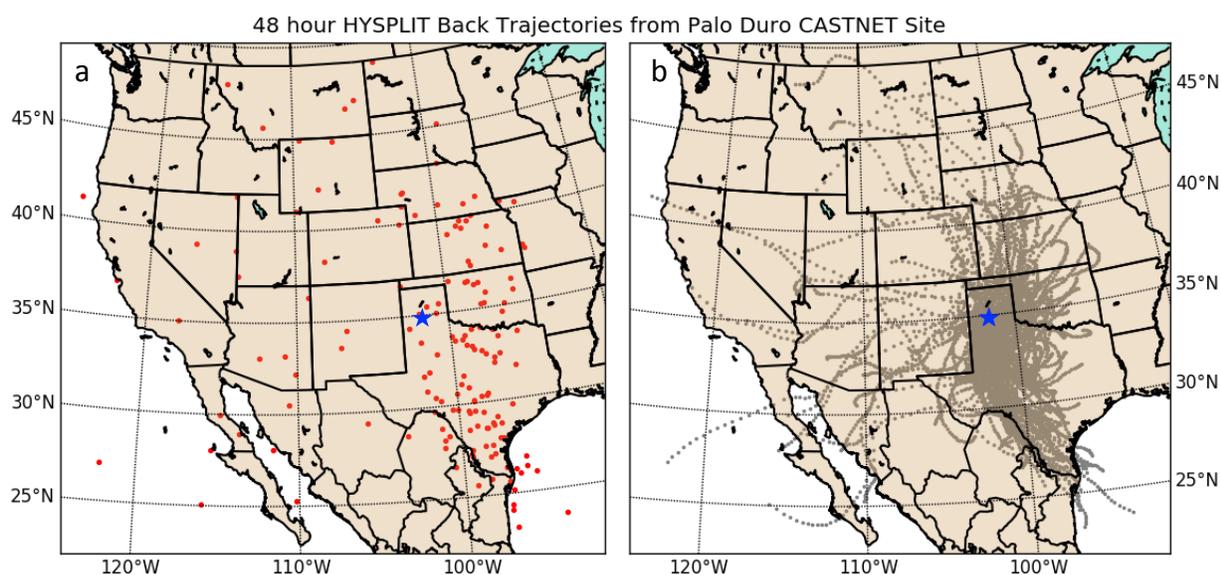


Figure 18. Figure. a) A map of the end points for 48-hour HYSPLIT back trajectories from the hours of MDA8 ozone concentrations that exceed 63 ppb originating from the Palo Duro CASTNET site (blue star) b) Same as a) but for entire back trajectory.

## 6 Biomass Burning Identification Tool

We acquired yearly Fire Inventory from NCAR (FINN) version 1.5 fire emissions files (Wiedinmyer et al., 2011) for the 8 years of interest for this study (2008-2015). These emissions files were developed with the goal to provide a consistent framework for modeling local and global air quality related to biomass burning. They are available at: <http://bai.acom.ucar.edu/Data/fire/>. Each FINN CSV file contains global estimates of daily biomass burning emissions, which include wildfires, agricultural burns and prescribed fires. Specifically, a yearly file contains the Julian day of a fire occurrence, the time of the satellite overpass/observation of that fire, a vegetation type, the latitude/longitude of the fire, the area of the fire and 40 species emissions with rates in moles or mass per day. If a fire burns for multiple days, there is a record for each day the fire burns. The FINN files do not currently contain emissions estimates of biofuel or trash burning, which are only available on a yearly time scale (Wiedinmyer et al., 2011), but these burns would not qualify as exceptional or natural events.

We then created intermediate files that contain re-gridded fire emissions to the NAM12 12km × 12km grid. The NAM12 domain was chosen in order to be consistent with our emissions preprocessor developed for the STILT-ASP model in our companion TCEQ project (WO# 582-16-62311-03) and our HYSPLIT back trajectories. We treat each fire each day as a point source, identify which grid box this point source fire is located in, and flag that grid box as a ‘fire grid box’. We then map all of our 48-hour HYSPLIT back-trajectories originating from the Palo Duro CASTNET site to this re-gridded fire emissions dataset for each day identified as having a MDA8 ozone exceeding 63 ppb. If a HYSPLIT trajectory intercepts a fire grid box, that trajectory is identified as having fire influence for that day. Of the 175 days that had a MDA8 ozone exceeding 63 ppb (for all years), 12 intersects were flagged as having fire influence (Table 5 below).

Table 5. HYSPLIT trajectories that were flagged as passing through a 12 km × 12 km grid box that contained a biomass-burning event for that day. The beginning date of the HYSPLIT back trajectory, the MDA8 value on that day, date of the actual intercept, hour of the intercept, and lat/lon of the intercept are shown. Blue highlights indicate a day with two events flagged along the same trajectory and red indicates transects that encountered fires outside of Texas.

