APPENDIX B

CONCEPTUAL MODEL FOR THE BEXAR COUNTY NONATTAINMENT AREA FOR THE 2015 EIGHT-HOUR OZONE NATIONAL AMBIENT AIR QUALITY STANDARD

State Implementation Plan Revision for the 2015 Eight-Hour Ozone National Ambient Air Quality Standards

Project Number 2022-025-SIP-NR
Proposal
May 31, 2023

EXECUTIVE SUMMARY

Ground-level ozone addressed by this State Implementation Plan (SIP) revision is formed through a photochemical reaction with nitrogen oxides (NO_X) and volatile organic compounds (VOC). This conceptual model provides a detailed examination of ozone formation in the Bexar County 2015 ozone National Ambient Air Quality Standard (NAAQS) nonattainment area with a focus on ozone levels above 70 parts per billion (ppb). Most of the analyses in this conceptual model focus on ozone season (March through October) data from 2012 through 2021 and recent changes in how, when, and where ozone.

Ozone concentrations in the Bexar County 2015 ozone NAAQS nonattainment area decreased significantly from 2012 through 2021, with the eight-hour ozone design value decreasing 9%. However, the trend slowed in recent years, with no change in eight-hour ozone design values between 2016 and 2021. From 2012 through 2021, the area's maximum daily NO_X concentrations decreased by 28%, but VOC concentrations have not observed any significant change.

Ozone precursor emissions in the Bexar County 2015 ozone NAAQS nonattainment area declined from 2012 through 2021. Mobile source VOC and NO_X emissions decreased and point source NO_X emissions decreased. While the overall quantity of point source VOC emissions has not changed notably, the spatial distribution of the emissions has shifted. The analyses conducted for this conceptual model support the following conclusions regarding ozone formation in the Bexar County 2015 ozone NAAQS nonattainment area.

- Ozone concentrations peak from May through June and then again from August through October, with a minimum occurring in July. The latter half of the ozone season generally sees higher ozone than the first half.
- High ozone typically occurs on hot sunny days with dry conditions and slow wind speeds out of the southeast and northeast. The highest ozone days often have recirculating winds that exacerbate ozone accumulation.
- The synoptic-scale meteorological conditions that allow for high local ozone formation also create high levels of regional background ozone, which combines with the locally formed ozone and emissions to produce eight-hour ozone levels more than 70 ppb.
- Emissions located south, southeast, and east of the Bexar County 2015 ozone NAAQS nonattainment area combine with urban area mobile source emissions to create ozone and transport it to the monitors located in the northwest of the Bexar County 2015 ozone NAAQS nonattainment area.
- Ozone formation appears to be predominantly NO_X limited at the monitors with the highest ozone concentrations. Control of VOC emissions would be expected to have less effect on ozone concentrations in the Bexar County 2015 ozone NAAQS nonattainment area compared to NO_X controls.

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Disclaimer: Maps in this document were generated by the Air Quality Division of the Texas Commission on Environmental Quality. The products are for informational purposes and may not have been prepared for or be suitable for legal, engineering, or surveying purposes. They do not represent an on-the-ground survey and represent only the approximate relative location of property boundaries. For more information concerning these maps, contact the Air Quality Division at 512-239-1459.

CHAPTER 1: INTRODUCTION

Ozone formation conceptual models characterize ozone trends, precursors, formation, and transport in a geographic area. This information provides a comprehensive picture of not only where and when ozone forms, but also how and why ozone forms in a geographic area. Conceptual models, also known as conceptual descriptions, are required by the United States (U.S.) Environmental Protection Agency (EPA) to accompany ozone photochemical modeling performed for State Implementation Plans (SIP) (EPA 2018). Although Bexar County is the only county in the San Antonio (SAN) area to be designated as nonattainment, this conceptual model will focus on ozone formation for the Bexar County 2015 ozone National Ambient Air Quality Standard (NAAQS) nonattainment area as well as relevant analyses of SAN area for the 2015 eight-hour ozone NAAQS of 70 parts per billion (ppb). This section discusses general ozone formation and includes a summary of the previous conceptual models for the San Antonio area.

1.1 GENERAL DESCRIPTION OF OZONE FORMATION

Ozone is not directly emitted into the atmosphere; it is formed through a complex series of chemical reactions of nitrogen oxides (NO_X) and volatile organic compounds (VOC) in the presence of sunlight. Ozone production requires two factors: sunlight and availability of reactants. Generally, these factors are present when there are clear skies, light winds, abundant sunshine, and warm temperatures. Typically, these meteorological conditions are associated with high-pressure areas that migrate across the U.S. during the summer season. High-pressure areas have two characteristics that encourage ozone formation: light winds and subsidence inversions. Typically, winds circulating around a high-pressure system are too weak to ventilate an urban area well, so local emissions tend to accumulate. Subsidence inversions cap the vertical mixing, further aggravating the situation by concentrating local pollutants near the surface. These meteorological conditions are further affected by the area's geography. Areas near the coast may experience air-mass flow reversals and valleys near mountainous areas may experience air inversions that trap pollution in the air near the surface.

1.2 SAN ANTONIO AREA MONITORS

The San Antonio area has numerous regulatory and non-regulatory monitors. Table 1-1: *Monitors in the San Antonio Area* lists each monitor in the area, along with its Aerometric Information Retrieval System (AIRS) number, Continuous Ambient Monitoring Station (CAMS) number, and county. There are 12 ozone monitors in the San Antonio area, eight in Bexar County 2015 ozone NAAQS nonattainment area. Three are regulatory: San Antonio Northwest, Camp Bullis, and Calaveras Lake. There are four VOC monitors, two in Bexar County 2015 ozone NAAQS nonattainment area and one each in Karnes and Wilson Counties. There are 24 meteorological monitor sites. There are 14 sites that measure NO_X, six of which are in Bexar County 2015 ozone NAAQS nonattainment area. Overall, this network of monitors allows for comprehensive spatial coverage and analysis of San Antonio area ozone formation.

Table 1-1: Monitors in the San Antonio Area

Site Name	AIRS number	CAMS number	County
San Antonio Northwest	480290032	0023	Bexar
Camp Bullis	480290052	0058	Bexar
Calaveras Lake	480290059	0059	Bexar
Old Highway 90	480290677	0677	Bexar
CPS Pecan Valley	480290055	0678	Bexar
Frank Wing Municipal Court	480290060	9999	Bexar
Elm Creek Elementary	480290501	0501	Bexar
Fair Oaks Ranch	480290502	0502	Bexar
Heritage Middle School	480290622	0622	Bexar
Gardner Rd. Gas Sub-Station	480290623	0623	Bexar
Gate 9A CPS	480290625	0625	Bexar
Gate 58 CPS	480290626	0626	Bexar
San Antonio Interstate 35	480291069	1069	Bexar
San Antonio Gardner Road	480291080	1080	Bexar
San Antonio Bulverde Parkway	480291087	1087	Bexar
San Antonio Red Hill Lane	480291091	1091	Bexar
Calaveras Lake Park	480291609	1609	Bexar
Government Canyon	480291610	1610	Bexar
Bulverde Elementary	480910503	0503	Comal
City of Garden Ridge	480910505	0505	Comal
New Braunfels Oak Run Parkway	480911088	1088	Comal
New Braunfels Airport	481870504	0504	Guadalupe
Seguin Outdoor Learning Center	481870506	0506	Guadalupe
Karnes County	482551070	1070	Karnes
Boerne Lake	482591622	1622	Kendall
Floresville Hospital Boulevard	484931038	1038	Wilson
Von Ormy Highway 16	480131090	1090	Atascosa
AACOG Pecan Street Poteet	480131627	1627	Atascosa

Figure 1-1: *Map of Ozone,Nitrogen Oxides, and Volatile Organic Compounds Monitors in the San Antonio Area* shows the monitors used for these analyses. Ozone monitors are shown with yellow, NO_X with blue, and VOC with purple. Regulatory ozone monitors are outlined in black. The Eagle Ford Shale is shaded with dots to contextualize the measurements from the Floresville Hospital Boulevard and Karnes County monitors.

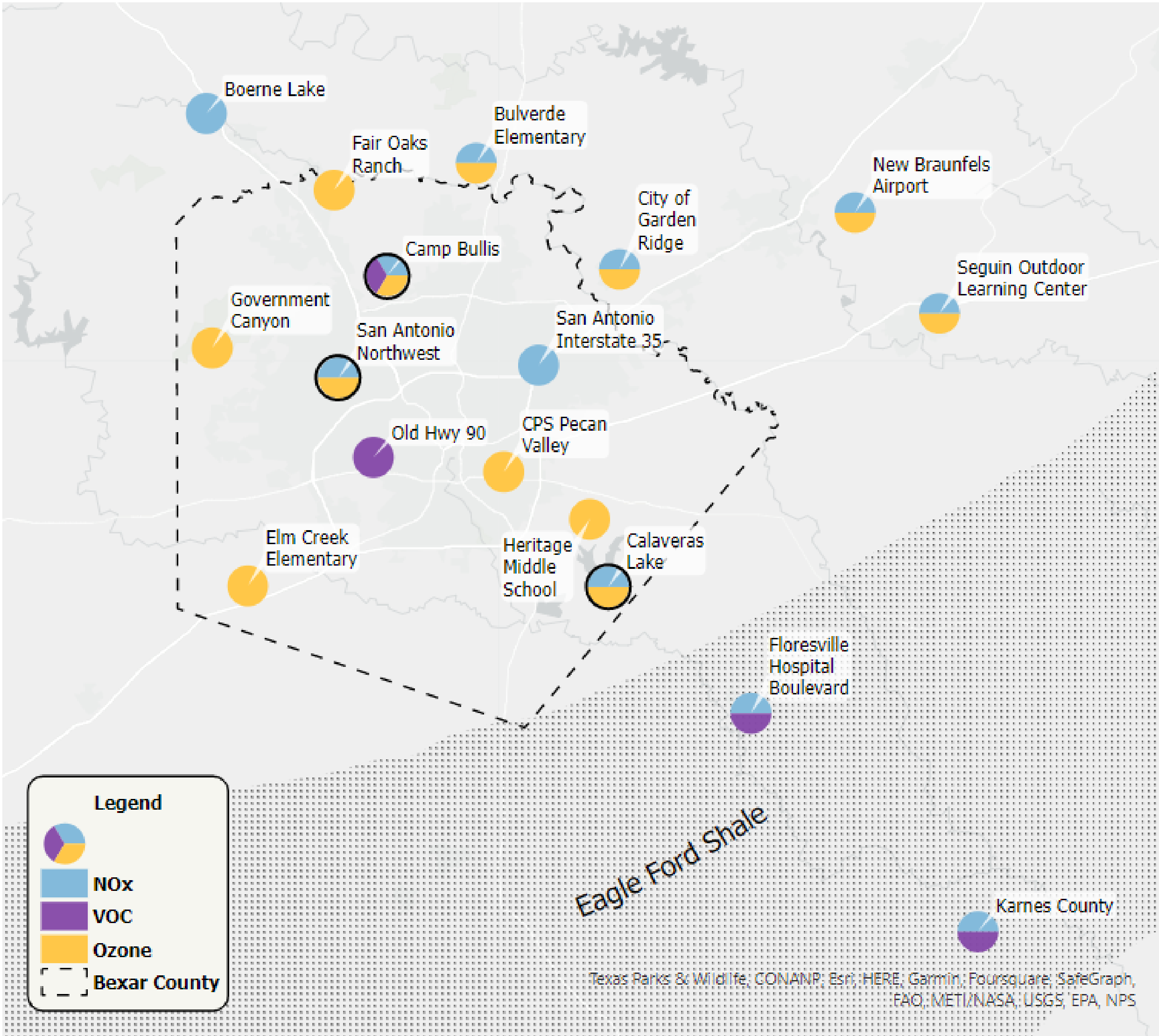

Figure 1-1: Map of Ozone, Nitrogen Oxides, and Volatile Organic Compounds Monitors in the San Antonio Area

1.3 PREVIOUS UNDERSTANDING OF SAN ANTONIO AREA OZONE FORMATION

The city of San Antonio is in Bexar County. Bexar County has experienced a steadily increasing population and in 2021 had a population of over 2 million, compared to a population of 1.7 million in 2010 (U.S. Census Bureau, 2021). Despite the increase in population, this area has observed modest improvements in air quality. The area is currently measuring attainment of the one-hour ozone NAAQS of 0.12 parts per million (ppm), the 1997 eight-hour ozone NAAQS of 0.08 ppm, and the 2008 eight-hour ozone NAAQS of 0.075 ppm.

The previous conceptual model for the San Antonio area was prepared by the Texas Commission on Environmental Quality (TCEQ) in 2019 and adopted in 2020 (TCEQ 2020). That conceptual model focused on ozone over the 2015 ozone NAAQS of 70 ppb and covered 2009 through 2018. That analysis established the following findings about ozone formation in the San Antonio area:

- Meteorological conditions linked to high ozone in the San Antonio area include high temperatures, low relative humidity, and slow wind speeds. On high ozone days, surface winds are slow with two reversals in direction, from the southeast to the northwest, and then from the northwest back to the southeast. Upper-level wind data show that the highest ozone concentrations occur when continental air is brought into the area or when winds are slow and there is recirculation.

- Like many other Texas areas, San Antonio experiences two seasonal peaks in ozone concentrations. The first occurs from April through June, and the second is from August through October.

- Long-range transport and high regional background ozone contribute the most early in the ozone season (March through July). From August through September, local contribution has a greater influence on ozone concentrations. There is year to year variability in local ozone production, but no overall trend from 2009 through 2018.

- Ozone peaks later in the day on high ozone days compared to low ozone days. On high ozone days, ozone first peaks near the center of San Antonio and then peaks later in the day on the outskirts of the city to the northwest. This indicates that ozone is first formed in the center of the city and then transported to the northwest, where the highest ozone concentrations typically occur.

- Ozone forms under NO_x limited to transitional conditions. Peak NO_x trended downward in the years studied, but median values at some monitors trended upward. Concentrations of VOC associated with mobile sources trended slightly downwards, but VOC associated with oil and gas production did not.

CHAPTER 2: OZONE CONCENTRATIONS AND TRENDS

To characterize the current ozone situation in the Bexar County 2015 ozone National Ambient Air Quality Standard (NAAQS) nonattainment area, this conceptual model will focus on ozone concentrations from 2012 through 2021. This section will look at ozone data in various forms to characterize where, when, and how ozone forms in the area.

The Bexar County 2015 ozone NAAQS nonattainment area has three ozone monitors that report data to the Environmental Protection Agency's (EPA's) Air Quality System (AQS) data mart; these three monitors are referred to as regulatory monitors. There are nine other ozone monitors in the San Antonio (SAN) area that do not report data to the EPA; they are commonly referred to as non-regulatory monitors. Many of these non-regulatory monitors sample ozone only from the months of March through October. These monitors cannot be used to determine compliance with the ozone NAAQS; however, they are useful to determine patterns in ozone formation. The following sections will note when regulatory or non-regulatory ozone monitors are used.

2.1 EIGHT-HOUR OZONE DESIGN VALUES

An ozone design value is a statistic used to compare an area's ozone concentration to the ozone NAAQS. The design value for the 2015 eight-hour ozone NAAQS is calculated by averaging the fourth-highest daily-peak eight-hour averaged ozone concentration over three years. Ozone design values are calculated for each monitor, and then the monitor with the highest design value sets the design value for the area. A monitor exceeds the 2015 eight-hour ozone NAAQS when its design value exceeds 0.070 parts per million (ppm), or 70 parts per billion (ppb).

The eight-hour ozone design value trend for the Bexar County 2015 ozone NAAQS nonattainment area is displayed in Figure 2-1: *Eight-Hour Ozone Design Values in the Bexar County 2015 Ozone NAAQS Nonattainment Area*. This area-wide trend only uses data from regulatory monitors. The trend shows that the design values have decreased by 7 ppb, or 8.8%. From 2012 to 2016, the design value decreased roughly 1.95 ppb per year on average. In more recent years, progress has slowed, with a decrease of about 0.25 ppb per year on average. The lowest design values recorded for the Bexar County 2015 ozone NAAQS nonattainment area were 72 ppb in 2018 and 2020.

The figure also indicates which monitor set the design value in each year. Camp Bullis had the highest design value for the first five years, then the highest design value switched to San Antonio Northwest for three years, before finally switching back to Camp Bullis. Both monitors had the same design values in 2016 and 2020. The other regulatory monitor, Calaveras Lake, was considered in this analysis but it typically measures lower ozone concentrations and has not set the design value in 10 years of analysis period.

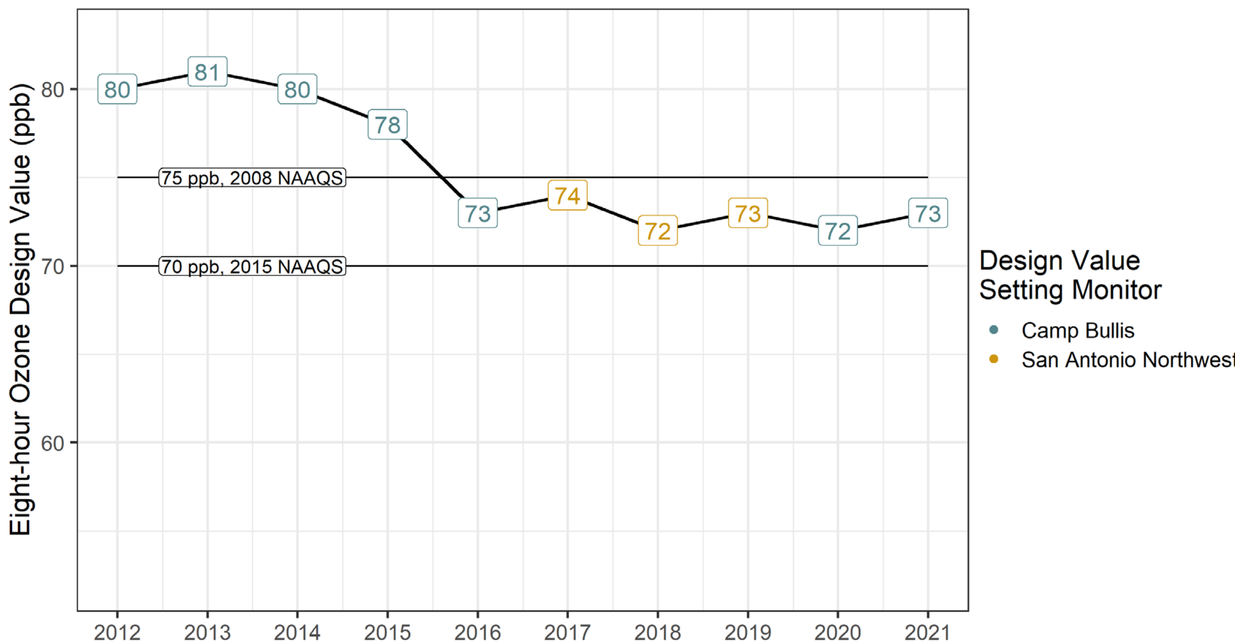

Figure 2-1: Eight-Hour Ozone Design Values in the Bexar County 2015 Ozone NAAQS Nonattainment Area

Looking at design value trends at each monitor provides additional insight into how ozone is changing across the entire San Antonio area and background ozone trends. Upwind monitors are often used to determine background concentrations.

Because the San Antonio area has only three regulatory monitors, all area monitors are shown in Figure 2-2: *Eight-Hour Ozone Design Values by Monitor in the San Antonio Area*. The regulatory monitors, San Antonio Northwest, Camp Bullis, and Calaveras Lake, are marked on Figure 2-2 with triangles and a solid line. The non-regulatory monitors are marked with dashed lines and circles. One of the non-regulatory monitors, Government Canyon, was activated mid-2017 and only has two valid design values.

Overall, all monitors in the San Antonio area show a decreasing trend in eight-hour ozone design values from 2012 through 2021. Some of the lowest design values ever recorded in the San Antonio area were observed for 2018 through 2021. CPS Pecan Valley and Heritage Middle School show decreases of over 23% from 2012 to 2021. The three regulatory monitors located inside the Bexar County 2015 ozone NAAQS nonattainment area show smaller, but still substantial, decreases; San Antonio Northwest decreased 8%, Camp Bullis decreased 10%, and Calaveras Lake decreased 6%.

The difference between the maximum design value and the minimum design value has increased by 5 ppb, from 12 ppb in 2012 to 17 ppb in 2021. This large difference between the lowest design value and the highest design value may indicate that there is more local ozone production occurring in the area recently.

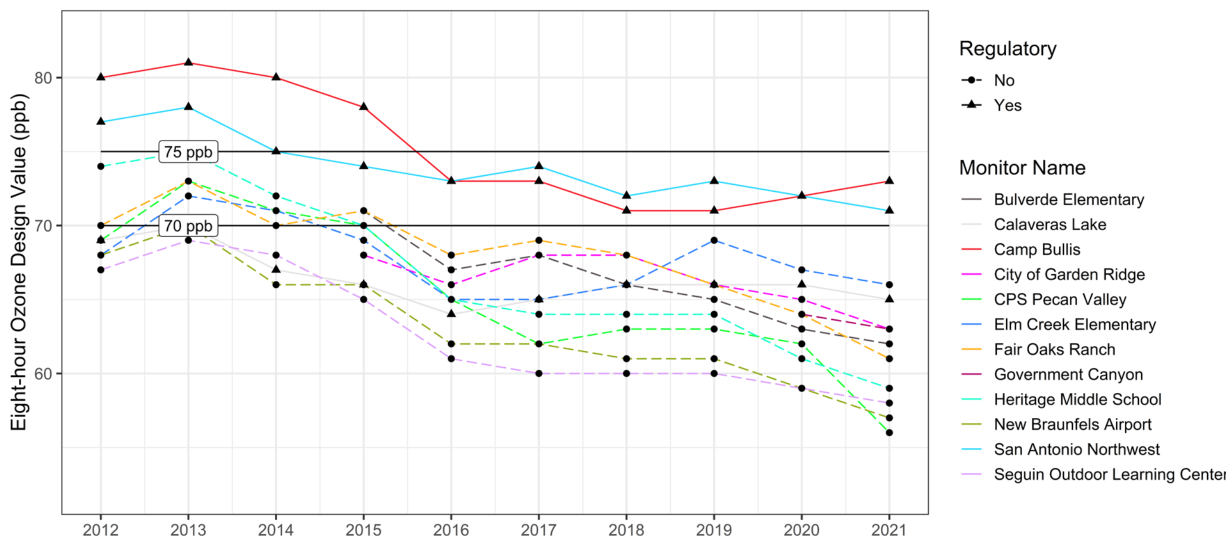

Figure 2-2: Eight-Hour Ozone Design Values by Monitor in the San Antonio Area

Displaying design values on a map can give better insight into ozone formation patterns. Eight-hour ozone design values in the San Antonio area from 2012, 2016, and 2021 were interpolated spatially using the kriging method. This analysis uses both regulatory and non-regulatory monitors to get better spatial coverage. Figure 2-3: *Eight-Hour Ozone Design Value Maps for the San Antonio Area* shows maps of design values from 2012, 2016, and 2021. The new Government Canyon monitor provides increased western spatial coverage in the 2021 map. The regulatory monitors are marked with stars.

The maps demonstrate how much eight-hour ozone design values have decreased across the entire San Antonio area. In addition to overall decreases, increased spatial heterogeneity is observed in 2021 compared to 2012. While values have changed dramatically, a consistent spatial pattern is observed across the study period. In 2012, the highest design values were concentrated in the northwest part of the city and the monitors east of the city have the lowest design values, a pattern that still holds true. This suggests prevailing winds from the east or southeast carry precursors and ozone across downtown San Antonio to the northwest of the city. However, there has been a shift in ozone concentrations observed southwest of the city at the Heritage Middle School monitor. In 2012, it recorded a design value on par with monitors north of town, 75 ppb. However in 2016 and 2021, its design value was considerably lower than the northern monitors. As discussed in Section 3.3.4. this may be evidence of the positive effects from lowered electric generating units (EGU) NO_X emissions southeast of town.

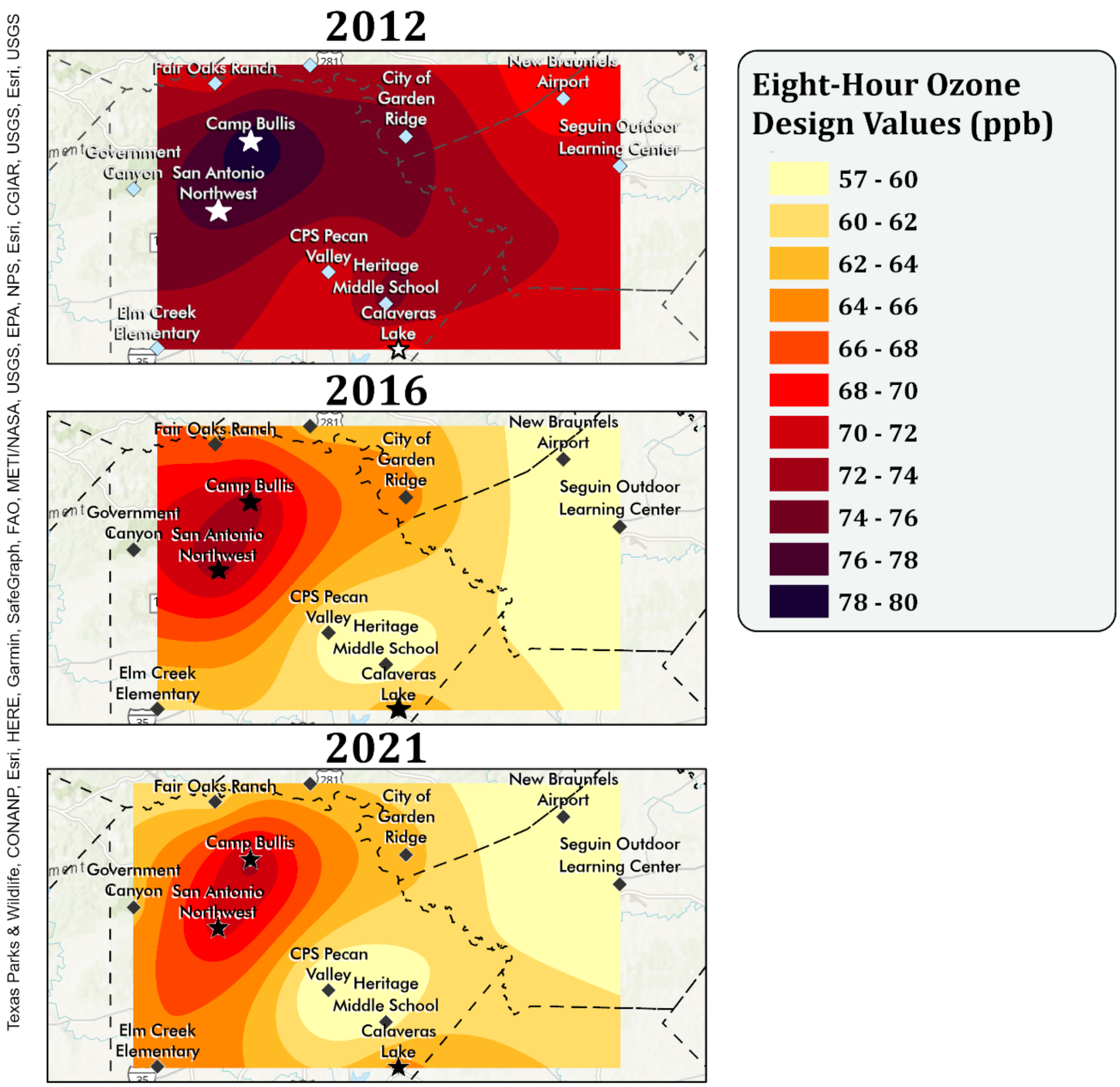

Figure 2-3: Eight-Hour Ozone Design Value Maps for the San Antonio Area

2.2 FOURTH-HIGHEST EIGHT-HOUR OZONE

Since design values are averages of three years of data, it is also useful to examine the trends in each monitor's fourth-highest daily maximum eight-hour average (MDA8) ozone concentrations for each year. Variability in fourth-highest MDA8 concentrations can help determine what years may have been affected by unusual meteorology or by local events.

Figure 2-4: *Fourth-Highest Eight-Hour Ozone Values in the San Antonio Area* shows there is high year to year variability, but overall the fourth-highest MDA8 ozone concentrations are trending downward. The year-to-year variability is experienced by all monitors, indicating climatological influences. The regulatory monitors, San Antonio Northwest and Camp Bullis, exhibit the highest values across the San Antonio area. The Camp Bullis monitor observed a sharp increase in ozone in 2020 and 2021 consistent with the pattern of many other monitors. The third regulatory monitor, Calaveras Lake, exhibits lower ozone values compared to San Antonio Northwest and Camp Bullis for all years studied.

The highest eight-hour ozone in the area occurred in 2012, 2013, and 2015, resulting in the elevated eight-hour ozone design values from 2012 through 2015. The lowest values for the area were also higher during 2012, 2013, and 2015, indicating high background ozone during those years

Fourth-highest eight-hour ozone value trends can help determine which years may have been influenced by meteorology. When all the monitors show either an increase or a decrease in fourth-highest ozone values, climatological influence is possible. The fourth-highest eight-hour ozone values in San Antonio indicate that ozone in 2014, 2016, and 2018 may have been affected by unique meteorology. In 2014 and 2016 there was an area-wide decrease in fourth-highest eight-hour ozone values, and in 2018, there was an area-wide increase.

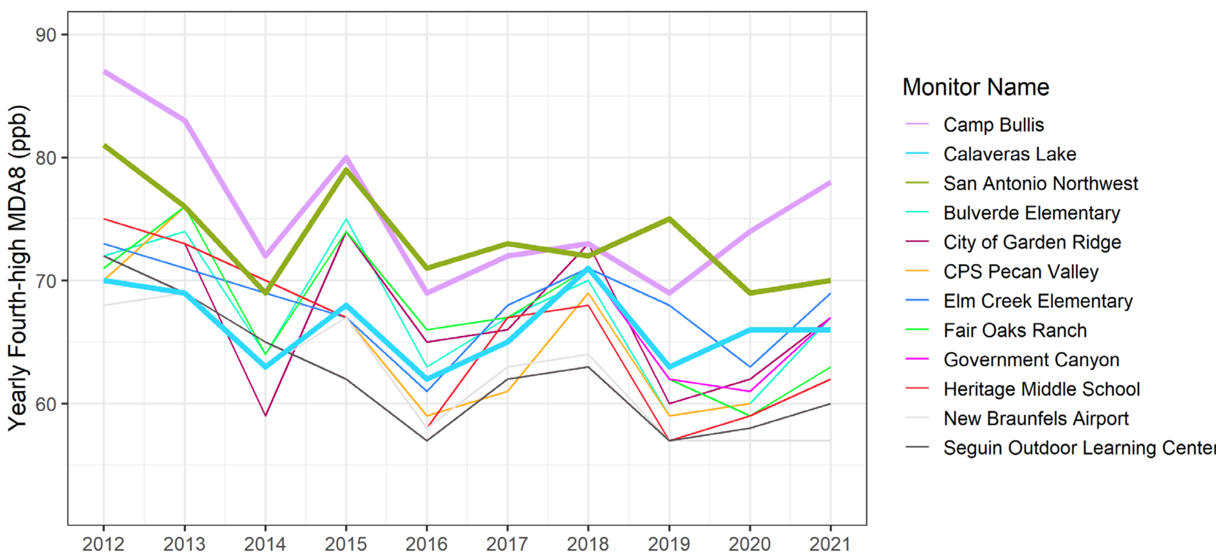

Figure 2-4: Fourth-Highest Eight-Hour Ozone Values in the San Antonio Area

2.3 EXCEEDANCE DAYS

An ozone exceedance day is defined as any day with at least one monitor measuring an MDA8 ozone concentration greater than a particular standard. If two monitors exceed in one day, that day is counted once. Examining the frequency and severity of exceedance days can further characterize each year's ozone season. The regulatory monitors and three eight-hour ozone standards were examined for this analysis. Figure 2-5: *Exceedance Days in Bexar County 2015 Ozone NAAQS Nonattainment Area* shows there is large variability in the number of exceedance days year-to-year. Since 2018, there have been no days when the MDA8 reached over 84 ppb, and they have been rare since 2016. There have been about half as many days that reached over 75 ppb in the most recent five years compared to the five years before that. Despite a sharp increase in 2020 and 2021, there were about 30% fewer days that reached over 70 ppb in the most recent five years compared to the prior five. Monitor level trends (not shown) reveal that most exceedance days occur at Camp Bullis and its trends align closely to what is seen area wide. San Antonio Northwest has shown a steady downward trend in its exceedance days for all three standards over the past ten years. Overall, the frequency of exceedance days indicates progress towards lowering ozone concentrations in the Bexar County 2015 ozone NAAQS nonattainment area.

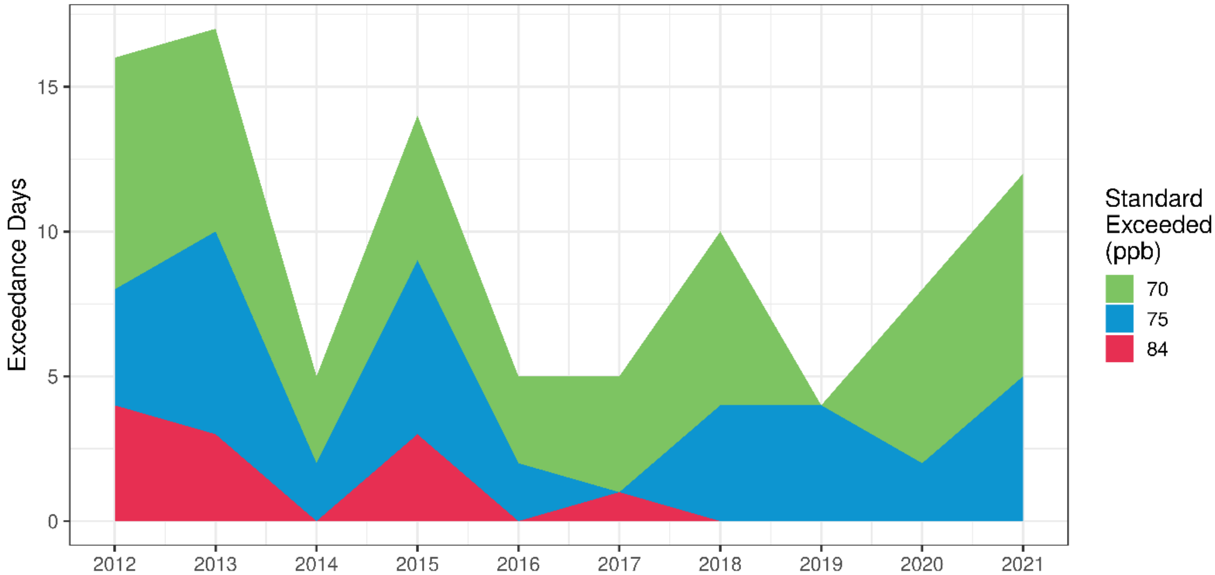

Figure 2-5: Exceedance Days in Bexar County 2015 Ozone NAAQS Nonattainment Area

2.4 OZONE SEASON

Analysis of the ozone season can provide insight into when ozone forms in the Bexar County 2015 ozone NAAQS nonattainment area. One way to determine the ozone season is to examine what months observe the most ozone exceedance days. Previous conceptual models for the Houston-Galveston-Brazoria area and the Dallas-Fort Worth area have shown that ozone season in many areas of Texas, including the Bexar County 2015 ozone NAAQS nonattainment area, has two peaks in ozone exceedance days (TCEQ 2019a, TCEQ 2019b). The first peak occurs in the late spring/early summer months of April through June, and the second peak occurs in the late summer/early fall months of August through October. These areas exhibit fewer high ozone days in July, commonly referred to as the mid-summer minimum in ozone concentrations. This minimum is likely caused by the dominance of high pressure in the southeast United States (U.S.), which results in air flow from the Gulf of Mexico over eastern Texas, therefore bringing cleaner and more humid gulf air into the region (Davis et al. 1998; Chan and Vet, 2010; Smith et al. 2013).

The frequency of exceedance days by month was used to characterize ozone season in the Bexar County 2015 ozone NAAQS nonattainment area. Figure 2-6: *Exceedance Days in the Bexar County 2015 Ozone NAAQS Nonattainment Area by Month* shows the frequency of exceedance days for the three eight-hour ozone standards from 2012 through 2021. This analysis corroborates the findings in Houston and Dallas; the ozone season exhibits two peaks with the mid-summer minimum occurring in July. Unlike Houston and Dallas, exceedances in Bexar County 2015 ozone NAAQS nonattainment area during March are quite rare, only one has occurred in this ten-year period. It is also apparent that most exceedance days typically occur in the latter half of the ozone season, August through October.

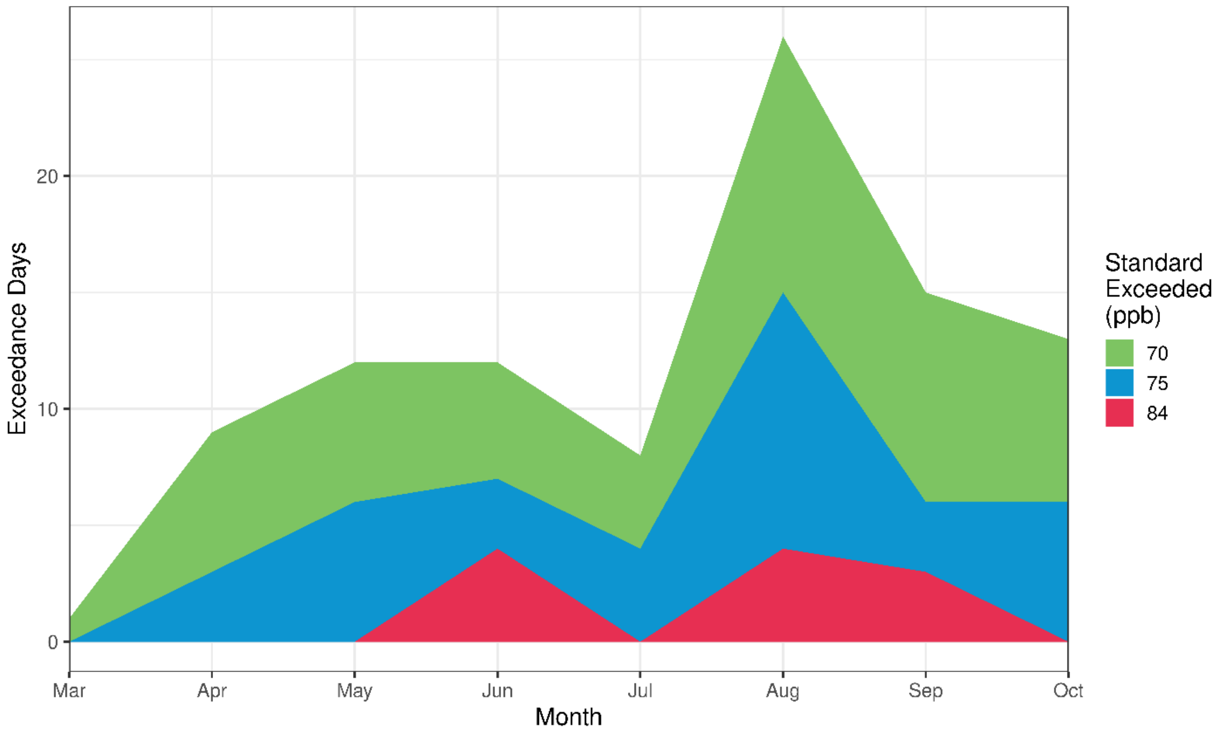

Figure 2-6: Exceedance Days in the Bexar County 2015 Ozone NAAQS Nonattainment Area by Month

The distribution of exceedance days was also analyzed for individual years. Figure 2-7: *Exceedance Days Over 70 ppb by Month and Year in the Bexar County 2015 Ozone NAAQS Nonattainment Area* shows that the distribution of exceedance days through the ozone season is not consistent across years. This is likely due to fluctuations in meteorology, as discussed in Section 2.3 and Chapter 5.