ORIG_DATE	MDA8 O <sub>3</sub> (ppb)	INTERCEPT_DATE	HOUR	HYSPLIT_LAT	HYSPLIT_LON
20080805	65	20080804	1	29.309	-99.205
20090520	65	20090518	20	31.281	-97.569
20090521	64	20090520	6	29.61	-98.24
20110524	68	20110523	1	29.641	-110.513
20110825	83	20110823	22	31.624	-101.719
20110826	78	20110826	8	34.78	-101.433
20110826	78	20110826	7	34.76	-101.32
20120424	66	20120423	10	31.901	-99.442
20120713	76	20120711	21	34.624	-98.672
20130526	64	20130525	10	29.791	-100.506
20130628	78	20130627	2	29.471	-99.994
20130629	63	20130628	14	35.392	-98.856

It can be seen in Figure 19 (below) that the trajectories flagged as having been influenced by biomass burning grid boxes occurred, for the most part, east of the Palo Duro CASTNET site except for one intersect (on May 24, 2011) originating in Mexico. Two other flagged trajectories occurred outside of the state of Texas on July 13, 2012 and June 29, 2013. There are also 2 intercepts that occur on the same trajectory (on August 26, 2011). The MDA8 ozone concentration for all flagged days range from 63 ppb to 83 ppb.

The results presented here show trajectories that passed within 1 grid box ( $12 \text{ km} \times 12 \text{ km}$ ). We also ran the trajectories through a coarser threshold to identify other potential influences of biomass burning on ozone at the Palo Duro CASTNET site. Instead of a 1-grid box threshold we set a 3-grid box threshold ( $36 \text{ km} \times 36 \text{ km}$ ). Of the 175 MDA8 ozone days exceeding 63 ppb, 40 of the days were flagged as having potential biomass burning influences on this coarser scale (not shown), which include the 11 days mentioned above.

#### 48 hour HYSPLIT Back Trajectories Flagged for Biomass Burning Interception

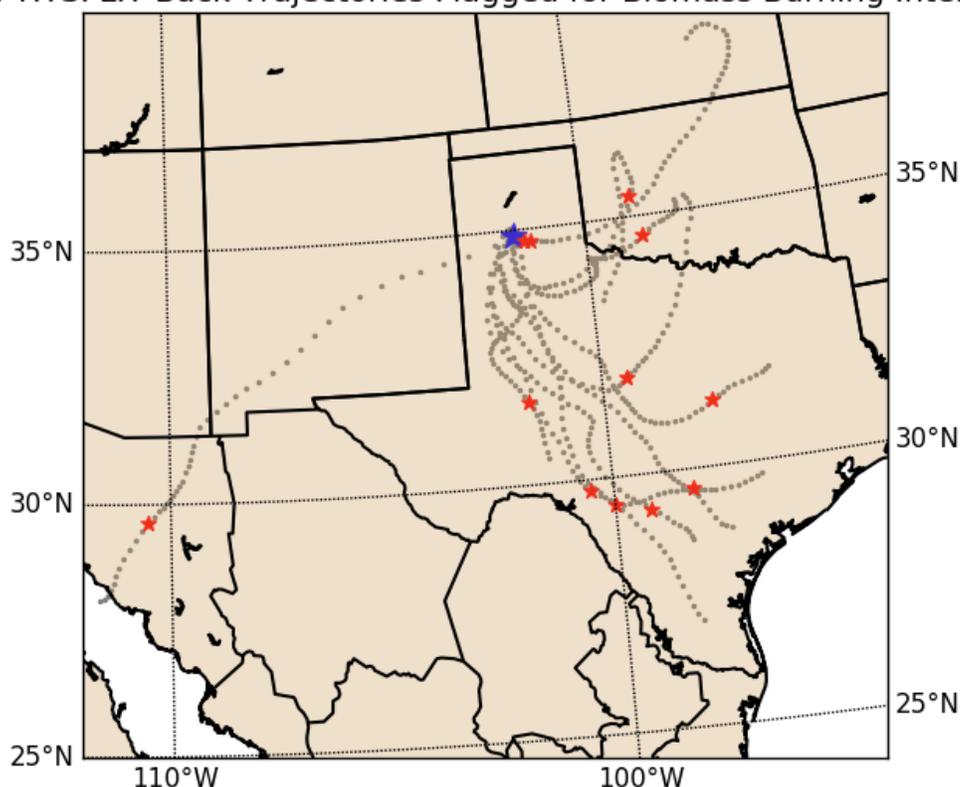


Figure 19. 48 hour HYSPLIT back trajectories originating from Palo Duro CASTNET Site. These trajectories intersected with a flagged biomass burning grid box on the day of intersect. Dots are the back trajectories, blue star denotes the Palo Duro CASTNET site and the red stars are the point of intersection with a flagged biomass burning grid box.