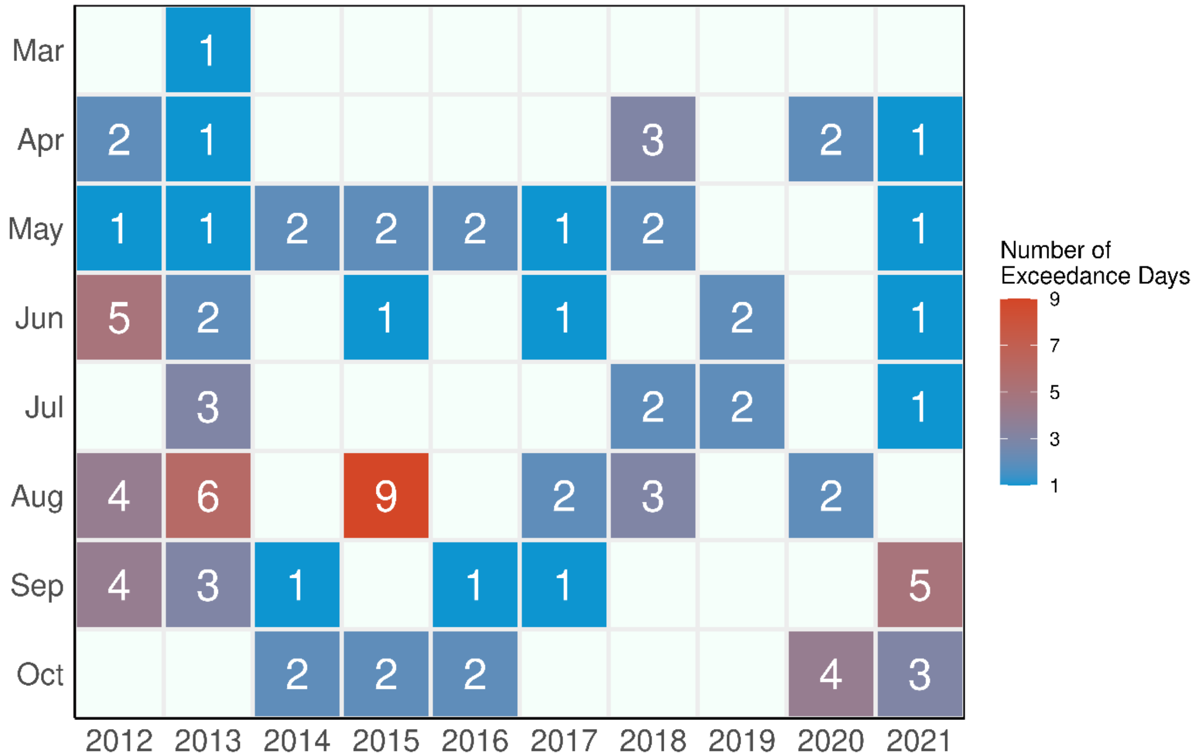

Figure 2-7: Exceedance Days Over 70 ppb by Month and Year in the Bexar County 2015 Ozone NAAQS Nonattainment Area

This analysis shows that the months conducive to ozone formation are March through October. The remainder of this conceptual model focuses on these months, which will be referred to as ozone season, unless otherwise noted.

2.5 TIME OF PEAK OZONE

Another way to investigate the temporal pattern of ozone is to look at the time of day when peak ozone occurs. In addition, differences in the time of peak ozone by monitor location may give insight into the origins of ozone formation in the area. The previous conceptual model for the Bexar County 2015 ozone NAAQS nonattainment area investigated the spatial-temporal variation in peak ozone in the San Antonio area (TCEQ, 2020). High ozone days and low ozone days were investigated separately, with high ozone days defined as any day with an MDA8 ozone greater than 70 ppb and a low ozone day as any day with an MDA8 ozone less than or equal to 70 ppb. This definition of high and low ozone days will be used throughout the remainder of the conceptual model. The analysis revealed that on low ozone days there is less variation in the time of peak ozone compared to high ozone days. On high ozone days there is increased temporal variation with ozone first peaking at monitors close to downtown followed by monitors in the northwest (often downwind of downtown). This delay is likely caused by the slow wind speeds that allow for ozone and precursor accumulation on high ozone days. The spatial relationship may indicate that ozone is first formed in the center of the San Antonio city area and then further photochemically aged while it moves to the outskirts of the city, leading to the higher concentrations observed at the northwestern monitors.

2.6 BACKGROUND OZONE

Regional background ozone can be defined as ozone present in the air entering a city from outside the city limits, or as ozone in the local air mass that has not been influenced by emissions from the city of interest. There are several ways that regional background ozone has been estimated, but none of those techniques are a perfectly accurate measure of the ozone that would be present in the absence of local emissions. Nonetheless, observational estimates of background ozone are important approximations of the magnitude of local emissions versus those outside the control of a particular city.

This analysis used the method described in Berlin et al. 2013 to estimate background ozone. This method identifies a subset of monitoring sites that lie on the periphery of the urbanized area and are not strongly influenced by nearby emission sources to estimate background ozone. In San Antonio, these monitors were Calaveras Lake, Elm Creek Elementary, Fair Oaks Ranch, Heritage Middle School, Government Canyon, Bulverde Elementary, City of Garden Ridge, New Braunfels Airport, and Seguin Outdoor Learning Center. The lowest MDA8 ozone observed at this subset of monitors is then considered the background ozone value for that day. This technique is conservative, in that if a gradient exists in background ozone, the technique will choose the low end of the gradient. In other words, based on observational data, the background ozone cannot be lower than the chosen value. Local ozone production is then approximated by finding the highest MDA8 ozone of all the monitors in the area and subtracting the estimated background value. Again, based on observational data, this allows for the most liberal estimate of local ozone production by using the lowest possible value for background ozone and the highest possible concentration for resultant ozone. For all analyses in this section, a modified ozone season is used (April through October) because several non-regulatory monitors used to characterize the background ozone concentration do not monitor in March, causing misestimates for background ozone during March.

The trends observed in background ozone for the modified ozone season from 2012 through 2021 in the San Antonio area were separated into high ozone days and low ozone days. Results are shown in Figure 2-8: *Background and Locally Produced Ozone During the Modified Ozone Season for Years 2012 through 2021 Separated by High and Low Ozone Days in the San Antonio Area*. In the ten years analyzed, 134 days were identified as high ozone days and about 2,200 days were identified as low ozone days. This disparity in sample size may contribute to the lower variability observed on low ozone days and should be considered throughout this analysis. One of the monitors, Heritage Middle School monitor, which typically measures background ozone for about 100 days per year, was not functioning properly in 2018. This may cause artificially high background ozone estimates for that year.

Background ozone has high year-to-year variability but overall shows a slight downward trend for both high and low ozone days. There have been no abnormal peaks in background ozone. A few abnormal dips occurred in 2016 and 2020, especially on the high ozone days. The anomaly in 2016 may be explained by atypical meteorology, which is estimated to have caused lower ozone values at sites in San

Antonio area and throughout the South (EPA 2022), see Section 2.4 for more details. For both high and low ozone days, estimated background ozone was the lowest in 2020.

Local ozone production is trending slightly upward for both high and low ozone days and shows similar amounts of yearly variability. Locally produced ozone on high ozone days has been the most variable in the past six years, fluctuating between 17 ppb in 2018 up to 32 ppb in 2020. In 2021, it returned to a level more consistent with past years, 22 ppb. Low ozone days are more consistent across the ten-year period.

When investigating percent contributions, on average over the past ten years, background ozone has contributed about 73% to MDA8 ozone concentrations on low ozone days, meaning that locally produced ozone contributes roughly 27%. These contribution averages are nearly identical for high ozone days, 72% and 28% respectively. On low ozone days, the contribution of locally produced ozone ranges from 22% in 2015 to 39% in 2020. On high ozone days, it ranges from 23% in 2018 to 42% in 2020. The percent contribution of background ozone for each year follows the same pattern in the high and low ozone day datasets. This indicates that large scale meteorological patterns likely influence each year's ozone season.

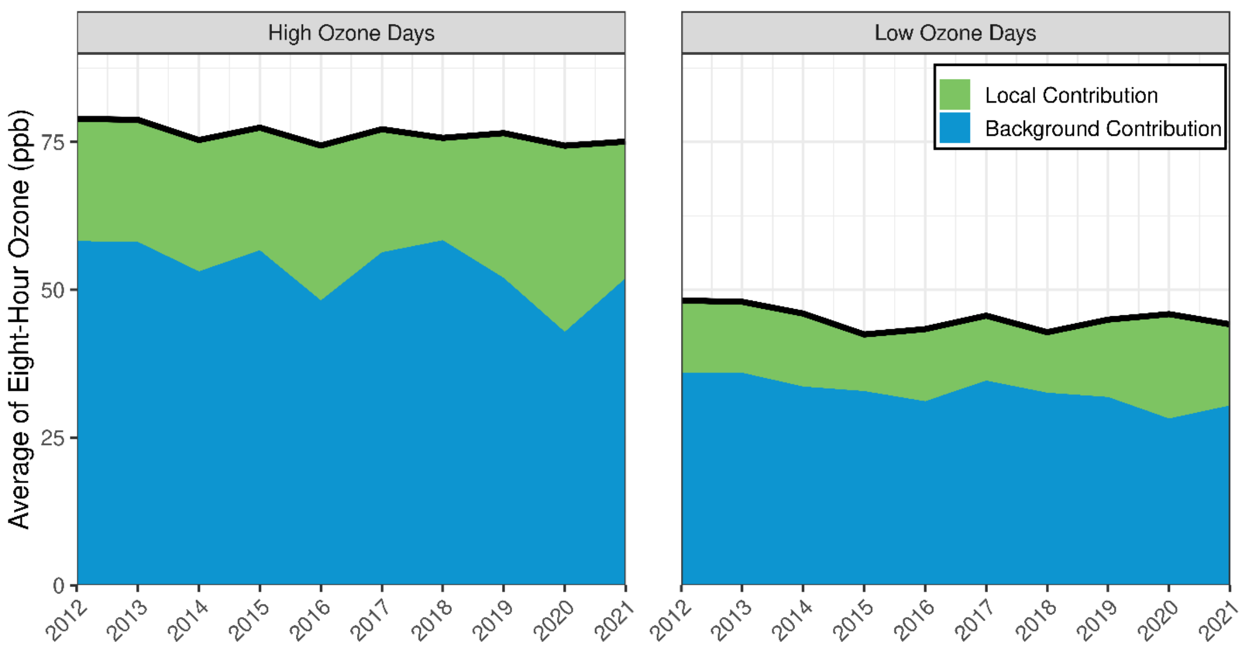

Figure 2-8: Background and Locally Produced Ozone During the Modified Ozone Season for Years 2012 through 2021 Separated by High and Low Ozone Days in the San Antonio Area

Figure 2-9: *Background Ozone for All Days in the Modified Ozone Season in the San Antonio Area* shows days with a scatter plot of background contribution values, with those over 55 ppb in red and a line of best fit, fitted using a generalized additive model, in green. The downward trend in background ozone is evident both from the downward trend of the fitted line (starting at around 39 ppb in 2012 and ending around 30 ppb in 2021) and from the decreasing frequency of days with background ozone over 55 ppb.

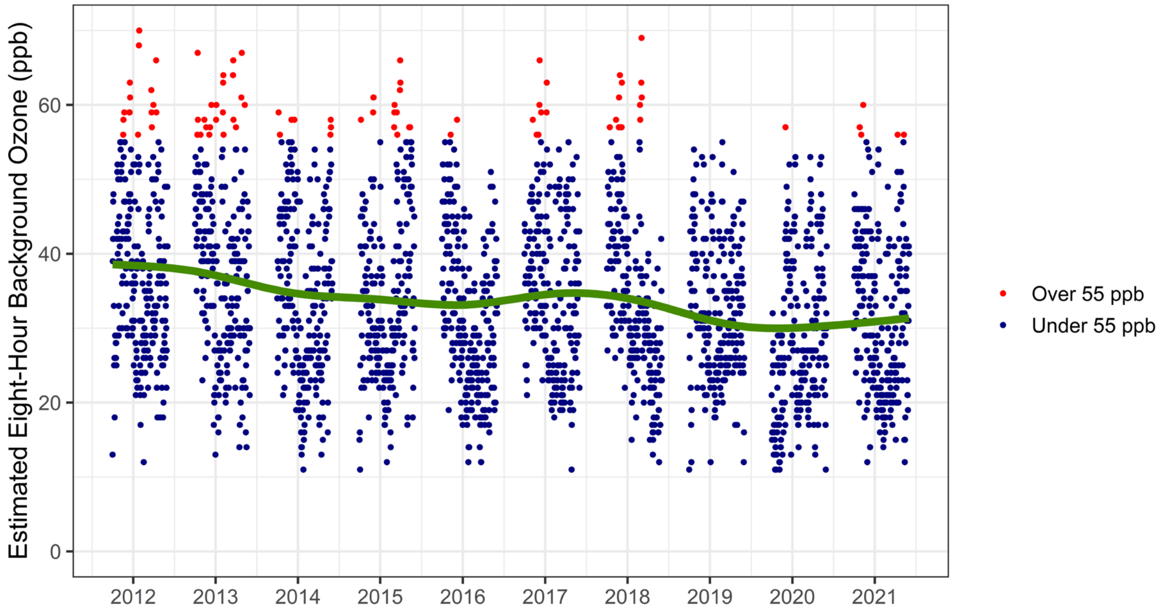

Figure 2-9: Background Ozone for All Days in the Modified Ozone Season in the San Antonio Area

Figure 2-10: *Estimated Locally Produced Ozone for All Days in the Modified Ozone Season in the San Antonio Area* shows a scatter plot of locally produced ozone contributions. Days with an estimated local contribution over 30 ppb are highlighted in red and a line of best fit, fitted using a generalized additive model, is shown in green. The local ozone production lacks the distinct trend that background ozone estimates showed. Local ozone production was abnormally high in 2020. The level of the lower values has increased, causing a slight increasing trend in local ozone production.

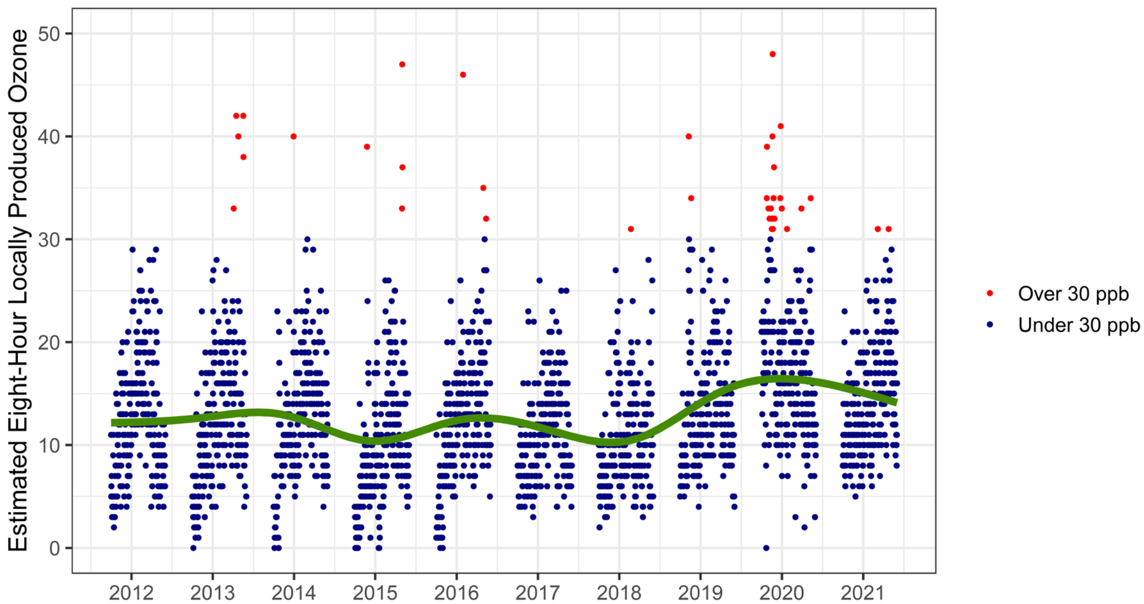

Figure 2-10: Estimated Locally Produced Ozone for All Days in the Modified Ozone Season in the San Antonio Area

To understand how time of year affects ozone, the background and locally produced ozone was investigated on a monthly basis. Results are shown in Figure 2-11: *Background and Locally Produced Ozone Averaged by Month for Years 2012 through 2021 Separated by High and Low Ozone Days in the San Antonio Area*. As previously discussed, the sample size for low ozone days was bigger than for high ozone days for all months.

Background ozone exhibits a very different pattern on high versus low days. On high ozone days, background ozone shows maximums in June and August, minimums in April and October, and a small dip in July. Low ozone days show maximums in April and May, and a minimum in July. Background ozone is more variable on low ozone days, varying 32%, from 28 ppb in July to 37 ppb in May and August. Conversely, background ozone on high ozone days only varies 9%, from 53 ppb in April to 58 ppb in June and August. The evidence suggests that background ozone is more influenced by month-to-month meteorological patterns on low ozone days. This corroborates with the heuristic that ozone forms best under specific weather conditions such as high temperature, slow wind speed, and further suggests that these weather conditions are likely synoptic, causing high ozone production at a regional scale.

As discussed in the previous section and in Chapter 5, a mid-summer minimum is caused by a shift in the Bermuda High during July which causes winds to prevail from the gulf most days. This phenomenon explains the pattern observed in the low ozone days' background concentrations. Locally produced ozone varies little across months. On high ozone days, locally produced ozone is slightly higher in April, September and October. On low ozone days, locally produced ozone is slightly higher in July and August. While these month-to-month differences are small, it is interesting that the pattern observed in the high versus low ozone datasets are opposite of one another.

Looking at the percent contribution of background and locally produced ozone shows that background ozone contributes the most to ozone concentrations in the San Antonio area.