## 7 Stratospheric Intrusion Identification Tool

The total amount of ozone in the troposphere is an order of magnitude smaller than in the stratosphere, thus the transport or mixing of stratospheric air into the troposphere can result in an increase in ambient ozone in the troposphere that can lead to elevated surface ozone levels. Stratospheric air transported or mixed into the troposphere, known as a stratospheric intrusion, is often associated with a tropopause fold resulting from the development of an upper-level baroclinic disturbance near the jet stream. Tropopause folds can be identified by potential vorticity in the range of 1.5 to 2.0 PVU at 500 mb (1 Potential Vorticity Unit =  $10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ K kg}^{-3}$ , Holton et al., 1995). Potential vorticity is the product of absolute vorticity and static stability and increases from the troposphere to stratosphere. In addition to potential vorticity, elevated total ozone column values can also be used to identify regions of stratospheric air associated with tropopause folding (Reader and Moore, 1995; Bonsani et al., 2000; Wimmers et al., 2003; Bonasoni Zavodsky et al., 2013; Berndt et al., 2015).

Previous studies of stratospheric intrusions have used the Modern-Era Retrospective Analysis for Research and Applications (MERRA) dataset (Rienecker et al., 2011, <http://disc.sci.gsfc.nasa.gov/uui/datasets?keywords=%22MERRA-2%22>), which is an integrated reanalysis of many climate variables using observing systems from the NASA GEOS-5 data assimilation system to identify possible stratospheric intrusions. They used a combination of MERRA potential vorticity (PV) and total ozone column ( $\text{TO}_3$ , Wargan, 2012). Since these MERRA datasets are available at a temporal resolution of 3 hours and contain dozens of atmospheric variables, the datasets are extremely large. Thus, we have only analyzed days at the Palo Duro CASTNET site that both exceeded the MDA8 ozone value of 63 ppb and had a 48 hour HYSPLIT back trajectory that traveled above an altitude of 1500 m, with higher altitude air masses being more likely to have been influenced by stratospheric air. Table 6 summarizes days that met these constraints.

If these HYSPLIT back trajectories flew over or near a region of high total ozone column and/or a PV of greater than 1.5 PVU at 500 mb, then that day has been flagged as being possibly influenced by a stratospheric intrusion (red shading). Figure 20 shows an event from May 2<sup>nd</sup>, 2008, which contains a HYSPLIT back trajectory from the Palo Duro CASTNET site (black dots), the background as MERRA  $\text{TO}_3$  (Dobson Units), and the contours as PV at 500 mb (PVU units). Initiating from 48 hours prior, the trajectory began in the northwest in an area of high  $\text{TO}_3$  ( $\sim 400$  DU) and crosses a contour of 1.5 PVU. Thus, we have flagged this day as being possibly influenced by a stratospheric intrusion. Of the 25 days that were identified as having a back trajectory travel above 1500 m, we have flagged 9 to be possibly influenced, including May 2<sup>nd</sup>, 2008. Appendix B includes the  $\text{TO}_3$ /PV plots for all 25 days listed in Table 6.

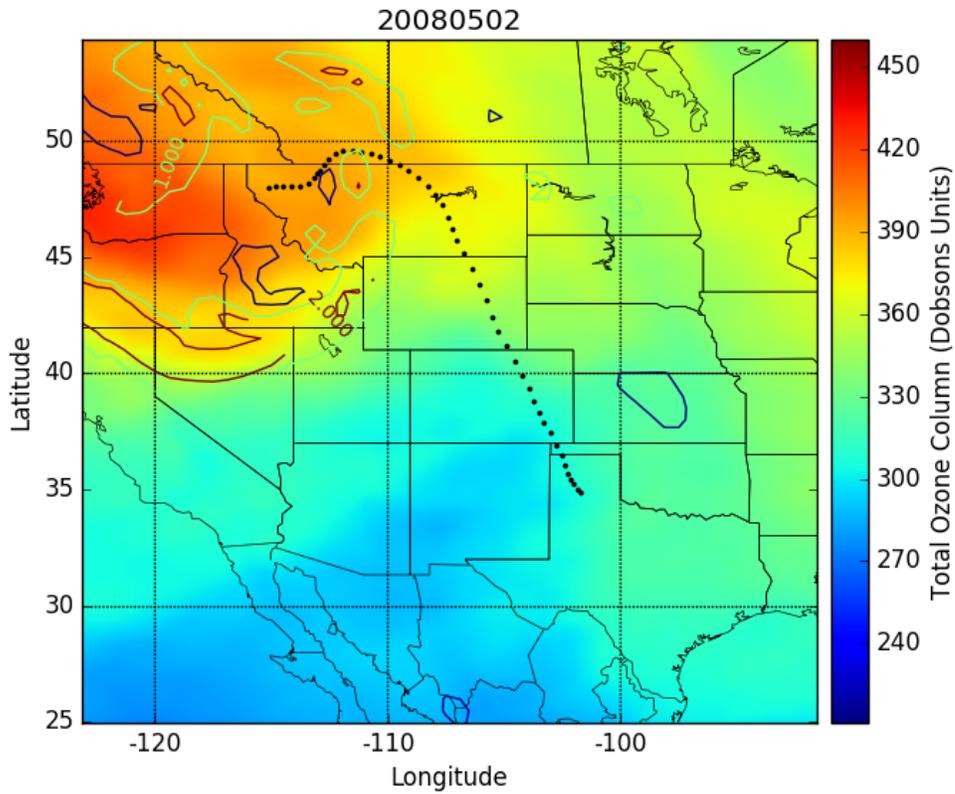


Figure 20. HYSPLIT back trajectory on May 2, 2008 from the Palo Duro CASTNET site (black dots), the background as MERRA Total Ozone Column ( $TO_3$ ), and the contours as potential vorticity (in potential vorticity units, PVU, red contour = 2.0, green contour = 1.0) at the 500 mb pressure level.

Table 6. 48 hour HYSPLIT back trajectories (of the 175 days exceeding 63 ppb MDA8 O<sub>3</sub>) originating at the Palo Duro CASTNET site that exceeded an altitude of 1500 m. Red shaded days have been flagged as influenced by stratospheric intrusions, and blue shaded are days both influenced by biomass burning and stratospheric intrusions.

<b>Date</b>	<b>MDA8 O<sub>3</sub> (ppb)</b>	<b>Maximum altitude (m)</b>
20080502	65	3929.2
20080509	64	1779.0
20080630	63	2895.5
20100512	63	1845.5
20110412	66	1819.6
20110531	65	3618.8
20110614	68	2056.0
20110619	64	3706.9
20110829	68	1745.6
20110830	65	1692.6
20110911	66	2229.2
20120426	64	1830.0
20120528	75	3149.0
20120529	79	1770.4
20120611	63	3324.1
20120808	82	1959.5
20120825	68	2285.4
20130520	70	3590.7
20130522	68	1562.3
20130530	67	1589.0
20130531	71	2223.0
20130730	64	1695.6
20130807	64	3529.3
20140425	63	1638.9
20140527	67	2063.9

## 8 Summarizing Influences of MDA8 Ozone in Palo Duro

Excluding days that are potentially influenced by biomass burning (Section 6) or stratospheric intrusions (Section 7), and assuming these influences created a high ozone event (MDA8 O<sub>3</sub> > 63 ppbv) (up to 2 days following that influenced day), reduces the number of high ozone days from 175 to 125. Figure 21 and 22 show the updated trends by day of week and hour of day, respectively. There is a slight shift towards the middle of the week, and the most common start of the MDA8 ozone window is now 12:00 (CST) for days having a MDA8 ozone greater than 63 ppb, consistent with the 70 ppbv days. There is also no longer a double peak around 10:00 for days with greater than 70 ppb. Figure 23 shows the number of days per year with a MDA8 ozone exceeding 63 ppb (left) and 70 ppb (right) with the same outcome as Figure 4 - there is an obvious decrease in the number of days that have a MDA8 ozone exceeding 63 ppb and 70 ppb from 2012 until 2015, however the year with the fewest high ozone days is 2010 as well as 2009, and 2014 for days exceed 70 ppb.

After reanalyzing meteorological trends, the reduced number of days does not significantly change any of our prior conclusions from Section 3. The remaining days may be mostly influenced by anthropogenic sources to the south of Palo Duro. Figure 24 and Table 7 summarize the percentage of trajectories that originated in each quadrant surrounding the Palo Duro Canyon site. In summary, the majority of days (65.4%) had back-trajectories that originated south of Palo Duro Canyon. Emissions inventories for 2011 and 2014 indicate large and increasing NO<sub>x</sub> and VOC area sources in the region around Midland. Thus, emissions from this area may be influencing ozone formation in Palo Duro, TX.