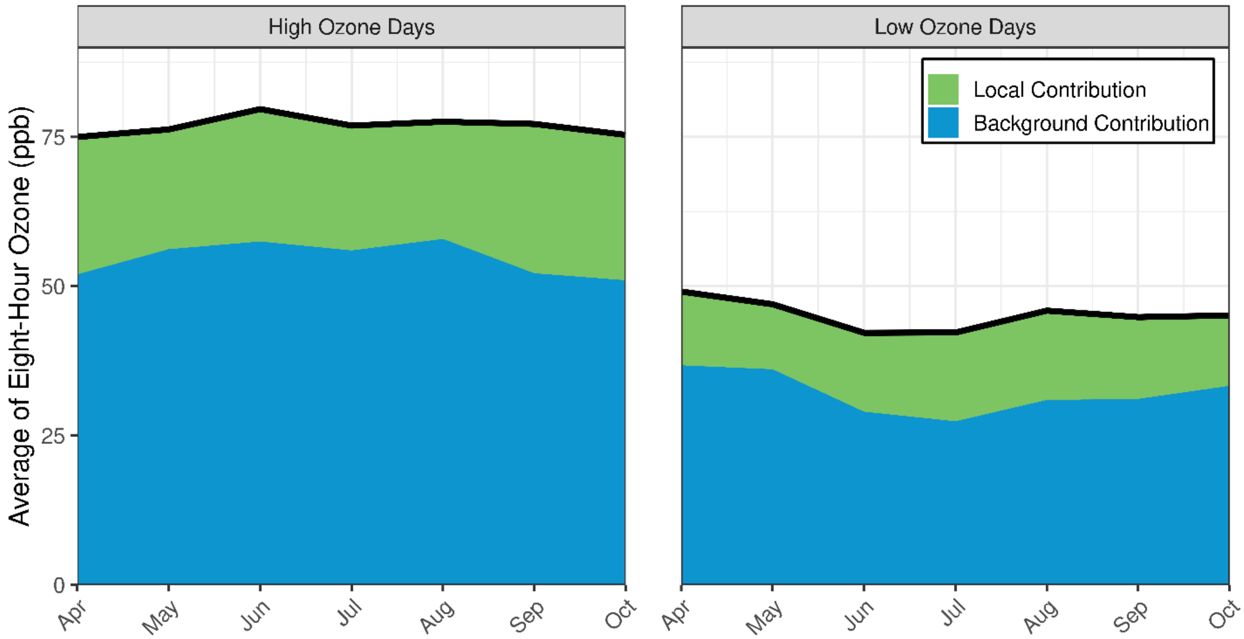

Figure 2-11: Background and Locally Produced Ozone Averaged by Month for Years 2012 through 2021 Separated by High and Low Ozone Days in the San Antonio Area

The findings of these analyses are further supported when combined with the results of the San Antonio Field Study, which investigated ozone production rates in San Antonio (Flynn et al. 2019). Over the course of several weeks ozone production rates were directly measured at sites up and down wind of the city core and modeled using in situ data at a site near downtown. Rates at the outer city sites were consistently under 15 parts per billion by volume per hour (ppbv/hour), with a median of 1 ppbv/hour (Anderson et al., 2019; Drexel, 2019). The estimated rate at the downtown site was 30-65 ppbv/hour (Anderson et al., 2019). These results support the finding that San Antonio has the potential to produce large amounts of ozone, as seen on high ozone days, but that typical rates of ozone production are quite low, as seen on low ozone days. It also reveals substantial spatial variation that may be explained by the location of precursor emissions, as will be explored in subsequent sections.

Trends in background ozone for both high and low ozone days correlate strongly with trends in MDA8 ozone. This is seen in Figure 2-12: *Daily Background Eight-Hour Ozone versus Daily Maximum Eight-Hour Ozone for the Ozone Season in the San Antonio Area from 2012 through 2021*. Ozone season data from 2012 through 2021 show that background ozone is well correlated with daily-maximum ozone, with a correlation coefficient of 0.75. This may indicate that trends in ozone concentrations for the San Antonio area are driven by changes in the background ozone. This also indicates that conditions that lead to high ozone within San Antonio also enhance ozone formation regionally (TCEQ, 2020). High ozone days are denoted with a line on the figure. With a few exceptions, high ozone days only occur on days with background ozone over 42 ppb, over twice that of the average background ozone seen on low ozone days.

The figure also indicates which year each point is from. Teal to navy color points are from recent years and yellow to green color points are from more distant years past. Upon inspection of this temporal relationship, an interesting pattern emerges. The data show that points under 70 ppb that are below the blue trend line are mostly from more distant years (green and yellow), while points above the trend line are more often from more recent years (teal and navy). Points below the trendline indicate that the resulting ozone concentrations were lower than may be expected for the level of background ozone estimated. Points above the trendline indicate the opposite, that the resulting ozone concentrations were higher than may be expected for the level of background ozone estimated. In more recent years on low ozone days, higher eight-hour ozone concentrations resulted from the same background ozone level, possibly indicating higher rates of local production on these days. This pattern is not seen in high ozone days. Most of the highest ozone concentrations were all recorded in more distant years. The exceedance days that associated with lower background concentrations are an almost equal mix of recent and distant years. Days with background concentrations over 60 ppb are very rare in recent years. This exemplifies the great strides that Texas has accomplished in its statewide air quality. It also indicates that exceedance days in the San Antonio region caused by extremely high background concentrations are diminishing.

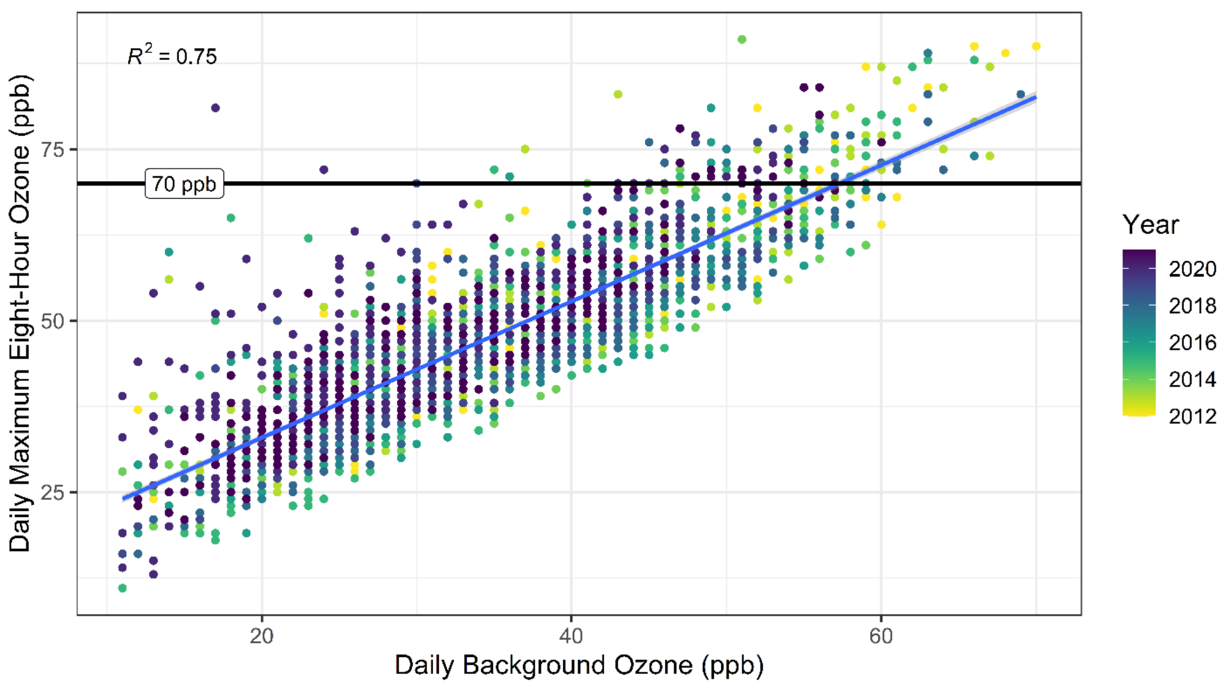

Figure 2-12: Daily Background Eight-Hour Ozone versus Daily Maximum Eight-Hour Ozone for the Ozone Season in the San Antonio Area from 2012 through 2021

CHAPTER 3: OZONE PRECURSOR CONCENTRATIONS AND TRENDS

As mentioned previously, ozone is not directly emitted into the atmosphere but formed through photochemical reactions with nitrogen oxides (NO_X) and volatile organic compounds (VOC). The complexity of ozone formation requires a comprehensive examination of these precursors to ozone formation. This section will focus on NO_X and VOC concentration trends, emission trends, and the chemistry that causes ozone formation in the San Antonio area.

3.1 AMBIENT NO_X TRENDS

NO_X, a precursor to ozone formation, is a variable mixture of nitric oxide (NO) and nitrogen dioxide (NO_2). NO_X is primarily emitted by fossil fuel combustion, lightning, biomass burning, and soil. Examples of common NO_X emission sources, which occur in all urban areas, are automobile, diesel, and small engines; residential water heaters; industrial heaters and flares; and industrial and commercial boilers. Mobile, residential, and commercial NO_X sources are usually numerous, smaller sources distributed over a large geographic area, while industrial sources are usually large point sources, or numerous small sources, clustered in a small geographic area. Sources of NO_X that are important to air quality in the San Antonio (SAN) area are mobile sources and large electric generation units (EGUs), especially in the area southeast of the city near Calaveras Lake. Previous studies also observed NO_X decreases from 2009 through 2018 (TCEQ, 2020).

There have been 15 NO_X monitors operated at some point from 2012 through 2021 in the San Antonio area; however, only three to eight NO_X monitors have 75% valid days in any given ozone season. In 2021, there were eleven NO_X monitors in the San Antonio area, with four in Bexar County. Five began collecting data in 2021. Calaveras Lake is the only NO_X monitor to have continuous, valid data for 2012 through 2021; however, several other monitors have at least seven years of data in that 10-year period. To focus on the monitors most pertinent to Bexar County air quality, the Floresville and Karnes County monitors are not included in this analysis.

NO_X trends are displayed in Figure 3-1: *Ozone Season Median Daily Maximum NO_X Trends for the San Antonio Area*. For this analysis, the daily maximum one-hour concentration at each monitor was determined and then the median calculated for all days in the ozone season. Only years that have at least 75% valid days (days with at least 75% of hours measured) for the ozone season are displayed and only monitors with at least three years of valid data are shown. The figure shows that the NO_X monitor located near the interstate, San Antonio Interstate 35, regularly measures NO_X concentrations twice that of the other monitors. San Antonio Northwest measures higher NO_X than the other non-roadside monitors and Camp Bullis measures the lowest NO_X.

Overall, there are not any strong trends in NO_X concentrations. There appears to be a slight downward trend in the yearly median at the Camp Bullis and San Antonio Northwest monitors, but the changes are subtle. In 2018 there was a large dip in the median daily-maximum NO_X at the San Antonio Interstate 35 (I-35) monitor, because 2019 also saw lower values, it is likely that 2018 did see moderate changes in anthropogenic activities, but there may have also been unique metrological phenomenon, likely wind direction and speed, that exacerbated these changes to activity.

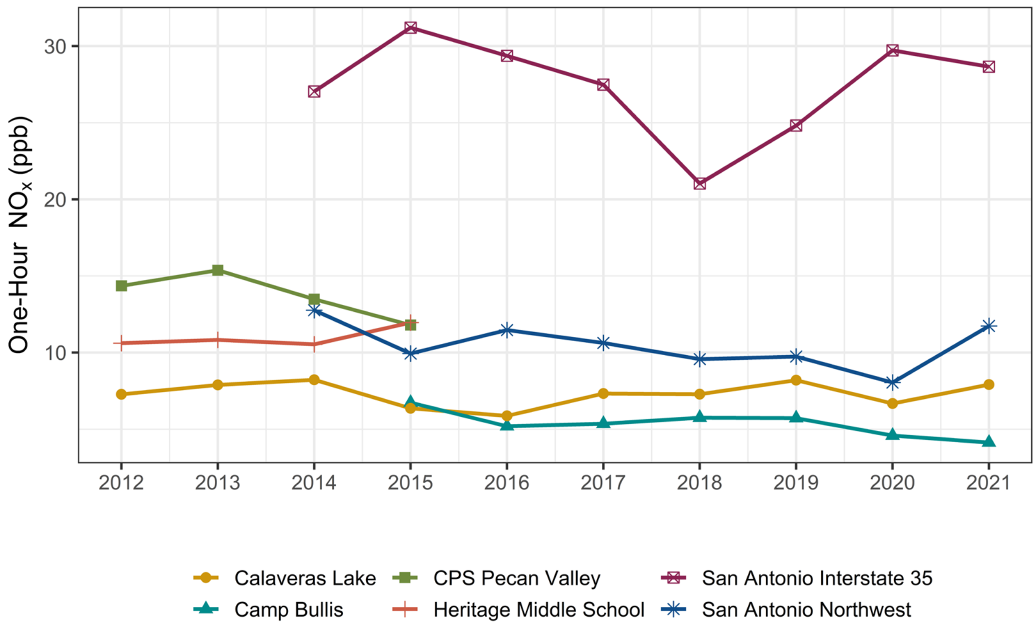

Figure 3-1: Ozone Season Median Daily-Maximum NO_x Trends for the San Antonio Area

Area-wide NO_x trends can also be examined to reveal more information about the distribution of NO_x concentrations and how they change over time. By looking at multiple percentiles of data more patterns can emerge. First, the daily maximum one-hour NO_x concentration for each monitor was determined. Then, the monitors were split up between roadside, i.e., San Antonio I-35, and non-roadside (all the other monitors). For each of these classifications, the highest daily maximum was selected for each day. Figure 3-2: *San Antonio Area Daily Maximum One-Hour NO_x Percentile Trends, Separated by Roadside (I-35) and Non-Roadside Monitors* shows the annual 98th, 75th, 50th, and 25th percentiles of that dataset. To ensure that yearly data were not artificially skewed by the addition or removal of monitors, only years with valid data for all three non-roadside monitors were included (2015 through 2021).

The 98th percentile of non-roadside monitors has decreased about 10 ppb over the six years studied. The roadside monitor's 98th percentile has also decreased significantly since 2014 but has been trending upward for the most recent four years. Different patterns emerge at lower percentiles. At the non-roadside monitors, there is a very slight downward trend in the 75th percentile, but no trend in the median or 25th percentile. For the roadside monitor, the 75th percentile exhibits a very similar pattern to the 98th percentile but does not show as much overall decrease over the eight year period. The median and 25th percentiles show no change. Overall, this indicates that the highest concentrations of NO_x are trending downward in most of the city but may be trending up in recent years near sources of high vehicle traffic. It also shows that median NO_x concentrations have not improved over the past six to eight years at any monitors in the city.

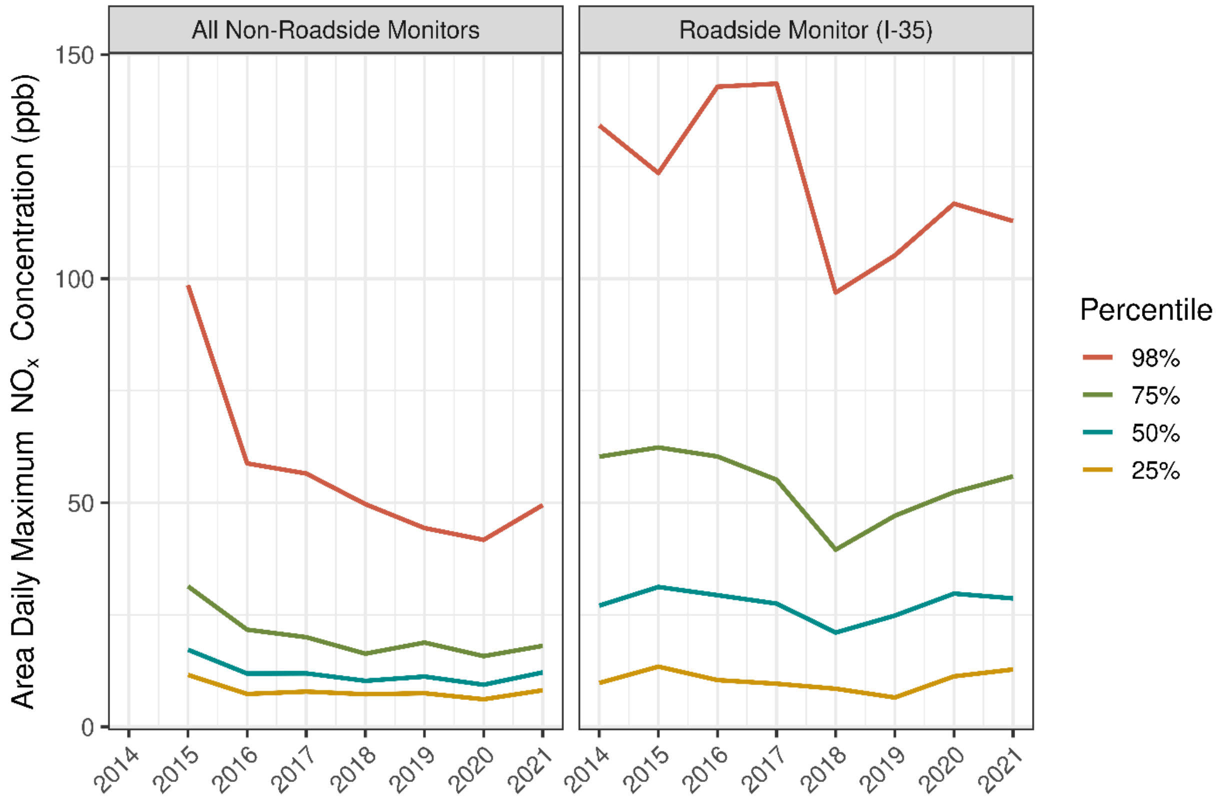

Figure 3-2: San Antonio Area Daily Maximum One-Hour NO_x Percentile Trends, Separated by Roadside (Interstate 35) and Non-Roadside Monitors

NO_x trends were also compared to ozone trends to see if there was any correlation in the trends between the two pollutants. The analysis used one-hour NO_x concentrations and one-hour ozone concentrations at the three sites with collocated ozone and NO_x monitors. Data from 2012 through 2021 was used for Calaveras Lake and San Antonio Northwest, but NO_x data at Camp Bullis was only available for 2015 through 2021. Data were filtered for days with at least 75% data validity during daylight hours, defined at 7:00 local standard time (LST) through 22:00 LST, then all daylight hours of ozone and NO_x data within the ozone season were averaged for each year. Values for 2015 were then normalized to 100% for all monitors. Normalizing the data allows for a more direct comparison of trends and can also easily show any percent change in the concentrations. By using the same year as the normalizing year for each monitor, the years may be compared more directly.

Results are displayed in Figure 3-3: *Normalized Annual Average NO_x and Annual Average One-Hour Ozone for the Ozone Season at Calaveras Lake (left), Camp Bullis (center) and San Antonio Northwest (right)*. Several things can be observed in the trends. At Calaveras Lake, it appears that one-hour ozone and NO_x are somewhat correlated, but fluctuations in NO_x are much larger than fluctuations in ozone. At Camp Bullis, NO_x and ozone appear to be correlated in 2015 through 2017, but from 2018 on, large decreases in NO_x did not result in changes to the average ozone concentration. San Antonio Northwest has high variability in NO_x averages from year-to-year, but much less movement in the ozone averages.