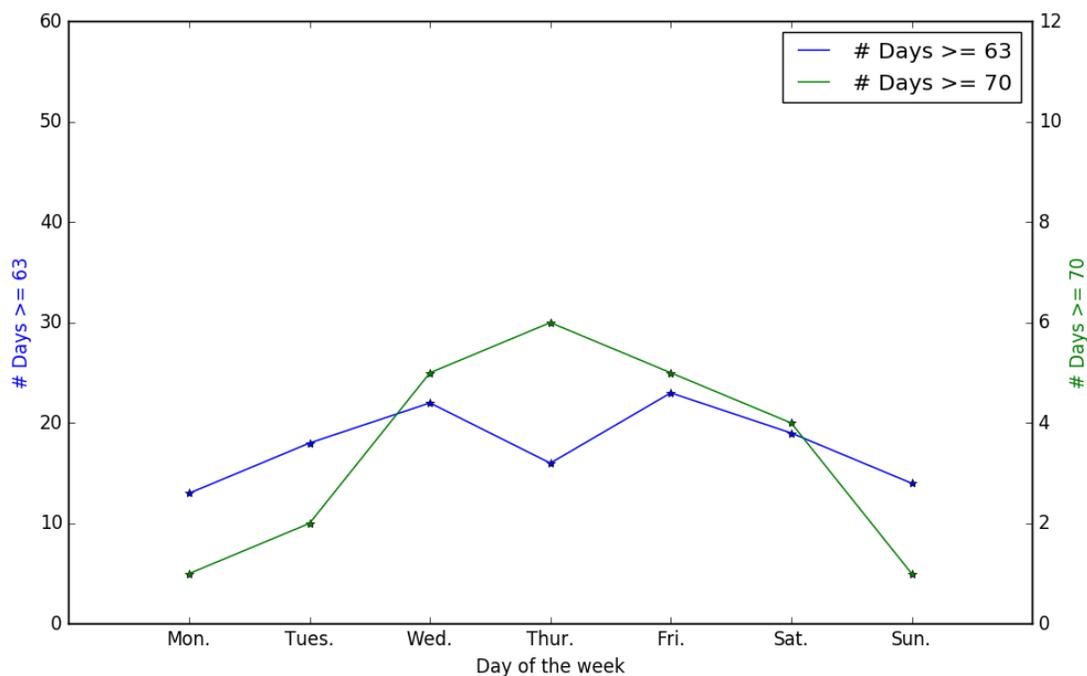


Figure 21. As Figure 7 but for the reduced number of days with a MDA8 ozone concentration exceeding 63 ppb.

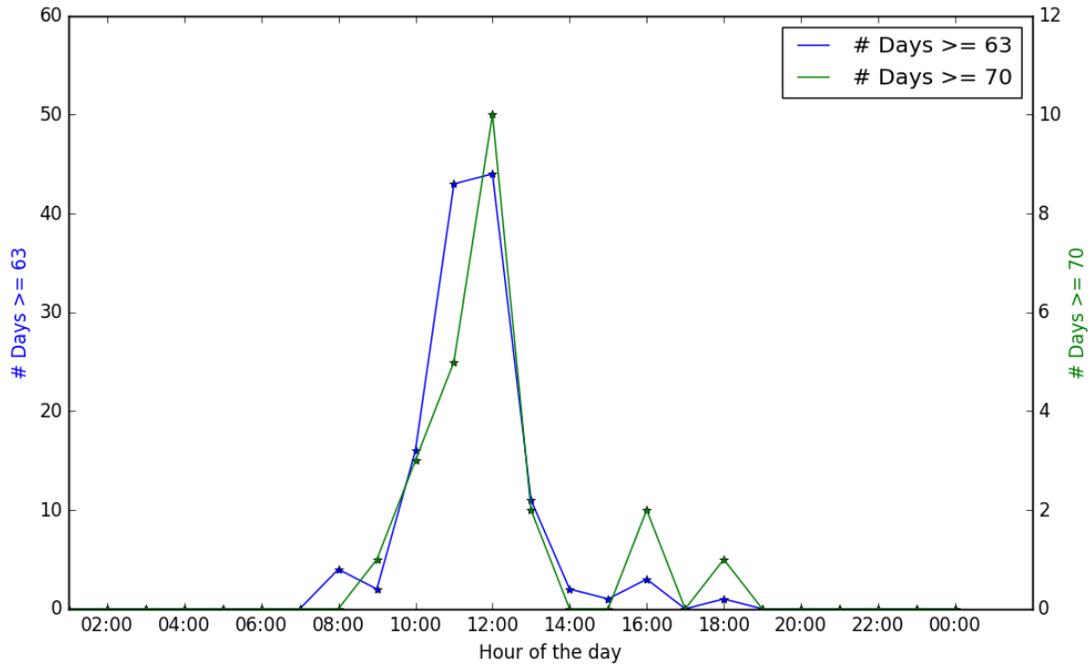


Figure 22. As Figure 8 but for the reduced number of days with a MDA8 ozone concentration exceeding 63 ppb.

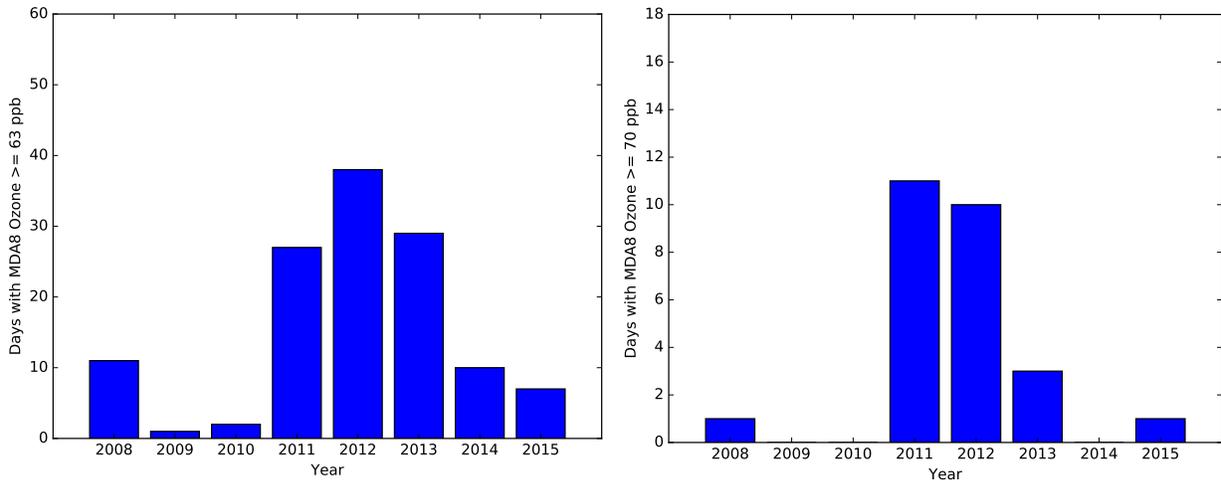


Figure 23. Same as Figure 4 but for days influenced by biomass burning and stratospheric intrusions removed.

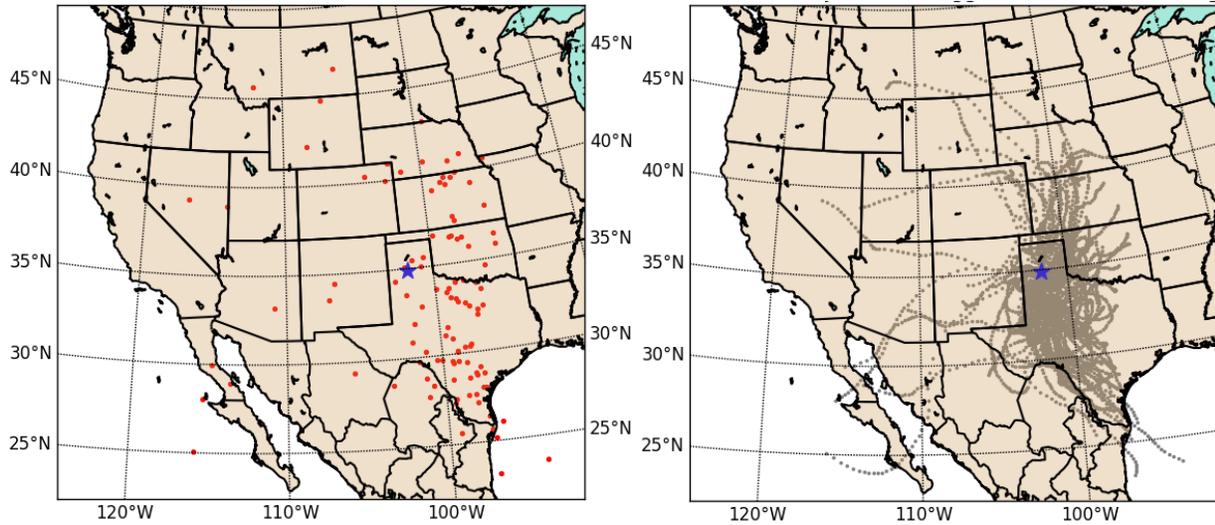


Figure 24. As in Figure 18 but after filtering for potential influence of biomass burning and stratospheric intrusions.

Table 7. Percentage of HYSPLIT back trajectory origin points and average direction in each quadrant surrounding Palo Duro.

<b>Direction</b>	<b>% end points</b>	<b>% average trajectory</b>
Northeast	25.2	22.4
Northwest	9.3	9.3
Southeast	54.2	48.6
Southwest	11.2	19.6

## 9 Conclusions

We conclude for the Conceptual Model at Palo Duro Canyon, TX, based on results presented in this report, that of the days that have a MDA8 ozone concentration of greater than or equal to 63 ppb, 40 days may have been influenced by biomass burning and 9 days may have been influenced by stratospheric intrusion events. The majority of days with high O<sub>3</sub> events (~125 out of 175) show no evidence for fire or stratospheric ozone influence and are assumed to be influenced by other sources. On these days, the measured wind direction and the HYSPLIT 48 hour back trajectories are mostly from south of the site. The regions south of the site that have the highest NO<sub>x</sub> and VOC area and point emissions include the Midland-Odessa, TX region where there is a large oil and gas industry presence. High and increasing VOC and NO<sub>x</sub> area emissions from the 2011 and 2014 emission inventory support the theory that this area may impact ozone formation in the Palo Duro Canyon CASTNET monitoring site.