Overall, there appears to be no consistent correlation between the two pollutants. Analysis of different yearly percentiles of NO_x and ozone hourly data did not reveal any additional relationships. As will be discussed later in Section 4.1: VOC and NO_x Limitations, this is an unexpected result. When ozone formation is NO_x limited, as the analysis in 4.1 indicates, we would expect to see more correlation between ozone and NO_x levels. The results of these analyses may indicate that NO_x emissions are aging and reacting to form other compounds, such as ozone, before reaching the Camp Bullis or other monitors and that the data presented here are not representative of the entire region.

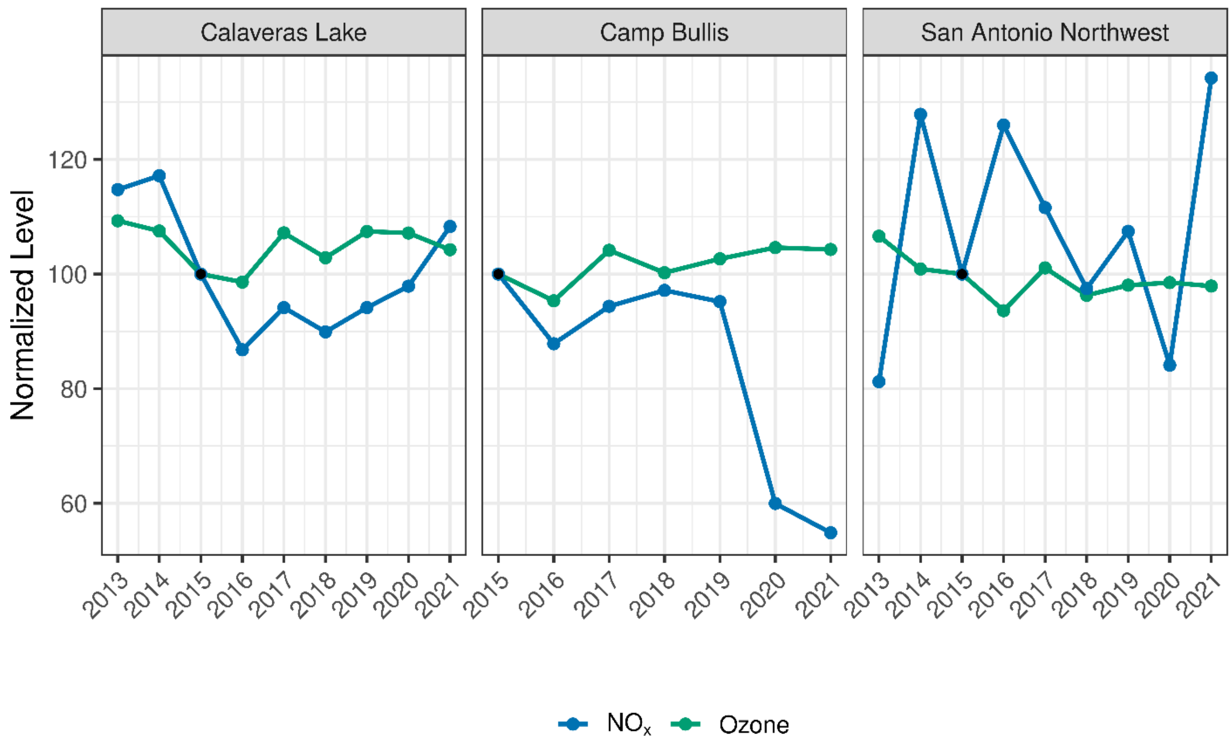

Figure 3-3: Normalized Annual Average NO_x and Annual Average One-Hour Ozone for the Ozone Season at Calaveras Lake (left), Camp Bullis (center) and San Antonio Northwest (right)

Comparing changes in the average of all hours of NO_x data and the average of only the daily maximum one-hour NO_x concentrations revealed key information. For all three monitors analyzed, Camp Bullis, San Antonio Northwest, and Calaveras Lake, the change in the annual average of daily maximums was greater than the change in the average of all hours. In fact, at San Antonio Northwest, the daily maximum average decreased by 25% from 2013 to 2021, but the average of all hours increased by 37%. This finding corroborates with the analysis of percentiles of NO_x hourly data presented in Figure 3-2 above. Both support the conclusion that high NO_x episodes are declining but the background or base NO_x concentrations are not changing or are rising slightly. This is further supported by the diurnal trends of NO_x concentrations, which were investigated in the previous conceptual model for Bexar County 2015 eight-hour ozone nonattainment area (TCEQ, 2020). The analysis revealed that San Antonio Northwest and Calaveras Lake exhibit peak NO_x concentrations in the morning, around 6:00 LST.

Over the years studied, the peak concentrations were decreasing but average concentrations during non-peak hours at San Antonio Northwest were higher in more recent years.

3.2 AMBIENT VOC COMPOSITION AND TRENDS

VOC play a central role in ozone production by oxidizing radicals. The San Antonio area has four VOC monitors. Two of these are in Bexar County 2015 ozone National Ambient Air Quality Standard (NAAQS) nonattainment area, an automated gas-chromatograph (auto-GC) at Camp Bullis and a canister sampler at Old Highway 90. There are two auto-GCs southeast of Bexar County at Floresville Hospital Boulevard (hereby Floresville) and Karnes County. auto-GC collect data in 40-minute intervals every hour and canister sites collect data in 24-hour intervals every six days. The data collected by the two methods are comparable but are typically analyzed separately due to the different time scales.

There is limited VOC data availability in San Antonio because the monitors are relatively new and have faced some quality assurance issues. The canister site at Old Highway 90 started measuring data in 2009 and is the most reliable for long term trends. The following analyses will use data from all four sites to investigate VOC composition and trends over the time periods of data available.

Some analyses will use a maximum incremental reactivity (MIR) index to weight the concentrations of VOC species. The MIR index is proportional to the ozone formation potential of a particular VOC (Carter, 2010). Scaling concentrations by the MIR can inform on which species may be contributing the most to ozone formation in an area.

3.2.1 VOC Composition

To understand ozone formation in San Antonio, it is important to first understand the overall composition of VOC and which VOC contribute the most to ozone formation. First, data from monitors within Bexar County will analyzed, then data from monitors outside Bexar County will be considered. For this analysis, two plots for each location will be shown. Each figure includes the 20 species in greatest abundance at each monitor. The plot on the left shows the median VOC concentrations for each species, ranked highest to lowest. The plot on the right shows the same median concentration weighted by MIR index, shown in the same order for comparison. This analysis considers data for all hours of the day during ozone season.

The median VOC concentrations, in parts per billion by volume (ppbV), for the top 20 VOC species at Camp Bullis from 2017 through 2021 are shown in Figure 3-4*: Camp Bullis VOC Species in ppbV (left) and Weighted by MIR Index (right)*. Camp Bullis is in a less urban area, about 13 miles from downtown, and this is reflected in its VOC composition. Low-reactivity alkanes ethane, propane, and n-butane are present in the greatest abundance at Camp Bullis. Of the non-alkane compounds, isoprene is present in the greatest amount.

However, when considering the median concentrations weighted by MIR, a different pattern emerges. When weighted by MIR, isoprene is over three times higher than any other species of VOC. Isoprene, known primarily as a biogenic VOC, is produced from trees and other vegetation. The area around Camp Bullis has a high density of oak trees and other vegetation, which is the likely cause for this high isoprene. The next group of VOC species with similar weighted concentrations includes low reactivity alkanes, that are present in high concentrations without weighted by MIR. Last group of VOC species, alkenes and aromatic compounds, such as ethylene, propylene, and toluene, that are highly reactive and have high ozone formation potential.

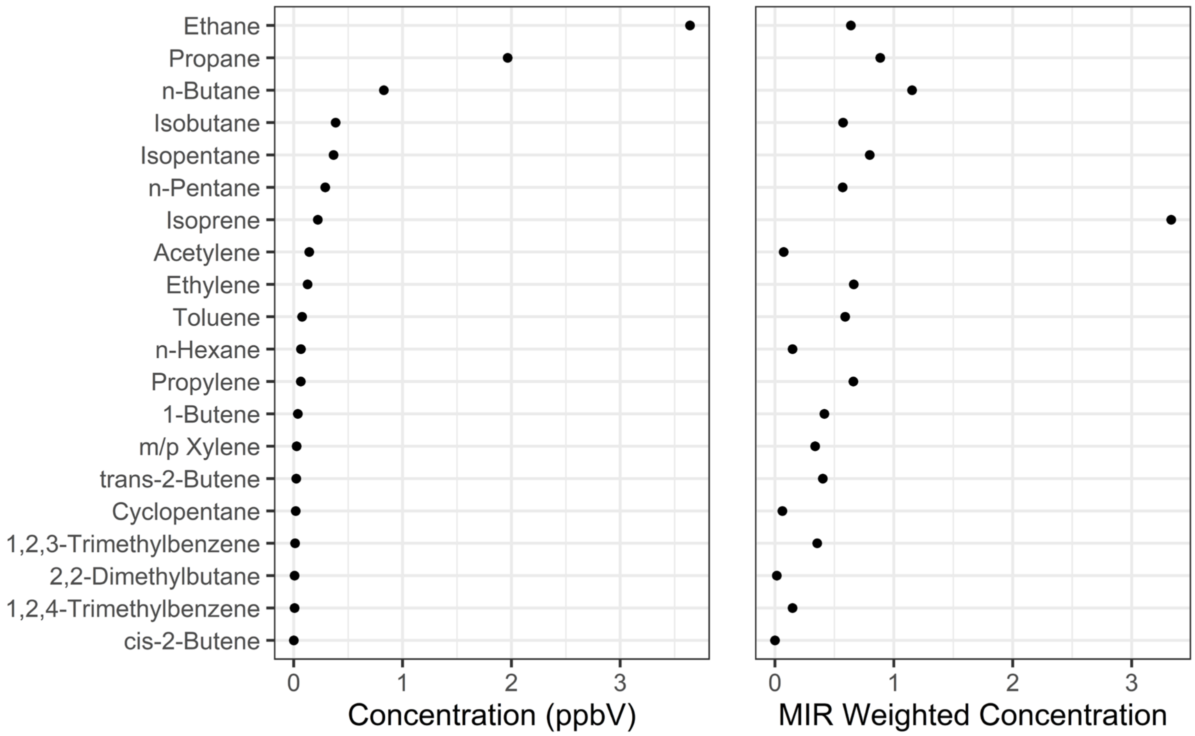

Figure 3-4: Camp Bullis VOC Species in ppbV (left) and Weighted by MIR Index (right)

The highest 20 VOC species at the Old Highway 90 canister site are shown in Figure 3-5: *Old Highway 90 VOC Species in ppbV (left) and Weighted by MIR Index (right)*. This analysis uses data from 2012 through 2021. This site is urban, just five miles almost due west of downtown San Antonio, which is evident in its VOC composition. Like Camp Bullis, ethane, propane, and n-butane contribute the most to total VOC at Old Highway 90. Compared to Camp Bullis, ethylene contributes more at Old Highway 90, but isoprene has a much lower contribution. When the MIR weighted concentrations are inspected, the data show that ethylene contributes much more to the total ozone formation potential than any other species. It is followed by toluene, another highly reactive species, and then n-butane and isopentane. Old Highway 90's proximity to consistent automobile traffic and location away from many biogenic sources drives most of the differences between it and Camp Bullis. This is evident in the higher ethylene contribution, which is attributed mainly to mobile sources, and lower isoprene contribution, which is attributed to biogenic sources.

The result of this analysis corroborates the findings from the San Antonio Field Study (SAFS), which also found that isoprene, along with formaldehyde and alkenes, contributed most to the VOC reactivity in the San Antonio area (Flynn et al. 2019, Flynn et al. 2018, Shrestha et al. 2022, Wood and Capps 2019, Yacovitch et al. 2017).

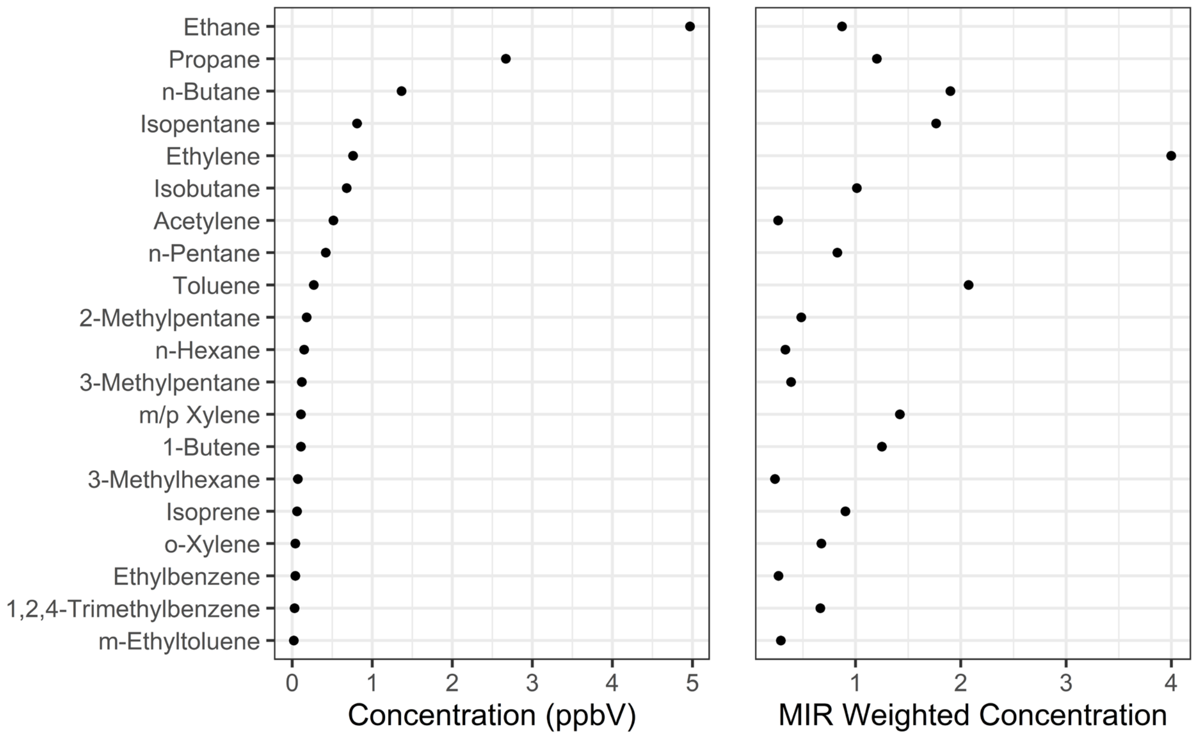

Figure 3-5: Old Highway 90 VOC Species in ppbV (left) and Weighted by MIR Index (right)

The data from outside of Bexar County 2015 ozone NAAQS nonattainment area were also analyzed to determine what VOC were coming into the area. The Floresville monitor is about 25 miles southeast of the city center and the Karnes County monitor is about 45 miles southeast of the city center. Both are located in the Eagle Ford Shale, an area with substantial oil and gas drilling operations. The scales on these figures are different from the scales on the two figures above, as the VOC concentrations at these two monitors are higher than those in the Bexar County 2015 ozone NAAQS nonattainment area.

Results for the Floresville monitor are shown in Figure 3-6: *Floresville VOC Species in ppbV (left) and Weighted by MIR Index (right)*. Like the Bexar County 2015 ozone NAAQS nonattainment area monitors, ethane, propane, and n-butane have the highest median concentrations; however, the MIR weighted plot presents several key differences compared to the Bexar County sites. Despite the very low reactivity of n-butane and propane (MIR index of 1.15 $gO_3/gVOC$ for n-butane vs. 9.00 $gO_3/gVOC$ for ethylene), they still have the greatest overall ozone formation potential at the Floresville monitor because of their sheer abundance.

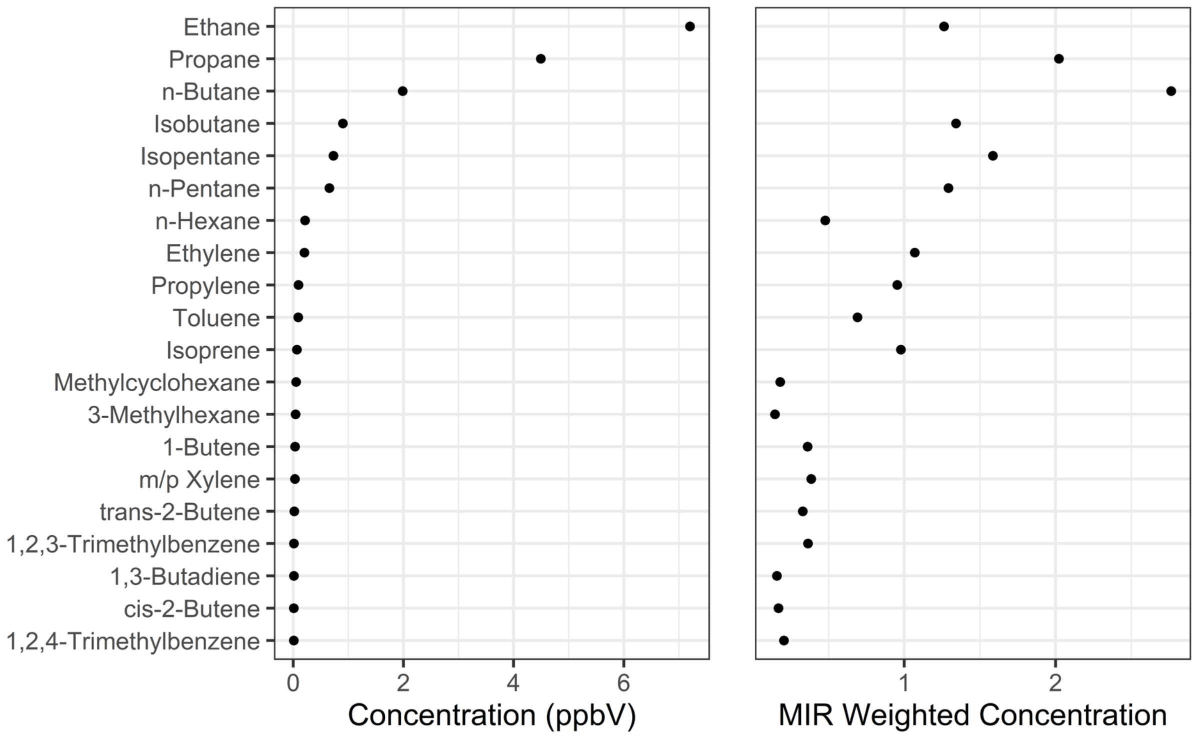

Figure 3-6: Floresville VOC Species in ppbV (left) and Weighted by MIR Index (right)

The top 20 VOC species at the Karnes County auto-GC are shown in Figure 3-7: *Karnes County VOC Species in ppbV (left) and Weighted by MIR Index (right)*. The composition at this monitor is very similar to that at the Floresville monitor. Ethylene is lower at the Karnes County monitor, possibly because it's located further from major roadways. The MIR weighted concentration of n-butane at the Karnes County monitor is even higher than the MIR weighted concentration of isoprene at the Camp Bullis monitor, an indication of the high concentration of low reactive VOC measured at the Eagle Ford Shale VOC monitors.

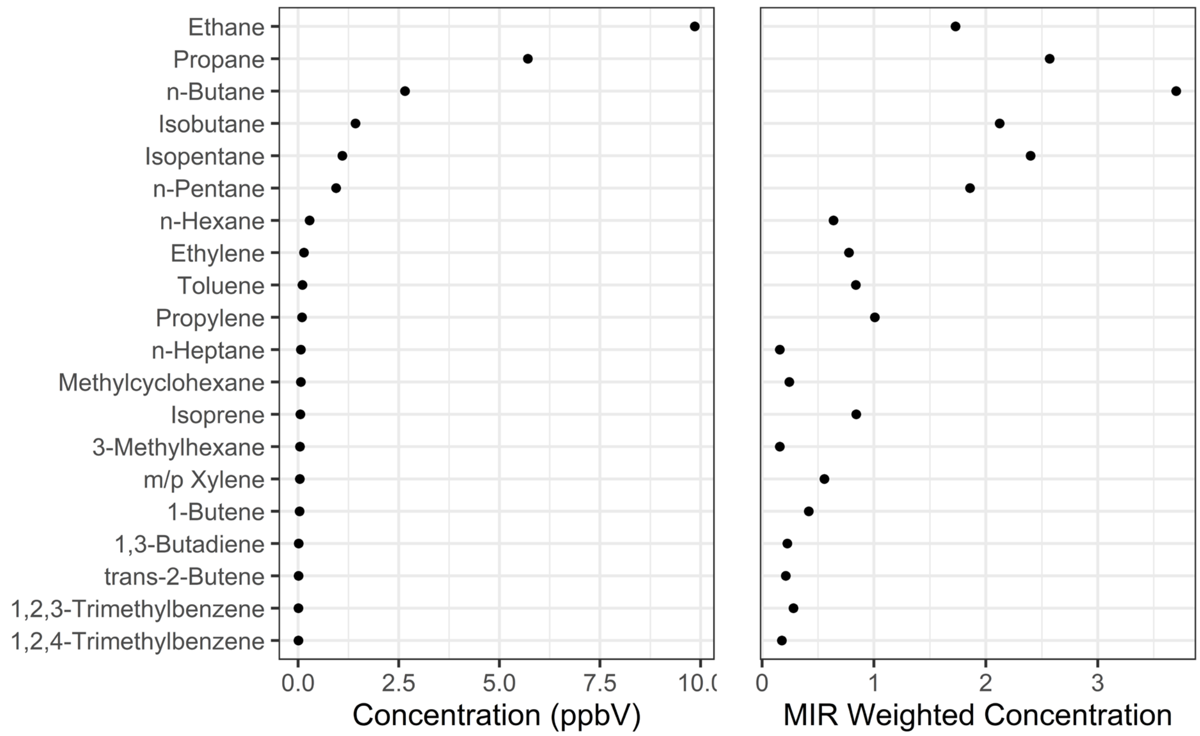

Figure 3-7: Karnes County VOC Species in ppbV (left) and Weighted by MIR Index (right)

3.2.2 Ambient VOC Trends in the San Antonio Area

Typically, the Texas Commission on Environmental Quality (TCEQ) investigates VOC classified as non-methane hydrocarbons. While methane is an organic compound, total non-methane hydrocarbons (TNMHC) is commonly used to distinguish the more reactive species of organic compounds from methane, which is naturally more abundant in the atmosphere, less reactive in the ozone formation process, and thus less relevant as a measure of precursor patterns. Trends in TNMHC concentrations, as a proxy for VOC, provide insight into variation in VOC levels. Unfortunately, there is no long-term TNMHC data available for Bexar County. Camp Bullis, the only auto-GC monitor in Bexar County, only started monitoring in 2016 and faced quality assurance issues in 2016 and 2019, leaving only four years with at least 60% data availability during the ozone season. Examination of this limited data can still offer insights into the area's air quality.

To explore the total VOC concentrations in the San Antonio area, all hours of TNMHC VOC data during the ozone season at each auto-GC site were considered. The canister site, Old Highway 90, was not included because a TNMHC value is not provided by this monitor type. Because the data is heavily skewed, looking at several percentiles can be more informative than the average or median. For this analysis, the 25th, 50th, 75th, and 95th percentiles were calculated for each year and the results displayed in Figure 3-8: *Yearly 25th, 50th, 75th, and 95th Percentiles of TNMHC Concentrations at auto-GC Sites in the San Antonio Area*. Only data during ozone season was included and only years with at least 60% data completeness during the ozone season are shown. An important note is that the scales for each site are different, with the total concentrations at Karnes County measuring at least ten times that at Camp Bullis.

At the Camp Bullis monitor, the VOC concentrations appear relatively consistent across the years studied, with slightly lower concentrations in 2021 than in 2017 for all percentiles; although with only four years of data it is difficult to decipher trends. At the Floresville monitor, a general upward trend since 2016 appears to be present in all percentiles of data. The data at Karnes County appears to be more variable and relatively flat over the seven years of data available, and the lower percentiles do not track with the 95th percentile.

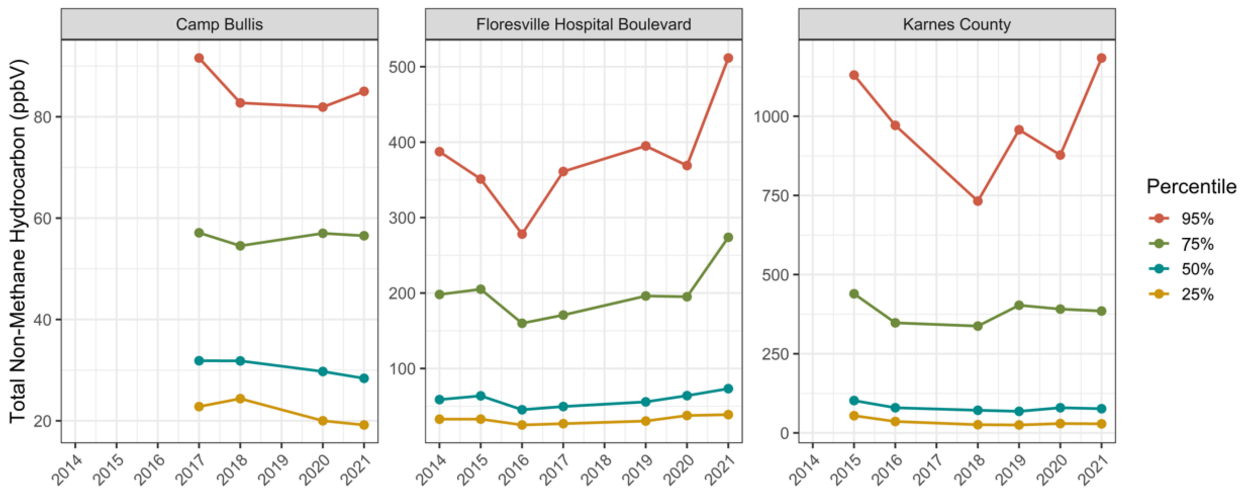

Figure 3-8: Yearly 25th, 50th, 75th, and 95th Percentiles of TNMHC Concentrations at auto-GC Sites in the San Antonio Area

VOC patterns may also be characterized by investigating trends in VOC groups. There are 17 distinct groups of VOC that share chemical characteristics and often source categories as well. A few species, such as propylene, ethylene, and 1,3-butatdiene, are distinct enough in their chemical properties, including their ozone formation potential, that they have their own groups. For this analysis, hourly concentrations of each species in each group were added together to reach a group total concentration in ppbV. Hours with less than 80% of species measured in a particular group were removed since they may allow for artificially low hours. Years with less than 60% valid hours were removed to avoid seasonal skewing of the data. The figures below, Figure 3-9: *Total Concentrations (ppbV) of VOC Groups at Camp Bullis auto-GC*, Figure 3-10: *Total Concentrations (ppbV) of VOC Groups at Old Highway 90 Canister Site*, Figure 3-11: *Total Concentrations (ppbV) of VOC Groups at Floresville auto-GC*, Figure 3-12: *Total Concentrations (ppbV) of VOC Groups at Karnes County auto-GC*, show the 10th through 90th percentiles of the groupings for each year that data were available in box plot format. Outliers were removed to improve readability of the figures. On each figure, a blank space indicates that year did not have enough valid data according to the criteria above, while a flat line indicates a value of zero for that year.

Figure 3-9 shows that there are no strong trends in the data for Camp Bullis. There does seem to be a slight downward trend in the median concentrations of isoprene, toluene, tri-methylbenzenes, and xylenes over the four-year period of data available.

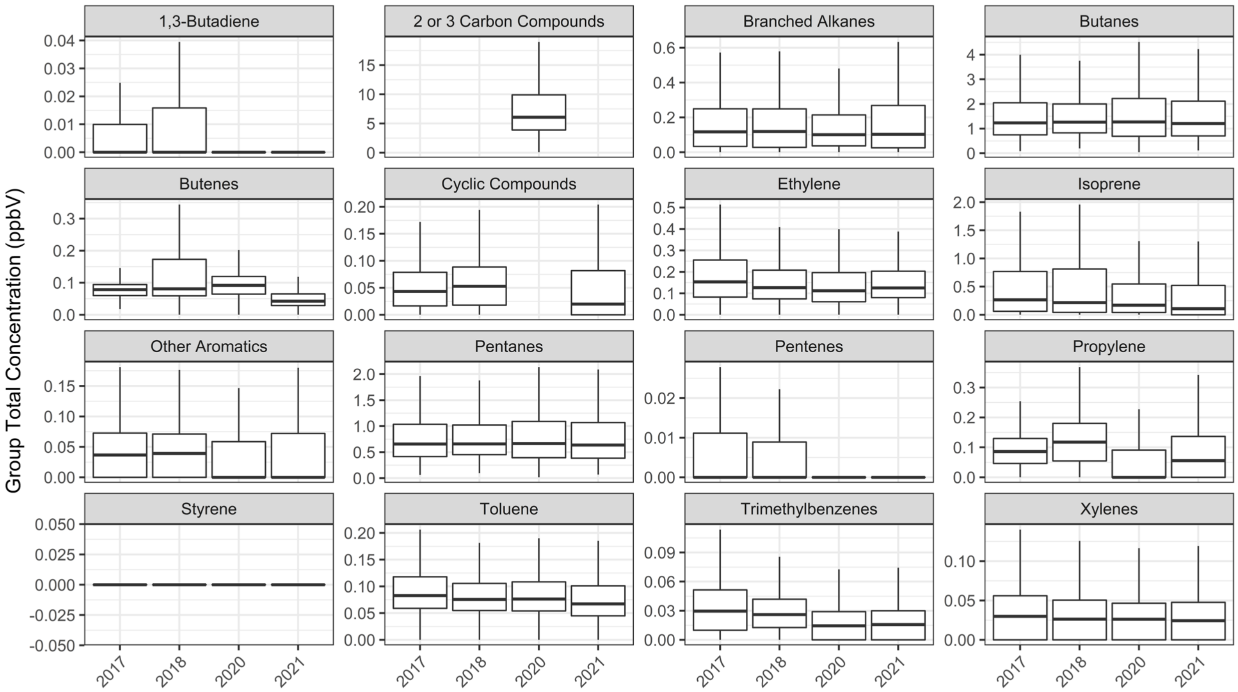

Figure 3-9: Total Concentrations (ppbV) of VOC Groups at Camp Bullis auto-GC

Figure 3-10 shows that, at the Old Highway 90 canister VOC monitor, most species exhibit a flat trend over the ten-year period. Substantial decreases in 1,3-butadiene, butenes, and pentenes are evident. There is a slight upward trend in isoprene, toluene, and xylenes. Styrene was consistently very low 2012 through 2019 but has measured higher levels in 2020 and 2021, indicating a possible source change. Across most species, 2020 seems to have a larger spread between the first and third quartile, represented by the edges of the box, and the medians are higher than the prior and following years.

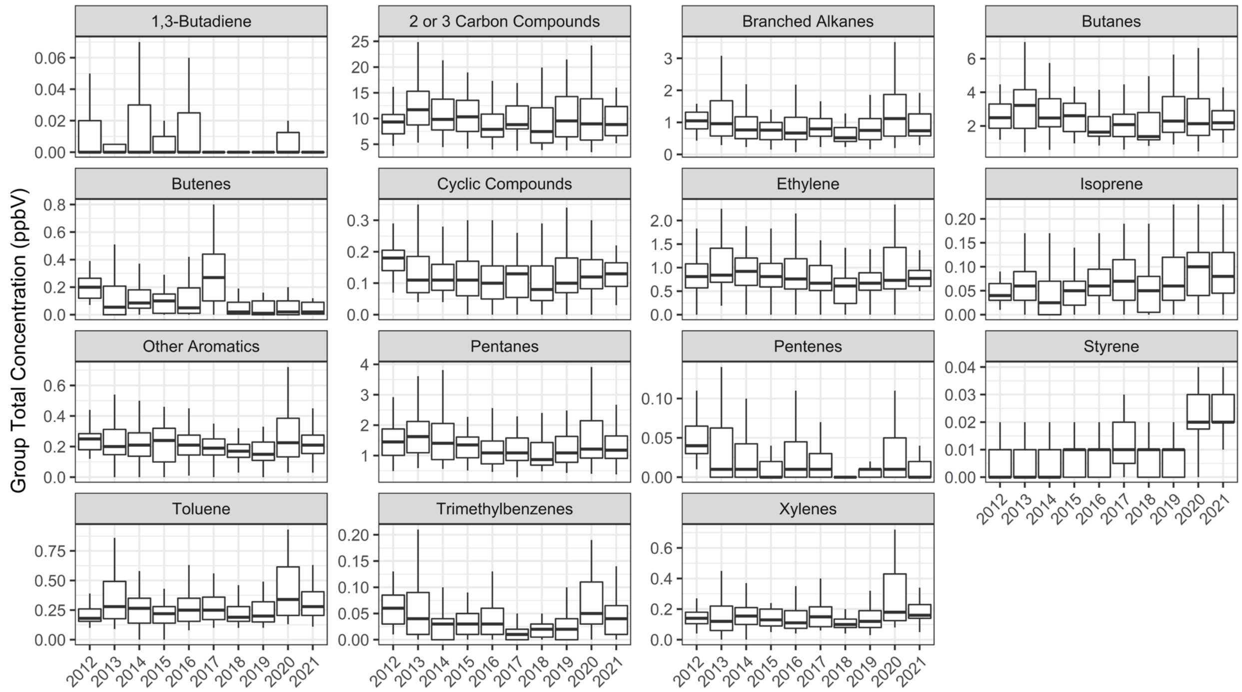

Figure 3-10: Total Concentrations (ppbV) of VOC Groups at Old Highway 90 Canister Site

Figure 3-11 shows that, at Floresville, seven years of data are available for some groups, so more trends can be discerned. Isoprene exhibits the most consistent trend, increasing over the seven-year period. Xylenes, toluene, trimethylbenzenes, and other aromatics appear to follow a similar year-to-year pattern. They each exhibited higher concentrations in the past two years compared to 2014 through 2016. Butenes have one anomaly year, in 2019, where the median concentration was over twice as high compared to all other years studied. This seems to correspond to an increase in 1,3-butadiene as well. These compounds are most commonly emitted from oil refining operations and chemical or plastics manufacturing. Analysis of point sources and their emissions in Section 3.3.1 also shows the presence of these VOC sources in San Antonio area.

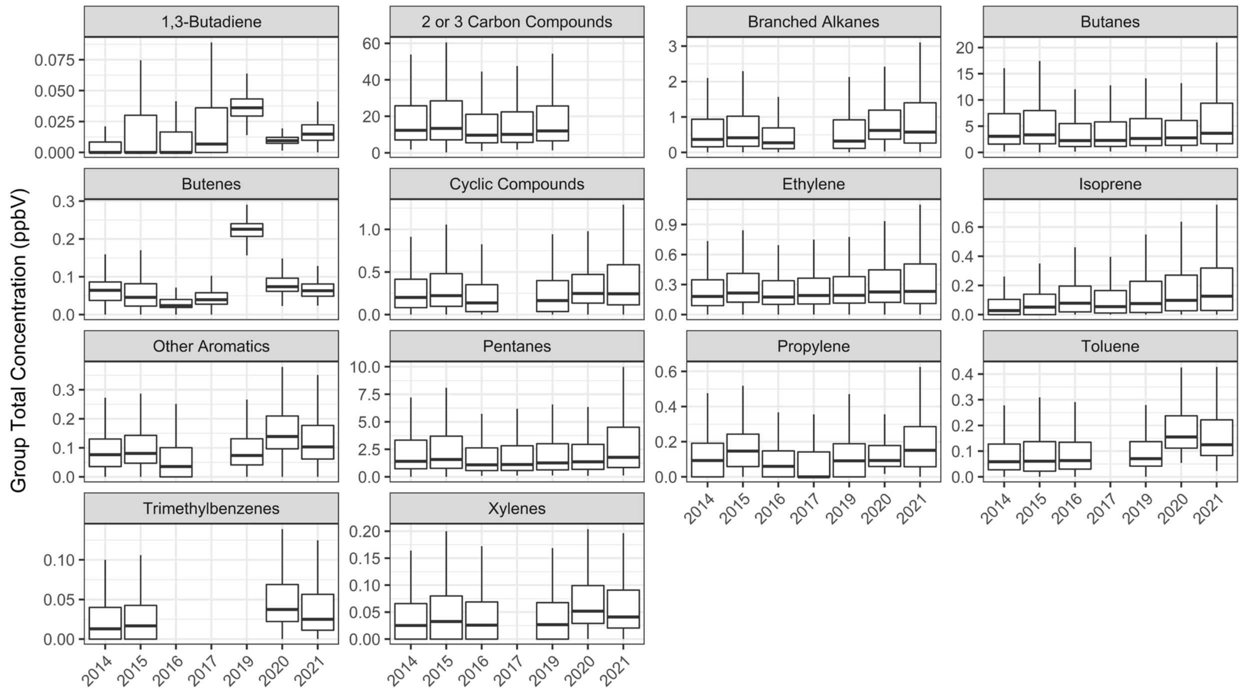

Figure 3-11: Total Concentrations (ppbV) of VOC Groups at Floresville auto-GC

Figure 3-12 shows that, at the monitor further southeast of Bexar County, Karnes County, there are six years of data available for most groups. Like Floresville, xylenes, toluene, trimethylbenzenes, and other aromatics appear to follow a similar year-to-year pattern. However, at the Karnes County monitors, they show a consistent decreasing trend. Propylene also shows a decreasing trend with the median measuring zero in the most recent three years.