The following provides answers to the conceptual model questions laid out in EPA's Draft Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, PM<sub>2.5</sub>, and Regional Haze (EPA, 2015):

- *What are the pollutants of concern in the area?*
  - This report focuses on ozone trends and formation in the area of Palo Duro, TX.
- *What are the current air quality levels in the area?*
  - The number of days with a MDA8 ozone concentration exceeding 63 ppb in the area since 2008 have decreased overall, however a large increase in the number of days over this threshold was seen between 2010 and 2011. Since we have no explanation as to why the number of days in 2011 and 2012 drastically increased, we cannot be certain that the current downward trend will continue. This same conclusion is true when excluding days influenced by biomass burning and stratospheric intrusion events.
- *What is the attainment/nonattainment status of the area?*
  - Currently the area is in attainment for the 2008 ozone NAAQS, and no designation has been made related to the revised 2015 ozone NAAQS.
- *What is the geographical scope of poor air quality?*
  - As we only explored ozone measurements at the Palo Duro CASTNET site in this study, and no other ozone measurements were available close by, the geographic scope of the poor air quality around the Palo Duro site is difficult to determine.
- *What is the temporal scope of poor air quality?*
  - Relative to all MDA8 ozone concentration days in Palo Duro between 2008-2015, the temporal scope of poorest air quality in the area appears to have occurred between 2011-2013 (Figure 4), with the maximum MDA8 ozone concentrations occurring in 2011-2012 (Figure 6). When analyzing all ozone days, the highest

concentrations occur between April and September, with the highest concentrations appearing in May and August (Figure 3). MDA8 ozone exceeds 63 ppb typically on days with a temperature greater than about 20 °C, when RH is below about 60 %, and wind direction is between 70 and 260 degrees, with little apparent dependence on wind speed. For days that exceed 70 ppb MDA8 O<sub>3</sub> the temperature is never below 25 °C, RH is never above 55 %, and wind direction is between 100 and 230 degrees (Figures 9, 10 and 11)

- *What are the air quality trends in the area? Is the problem getting better or worse?*
  - The number of days with a MDA8 ozone concentration exceeding 63 ppb in the area since 2008 have decreased overall, however a large increase in the number of days over this threshold was seen between 2010 and 2011, not declining to zero until 2014. Since we have no explanation as to why the number of days in 2011 and 2012 drastically increased, we cannot be certain that the current downward trend will continue. The same pattern appears when excluding days that have been influenced by biomass burning and stratospheric intrusions (Figure 23).
- *What are the suspected mechanisms for formation of poor air quality levels?*
  - While some days (<50 out of the 175) in which the MDA8 ozone concentration exceeds 63 ppb were possibly influenced by biomass burning events or stratospheric intrusion events, it appears that the remaining majority of days were influenced by NO<sub>x</sub> and VOC emissions coming from south of the Palo Duro site, likely transported from this area. Thus, the main mechanism for ozone formation in the Palo Duro area is likely photochemical production of ozone related to these emissions, with some days possibly influenced by biomass burning or stratospheric intrusion ozone. Highest ozone days occur between May and October, with maximum concentrations occurring May and August (Figure 3). Thus, temperature plays a role in ozone formation. Relative humidity is usually below 60 % on days with higher ozone, indicating the source region may have dryer air, or ozone formation may be forming in dryer conditions.
- *What are the sources of emissions that may contribute to poor air quality?*
  - Wind direction measurements and HYSPLIT back trajectory calculations indicate a large number of the MDA8 ozone concentration days exceeding 63 ppb with sources coming from the south/ (Figure 13 and 23). After exploring which of these days were possibly influenced by biomass burning events or stratospheric intrusion events, it appears that the remaining majority of days may be influenced by the high NO<sub>x</sub> and VOC emissions coming from the large source region around Midland, TX, with additional sources out of the east/south-east.

- *Are there unique meteorological influences on local air quality levels?*
  - MDA8 ozone exceeds 63 ppb typically on days with a temperature greater than about 20 °C, when RH is below about 60 %, and wind direction is between 70 and 260 degrees, with little apparent dependence on wind speed. For days that exceed 70 ppb MDA8 O<sub>3</sub> the temperature is never below 25 °C, RH is never above 55 %, and wind direction is between 100 and 230 degrees (Figures 9, 10 and 11).

## 10 Quality Assurance Steps and Reconciliation with User Requirements

All work on the project was done in accordance with the Quality Assurance Project Plan (QAPP). All scripts and data files used in this project were inspected by team members different from the original author to ensure they were correct, and any errors noted in early versions were fixed. Other required evaluations are contained within the report. In addition, if further analysis or feedback from TCEQ uncovers any errors in the provided files, we will correct those and provide TCEQ with corrected files.

## 11 Recommendations for Future Study

We recommend that future work focus on:

- The development of datasets in closer proximity to the Palo Duro CASTNET monitoring site in order to evaluate measured species and meteorological parameters. Additionally, measurements of the vertical profile of O<sub>3</sub> at this location would be useful. The addition of these measurements will allow for further validation of air quality impacts on the area, and the relative contribution from regional emissions as well as out of state emissions.
- Continued development of a biomass burning identification tool that contains additional HYSPLIT back trajectories, and a more detailed account of chemistry in order to account for biases and variability in meteorology and atmospheric species arriving at the Palo Duro CASTNET measurement site.
- Creating a Generalized Additive Model to relate the Palo Duro MDA8 O<sub>3</sub> to meteorological predictors to further understand O<sub>3</sub> formation in this area (reference last year's report).
- Investigating this site using TCEQ's 2012 CAMx modeling dataset, as that is the year with most days exceeding a MDA8 ozone concentration of 63 ppb at Palo Duro. Inputs for model set up are already available, thus increasing the ease of modeling tasks.