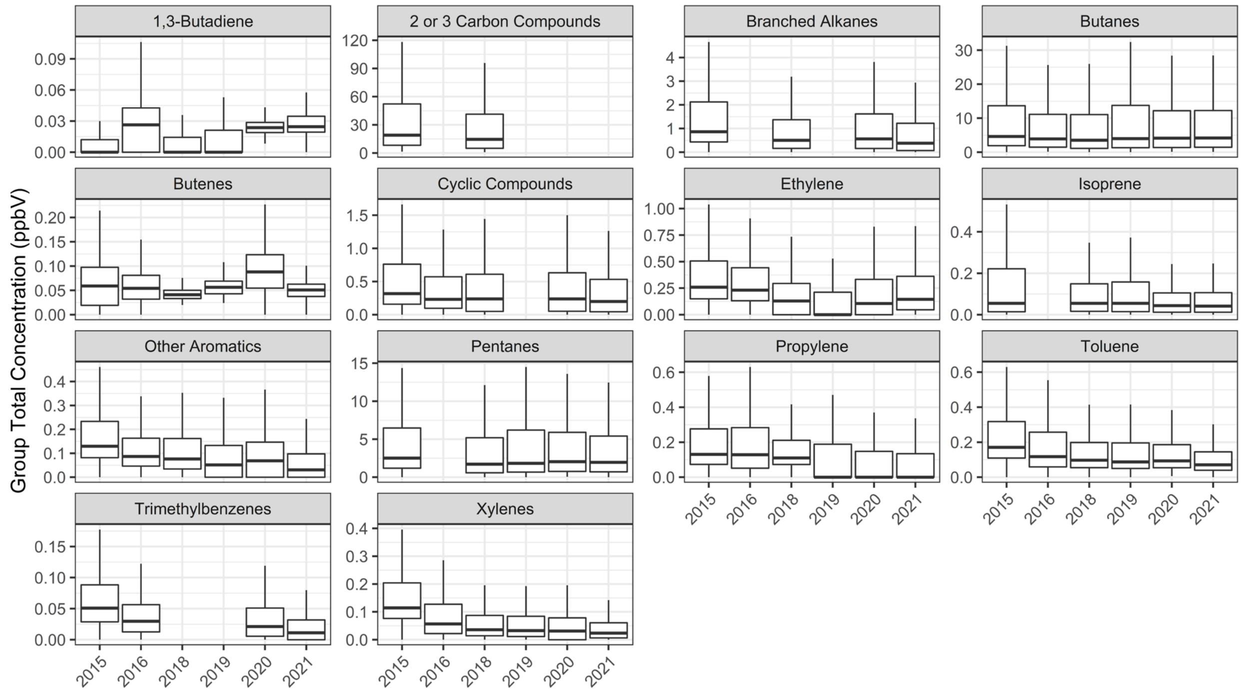

Figure 3-12: Total Concentrations (ppbV) of VOC Groups at Karnes County auto-GC

Overall, there are distinct differences between the patterns in VOC concentrations at each site and this analysis does not suggest a strong correlation between the sites. This may be due to dispersion, dry and wet deposition, or chemical transformations between monitoring sites, and is most likely some combination thereof.

Another analysis that can inform changing emission sources and patterns is a principal component analysis (PCA). A PCA analysis identifies species that trend together and are likely emitted from similar sources. In the previous SIP revision for Bexar County, PCA was performed on the VOC canister data from Old Highway 90 since it had the most data available at the time. The analysis identified three distinct factors. The most notable species in factor one were ethylene, propylene, m/p xylene, isopentane, and n-pentane. These species are indicative of an automobile source. Factor two consisted of five species of alkanes, including ethane, propane, and n-butane. These low-eight alkanes are indicative of oil and gas activities, possibly from the Eagle Ford Shale southeast of San Antonio. Factor three contained four species, but toluene was by far the most notable. The species in factor three do not have a known common source.

To identify any trends in Bexar County, each species from the identified factors were added for each collection period during the ozone season (one hour for the Camp Bullis auto-GC site and 24 hours for the Old Highway 90 canister site). Hours with less than 80% of species with data were filtered out and years with less than 60% of valid collection days were filtered out. To improve readability, outliers are not shown. This process was also repeated using the concentrations weighted by their MIR index and since no novel patterns were discerned, only the unweighted analyses are presented here. However, the relative scale on each of the factors changed dramatically, as discussed for each site.

The results for Camp Bullis are shown in Figure 3-13: *Total VOC Concentrations for Three Factors at Camp Bullis*. Because of the limited data availability, 2019 is excluded and there is little confidence in trends in the data. It does appear that the total concentration of species in factor three have decreased in recent years, and the same is possible for factor one. Factor two's medians are about seven times higher than factor one's and 100 times larger than factor three's. When weighted by MIR, however, factor one and two become roughly equal in magnitude and factor three is only ten times smaller than factor two. This indicates that at Camp Bullis, automobile and oil and gas activities may contribute similarly to ozone formation.

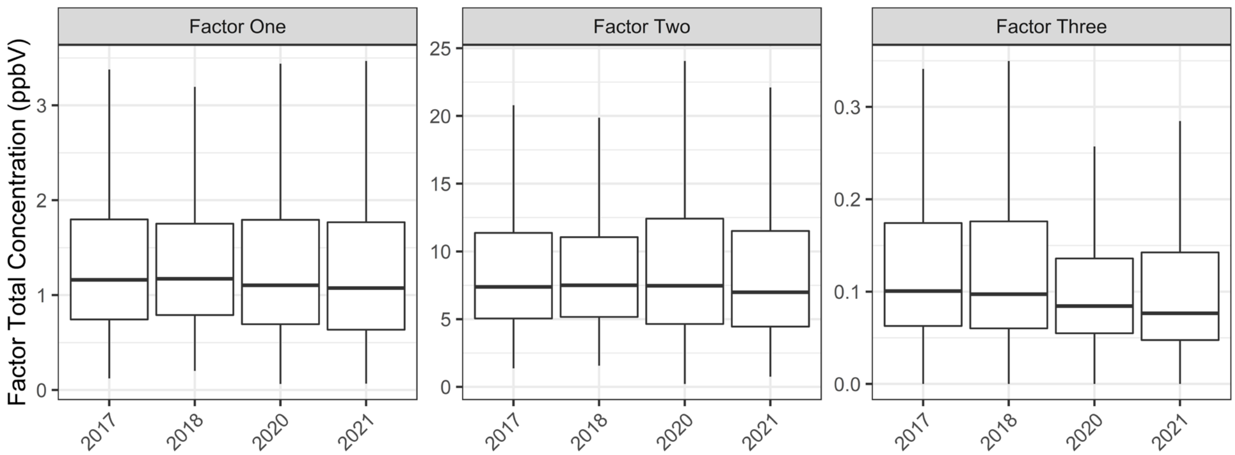

Figure 3-13: Total VOC Concentrations for Three Factors at Camp Bullis

The results for Old Highway 90 are shown in Figure 3-14: *Total VOC Concentrations for Three Factors at Old Highway 90*. Overall, a downward trend in factor one VOCs is evident from 2012 through 2018. From 2018 through 2021 there appears to be an increase, but no trends can be discerned unless these increases continue in the future. The decreases in factor one may be driven by fleet turnover, as cleaner and less emitting vehicles replace older and higher emitting ones. When compared to Camp Bullis. The concentrations of compounds in factor one are over three times as large at Old Highway 90, indicating more VOCs from vehicle emissions are present nearer to the city center. Factors two and three do not show any consistent trend over the ten-year period. However, the concentrations of factor two are comparable to the concentrations seen at Camp Bullis. The concentrations of factor three are roughly four times that at Camp Bullis. Upon further investigation, this is mostly driven by higher concentrations of toluene at Old Highway 90 as shown in Figure 3-9 and Figure 3-10. When weighted by MIR, factor one was twice the median of factor two and factor three was half the median of factor two. These shifts in relative weighted concentrations indicates that factor one contributes the most to ozone formation at Old Highway 90.

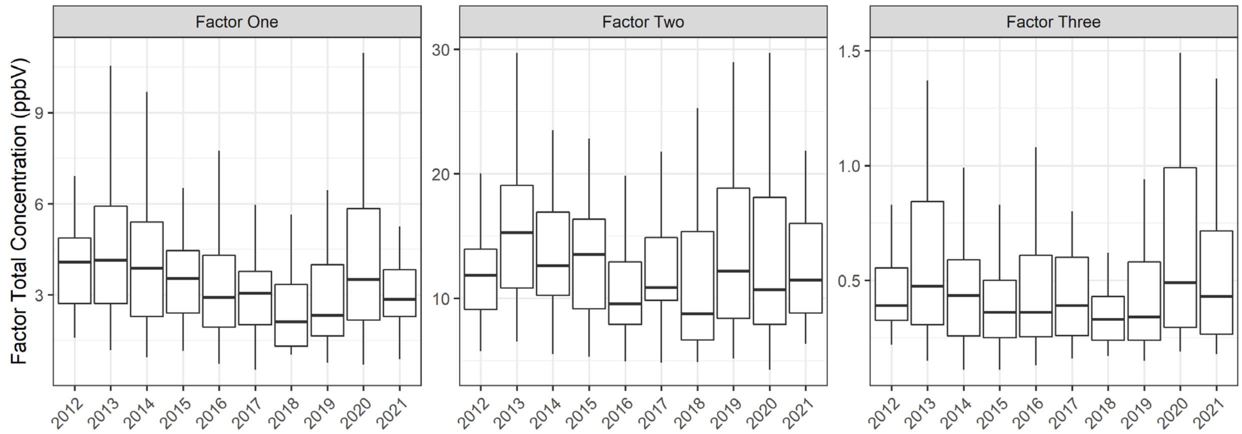

Figure 3-14: Total VOC Concentrations for Three Factors at Old Highway 90

The trends presented here are corroborated by the findings of the SAFS conducted in 2017. During the study VOC were studied at several locations in the city. Like the results of the factor analysis above, results of SAFS show strong mobile signatures in the San Antonio area, especially at the Traveler's World site, located about seven miles southeast of the Old Highway 90 monitor and three miles south of downtown (Flynn et al. 2019). The VOC measured downwind at the University of Texas San Antonio (UTSA) were determined to be more photochemically aged, with isoprene being the dominant VOC at that site, which aligns with the findings in the right panel of Figure 3-4 (Flynn et al. 2019, Wood and Capps 2019). Other research found that oil and gas VOC show local influence on ozone at the Floresville auto-GC but they were not able to tie those oil and gas VOC to ozone produced in Bexar County 2015 ozone NAAQS nonattainment area (Yacovitch et al. 2017).

3.3 OZONE PRECURSOR EMISSIONS

In addition to ambient concentrations and trends in ozone precursors, trends in ozone precursor emission inventories were also investigated. The categories of on-road, non-road, and electric generating units (EGU) have historically been primary sources of anthropogenic NO_x emissions in ozone nonattainment areas including for the San Antonio area. VOC emissions in San Antonio area are from area sources, oil and gas production sources, and on-road sources.

The TCEQ funded a study by the Texas Transportation Institute (TTI) to estimate on-road emissions trends throughout Texas from 1999 through 2050 using the 2014a version of the Motor Vehicle Emission Simulator (MOVES2014a) model (TTI, 2015). On-road NO_x and VOC emissions in the San Antonio area decreased from the early 2000's through 2021 and beyond. These reductions are projected to continue as older, higher-emitting vehicles are removed from the fleet and are replaced with newer, lower-emitting ones. Details can be found in the previous Bexar County nonattainment area conceptual model (TCEQ, 2020).

A similar pattern is reflected in a TCEQ non-road emissions trends analysis using the Texas NONROAD (TexN) model. Non-road emissions decreased from 1999 through 2021 and beyond, even as the number of non-road engines (equipment population) has increased. As with the on-road fleet turnover effect, reductions in non-road NO_x emissions are projected to continue as older higher-emitting equipment is removed from the fleet and replaced with newer lower-emitting equipment. Details can be found in the previous Bexar County nonattainment area conceptual model (TCEQ, 2020)

The rest of this section will focus on trends in point source NO_x and VOC emissions in the San Antonio area.

3.3.1 Point Source Emission Trends

Point source emission trends of NO_x and VOC were analyzed using data from the State of Texas Air Reporting System (STARS) database. To capture all nearby emissions affecting the Bexar County nonattainment area, NO_x emissions from all point sources in Bexar County were investigated. Figure 3-15: *NO_x Point Source Emissions from 2012 through 2021 in the Bexar County 2015 Ozone NAAQS Nonattainment Area* shows the recent trend in NO_x emissions. The six named point sources, based on 2021 emissions, make up 96% of NO_x emissions in 2021. The largest three point sources make up 86% of NO_x emissions in 2021. The largest NO_x emission source each year is the Calaveras Lake power plant, which supplies the majority of electricity to San Antonio. The Calaveras Plant NO_x emissions have fluctuated greatly year to year, likely in response to fluctuations in weather that influence electricity demand, but overall have been trending downward. The second and fourth largest emission sources are two cement plants, Alamo Cement 1604 Plant and Capitol Aggregates Portland Cement. The combined emissions of these two entities have not significantly changed over the decade studied. The remaining sources include smaller power plants, natural gas infrastructure, a steel mill, and other industrial entities. Overall, there have been decreases in NO_x emissions, but the rate has slowed more recently.

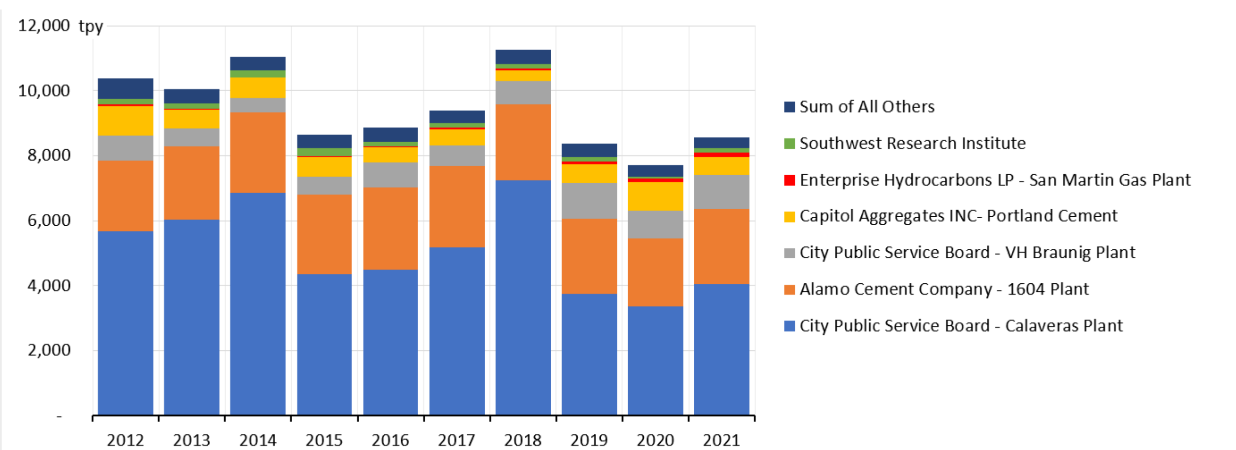

Figure 3-15: NO_x Point Source Emissions from 2012 through 2021 in the Bexar County 2015 Ozone NAAQS Nonattainment Area

Calaveras Plant has seen the greatest decrease in NO_x emissions over the ten year period. Compared to 2012 emissions, Calaveras Plant 2021 NO_x emissions decreased by 29%. There have been a few small sources to the southeast and southwest of the Camp Bullis monitor that have increased emissions, but these changes are minor compared to the decreases seen at other facilities throughout the area. The largest increases were from entities to the northwest and northeast of the city, just outside of Bexar County.

To further understand how emissions have changed over time, the percent change in NO_x point source emissions calculated for each year for facilities within Bexar County and those in counties adjacent to Bexar County. The results are shown in Figure 3-16: *Percent Change in NO_x Point Source Emissions in the San Antonio Area from 2012 through 2021*. There is a 13% decrease in NO_x emissions over the ten years studied, mainly from point sources inside Bexar County. Based on the 2021 emissions inventory, emission sources in Bexar County make up roughly 55% of NO_x emissions in the San Antonio area and the adjacent counties makes up roughly 45% of NO_x emissions in the San Antonio area.

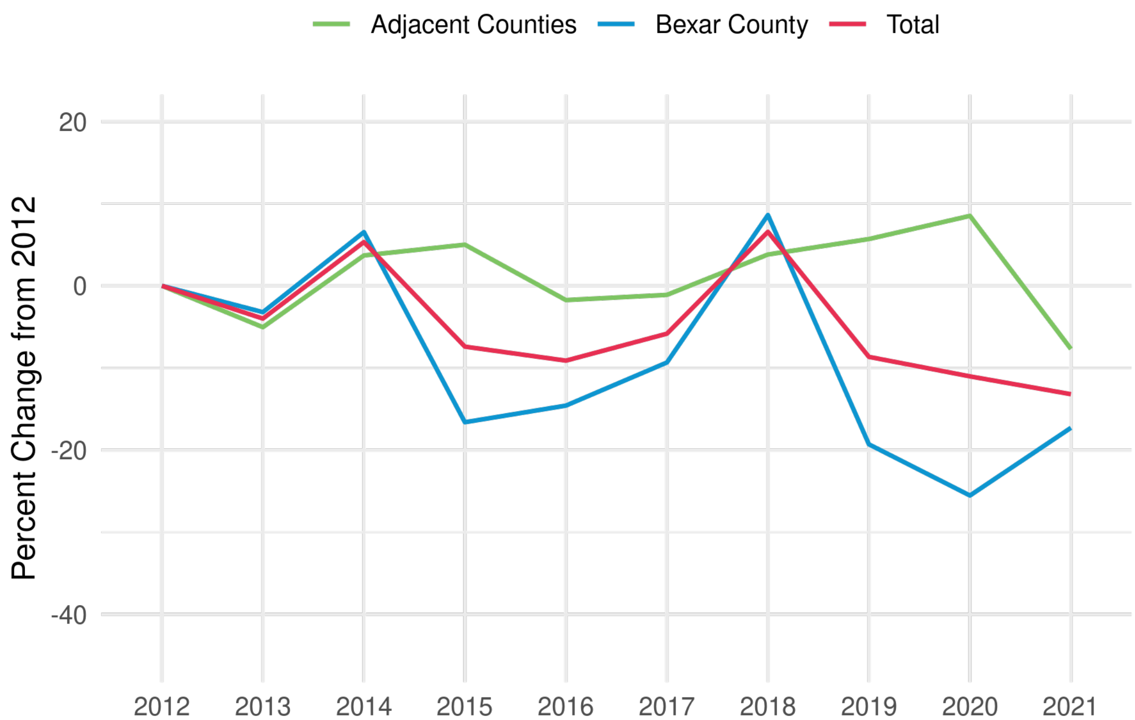

Figure 3-16: Percent Change in NO_x Point Source Emissions in San Antonio Area from 2012 through 2021

Understanding the spatial distribution of point sources is key to understanding how they may impact ozone photochemistry in an airshed. Sources upwind from monitors are more likely to contribute to ozone levels at that monitor than those that are downwind. To understand the spatial distribution of NO_x emissions, each point source was plotted on a map of the San Antonio area. The results are shown in Figure 3-17: *Map of 2021 NO_x Point Source Emissions in the San Antonio Area*. Each facility's 2021 NO_x emissions are shown by color and size of marker. While there are many small sources scattered throughout the area, the largest NO_x sources are concentrated southeast and east of the design value setting monitor, Camp Bullis. As will be discussed in Section 5.3.1, the prevailing wind patterns at the Camp Bullis monitor are out of the southeast and east-southeast, making the largest NO_x sources in Bexar County directly upwind of Camp Bullis. These large NO_x sources are all likely contributors to ozone formation in the air mass that reaches Camp Bullis.