## 12 References

- Berndt, E. B., B. T. Zavodsky, M. J. Folmer, 2015: Development and Application of Atmospheric Infrared Sounder Ozone Retrieval Products for Operational Meteorology, *IEEE Trans Geosci, Rem Sens*, 54, 958 -967.
- Bonasoni, P., F. Evangelisti, U. Bonafe, F. Ravegnani, F. Calzolari, A. Stohl, L. Tositti, O. Tubertini, T. Colombo, 2000: Stratospheric ozone intrusion episodes recorded at Mt. Cimone during the VOTALP project: 18 case studies, *Atmos Environ.*, vol. 34, no. 9, pp. 1355-1365.
- Draxler, R. R. and G. D. Hess (1998), An overview of the HYSPLIT\_4 modeling system for trajectories, dispersion, and deposition, *Aust. Meteorol. Mag.*, 47, 295-308.
- EPA, 1998. Guideline on Data Handling Conventions for the 8-Hour Ozone NAAQS, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Washington 1998, EPA-454/R-98-017.
- EPA, 2007, Federal Register, 40 CFR Part 50, Appendix P to Part 50 - Interpretation of the Primary and Secondary National Ambient Air Quality Standards for Ozone, U.S. Environmental Protection Agency, Washington 1998, EPA-454/R-98-017.
- U.S. Environmental Protection Agency. Draft Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, PM<sub>2.5</sub>, and Regional Haze. December 2014. [http://www.epa.gov/ttn/scram/guidance/guide/Draft\\_O3-PM-RH\\_Modeling\\_Guidance-2014.pdf](http://www.epa.gov/ttn/scram/guidance/guide/Draft_O3-PM-RH_Modeling_Guidance-2014.pdf), accessed June, 2016.
- Holton, J. R., P. H. Haynes, A. R. Douglass, R. B. Rood, and L. Pfister (1995), Stratosphere-troposphere exchange, *Rev. Geophys.*, 33(4), 403–439.
- Reader M. C. and G. W. K. Moore, 1995: Stratosphere-troposphere interactions associated with a case of explosive cyclogenesis in the Labrador Sea, *Tellus A*, vol. 47, no. 5, pp. 849-863.
- Rienecker, M.M., M.J. Suarez, R. Gelaro, R. Todling, J. Bacmeister, E. Liu, M.G. Bosilovich, S.D. Schubert, L. Takacs, G.-K. Kim, S.E. Bloom, J. Chen, D. Collins, A. Conaty, A. da Silva, W. Gu, J. Joiner, R.D. Koster, R. Lucchesi, A. Molod, T. Owens, S. Pawson, P. Pegion, C.R. Redder, R. Reichle, F.R. Robertson, A.G. Ruddick, M.Sienkiewicz, J. Woollen (2011), MERRA - NASA's Modern-Era Retrospective Analysis for Research and Applications, *J. Climate*, 24, doi: 10.1175/JCLI-D-11-00015.1.
- Wargan, Krzysztof, A Stratospheric Intrusion Event on 29 April 2012 Captured by the MERRA-2 Reanalysis, [http://gmao.gsfc.nasa.gov/research/science\\_snapshots/strat\\_intrusion\\_29Apr2012.php](http://gmao.gsfc.nasa.gov/research/science_snapshots/strat_intrusion_29Apr2012.php)
- Wiedinmyer, C., S. K. Akagi, R. J. Yokelson, L. K. Emmons, J. A. Al-Saadi, J. J. Orlando, and A. J. Soja. "The Fire Inventory from Ncar (Finn): A High Resolution Global Model to Estimate the Emissions from Open Burning." *Geoscientific Model Development* 4, no. 3 (2011): 625-41. (<http://www.geosci-model-dev.net/4/625/2011/gmd-4-625-2011.html>)
- Wimmers, A. J. , J. L. Moody, E.V. Browell, J. W. Hair, W. B. Grant, C. F. Butler, M. A. Fenn, C. C. Schmidt, J. Li, and B. A. Ridley, 2003: Signatures of tropopause folding in satellite imagery, *J. Geophys. 11 Res.*, vol. 108, no. D4, pp. 1984-2012.
- Zavodsky, B. T., A. L. Molthan, and M. J. Folmer, 2013: Multispectral imagery for detecting stratospheric air intrusions associated with mid-latitude cyclones, *J. Operational Meteor.*, vol. 1, no. 7, 71-83, Available at <http://dx.doi.org/10.15191/nwajom.2013.0107>.