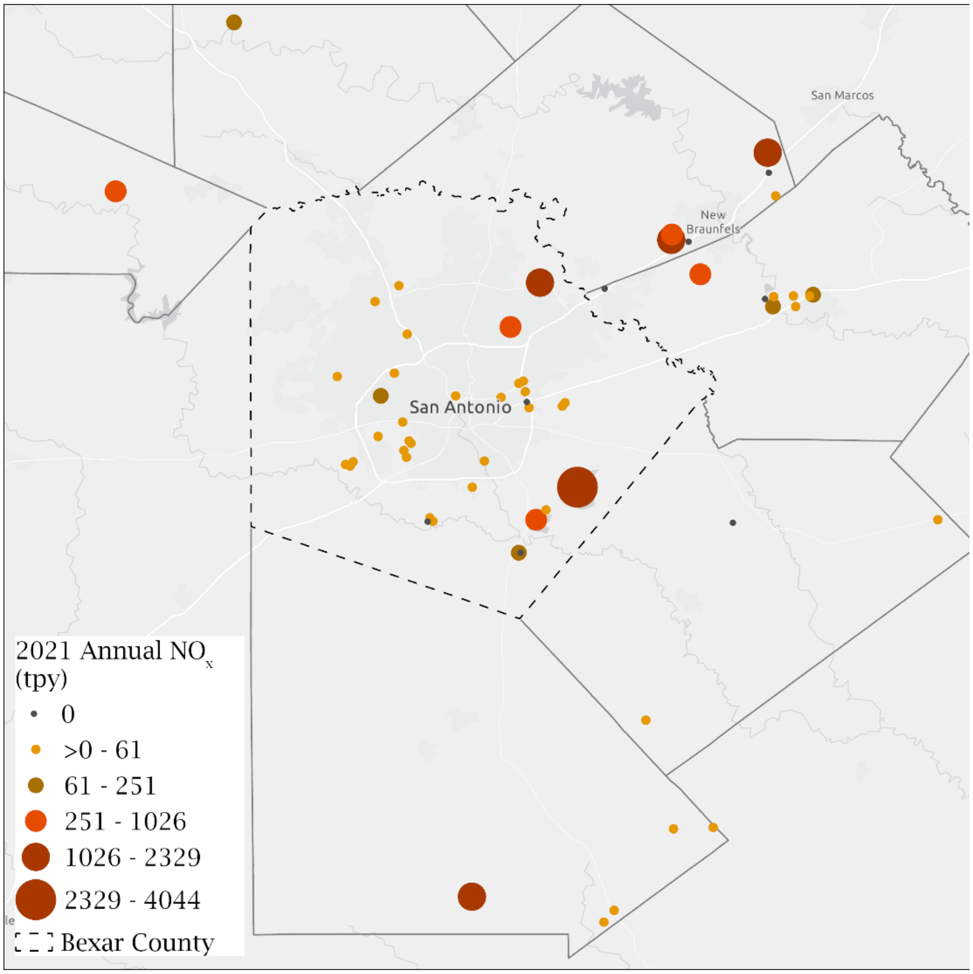

Figure 3-17: Map of 2021 NO_x Point Source Emissions in the San Antonio Area

Emissions of VOC from point sources in Bexar County 2015 ozone NAAQS nonattainment area were also investigated. The total VOC emissions inventory for 2012 through 2021 in the Bexar County 2015 ozone NAAQS nonattainment area is shown in Figure 3-18: *VOC Point Source Emissions from 2012 through 2021 in the Bexar County 2015 Ozone NAAQS Nonattainment Area*. Compared to NO_x sources, there are many more VOC sources of substantial size. The eight named point sources make up approximately 62% of total VOC emissions. The largest VOC point source is the Toyota Vehicle Assembly Plant with roughly 300 tons per year (tpy) of VOC emissions in 2021. The second largest VOC source is the San Antonio Petroleum Refinery, with 114 tons of VOC emissions in 2021. Other point sources include power plants, cement plants, oil and gas infrastructure, and other industrial, manufacturing, and research facilities. Compared to NO_x emissions, there is less year-to-year variability in VOC emissions, likely because VOC emissions are less affected by electricity demands that fluctuate with weather conditions. Overall, there is no clear trend in VOC emissions over the ten years studied.

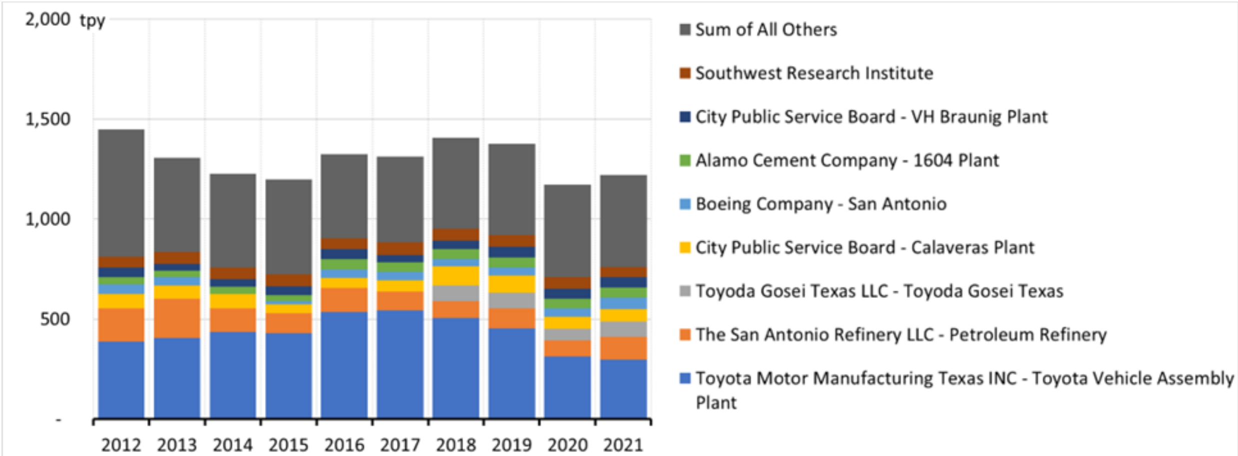

Figure 3-18: VOC Point Source Emissions from 2012 through 2021 in the Bexar County 2015 Ozone NAAQS Nonattainment Area

Year to year variability in VOC emissions is also seen in Bexar County 2015 ozone NAAQS nonattainment area VOC sources. The first and second largest VOC emissions sources show decreases of 24% and 31%, respectively, from 2012 to 2021.

To further understand how emissions have changed over time, the percent change in VOC emissions from 2012 was calculated for each year for facilities within Bexar County and those counties adjacent to Bexar County. The results are shown in Figure 3-19: *Percent Change in VOC Point Source Emissions in San Antonio Area from 2012 through 2021*. Comparing 2012 to 2021, VOC emissions decrease about 4%. VOC point sources in Bexar County have lower VOC emissions than in 2012. In contrast, VOC sources outside of Bexar County have had increased emissions in recent years. As will be discussed in Section 4.1, the area seems to be trending from a transitional regime to a NO_x limited regime, and changes in the NO_x and VOC point source emissions may be a key driver in that.

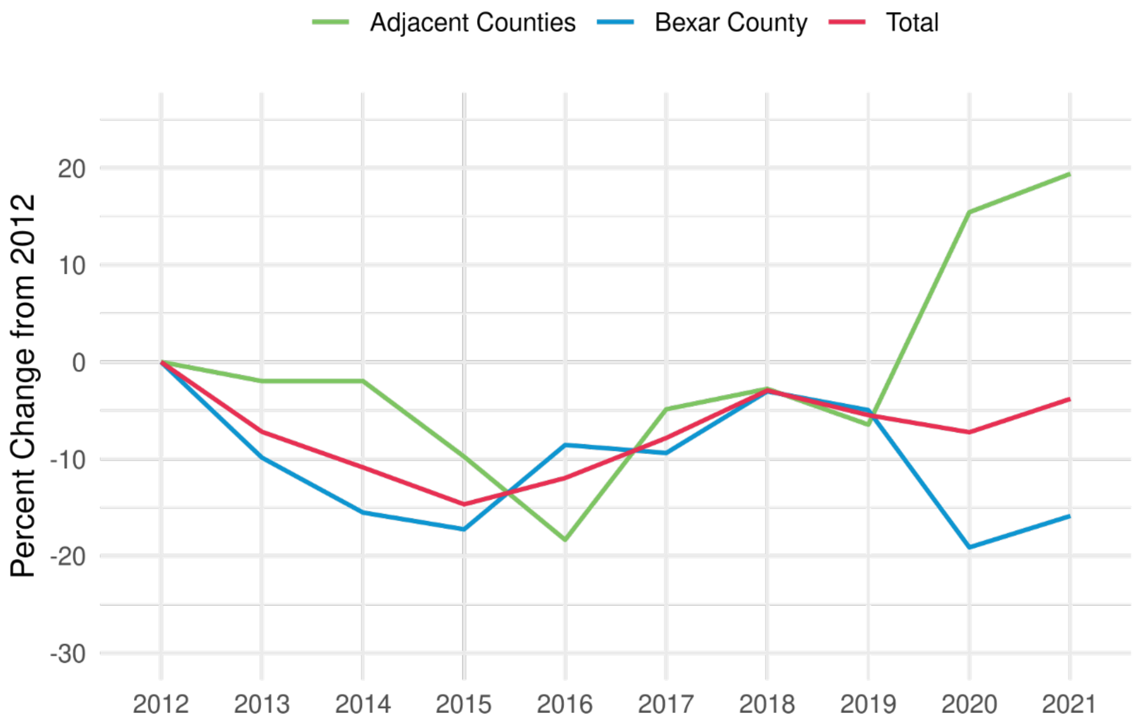

Figure 3-19: Percent Change in VOC Point Source Emissions in San Antonio Area from 2012 through 2021

As mentioned for NO_x emissions, understanding the spatial distribution of precursors emissions is vital to understanding their role in ozone formation. To investigate the spatial distribution of VOC point source emissions, each point source was plotted on a map of the San Antonio area. The results are shown in Figure 3-20: *Map of 2021 VOC Point Source Emissions in the San Antonio Area*. The largest point source in the area is the Toyota Vehicle Assembly Plant, which is located directly next to the Toyoda Gosei Plant (the third largest VOC point source in the area in 2021); they are located on the south side of Bexar County. The second largest VOC point source, San Antonio Petroleum Refinery, is also located south of the Camp Bullis monitor.

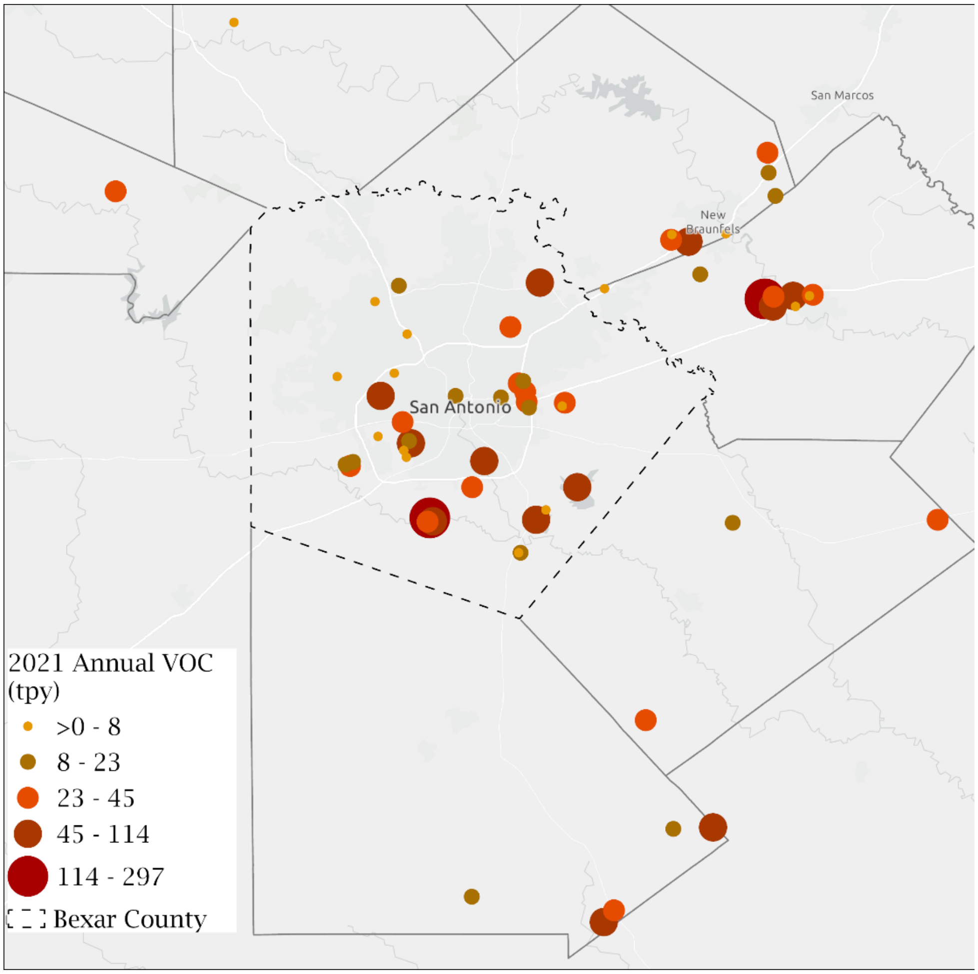

Figure 3-20: Map of 2021 VOC Point Source Emissions in the San Antonio Area

CHAPTER 4: OZONE CHEMISTRY

Previous chapters of this conceptual model focused on analysis and trends of ozone and its precursors separately. More detailed analysis of the interactions between ozone and its precursors will help to determine what precursors area most important to ozone formation in the San Antonio area. This section will explore ozone chemistry by investigating volatile organic compounds (VOC) and nitrogen oxides (NO_X) limitations and ozone formation on weekdays versus weekends in the Bexar County 2015 ozone National Ambient Air Quality Standard (NAAQS) nonattainment area.

4.1 VOC AND NO_X LIMITATIONS

The VOC and NO_X limitation of an air shed can help determine how immediate reductions in VOC and NO_X concentrations might affect ozone concentrations. A NO_X limited regime occurs when the radicals from VOC oxidation are abundant, and therefore ozone formation is more sensitive to the amount of NO_X present in the atmosphere. In these regimes, controlling NO_X would be more effective in reducing ozone concentrations. In VOC limited regimes, NO_X is abundant, and therefore ozone formation is more sensitive to the number of radicals from VOC oxidation present in the atmosphere. In VOC limited regimes, controlling VOC emissions would be more effective in reducing ozone concentrations. Areas where ozone formation is not strongly limited by either VOC or NO_X are considered transitional and controlling either VOC or NO_X emissions could reduce ozone concentrations in these regions.

One method of estimating if ozone formation occurs in a VOC or NO_X limited regime is by calculating a VOC-to-NO_X ratio. This ratio is calculated by dividing hourly total non-methane hydrocarbons (TNMHC) concentrations in parts per billion by carbon (ppbC) by hourly NO_X concentrations in parts per billion by volume (ppbV). TNMHC is used as proxy of VOC in this analysis. While ratio definitions for VOC limited, NO_X limited, or transitional atmospheric conditions vary, this analysis uses the cut points described in EPA's Photochemical Assessment Monitoring Stations (PAMS) training workshop (Hafner and Penfold, 2018). Ratios less than 5 ppbC/ppbV are considered VOC limited, ratios above 15 ppbC/ppbV are considered NO_X limited, and ratios between 5 ppbC/ppbV and 15 ppbC/ppbV are considered transitional. Due to the nature of the ratio calculation, NO_X values of 0 ppbV produce invalid results. To address this issue, only hours having non-zero values of VOC and NO_X were used for analysis. Because VOC and NO_X concentrations often exhibit steep spatial gradients, the concentrations must be from the same location to calculate a useful statistic. Therefore, calculation of VOC-to-NO_X ratios are limited by the number of collocated automated gas-chromatograph (auto-GC) and NO_X monitors available in the area.

The San Antonio area has three auto-GC monitors that are collocated with NO_X monitors, but only one is in Bexar County 2015 ozone NAAQS nonattainment area. Because there is such high spatial variation this analysis will focus on the monitor in Bexar County, Camp Bullis. Because the purpose of the analysis is to explore ozone formation in Bexar County, only months in the ozone season will be investigated. Due to limited hours of available data in 2019, results may not be representative of the true chemical regime for that year. Ratios were calculated for each hour of the day and then aggregated to determine the median ratio for each year. Results are shown in Figure 4-1: *Median VOC-to-NO_X Ratios During the Ozone Season at Camp Bullis*. Data show that, from 2016 through 2018, Camp Bullis saw transitional but close to NO_x limited conditions. After 2019, the monitor has measured NO_x limited conditions.

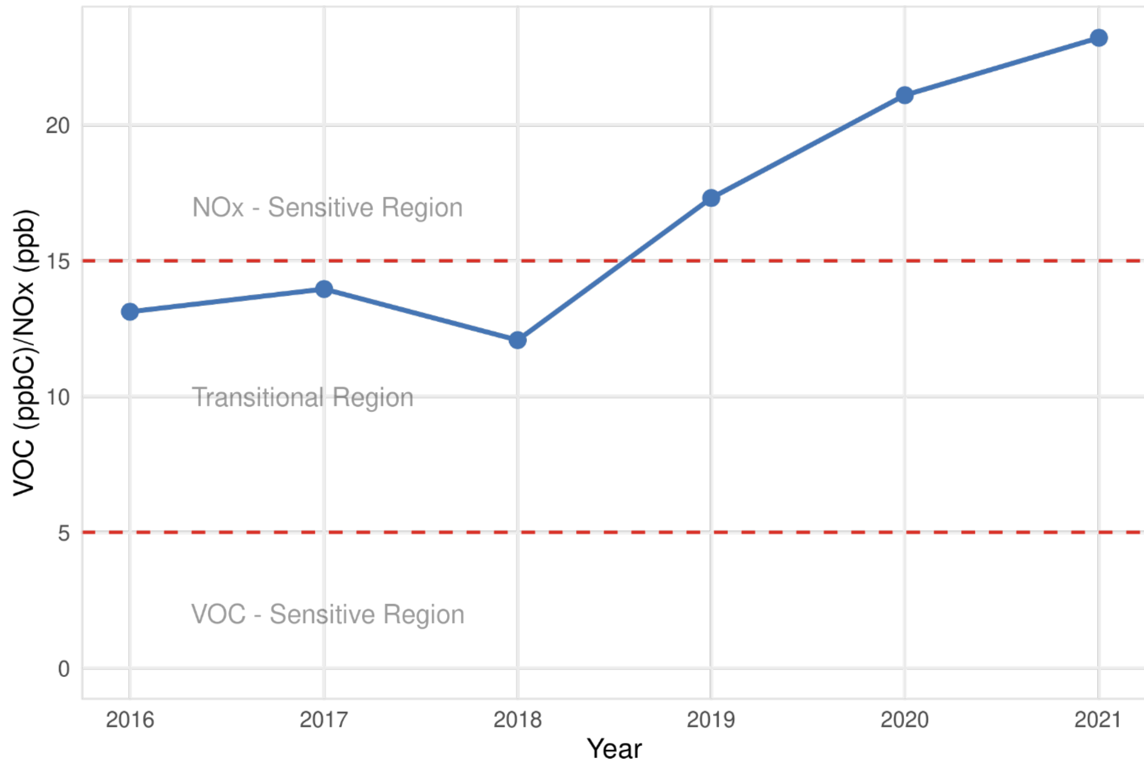

Figure 4-1: Median VOC-to-NO_x Ratios During the Ozone Season at Camp Bullis

VOC-to-NO_x ratios were also investigated by hour to determine how diurnal variability effects the chemical composition of the atmosphere. For each hour of available ozone season data from 2016 through 2021, the TNMHC concentration was divided by the NO_x concentration, and the results were aggregated for each hour of the day. Hourly medians for the ozone season from 2016 through 2021 at Camp Bullis are shown in Figure 4-2: *Median Hourly VOC-to-NO_x Ratios During the Ozone Season from 2016 through 2021 at Camp Bullis.*

The results show that the ratio fluctuates from NO_x limited in the overnight hours to transitional during the early morning hours. The ratios then return to NO_x limited in the daytime hours. The higher ratios that occur overnight are likely due to the lower levels of NO_x present overnight. The morning decrease in ratios is likely due to the increases in NO_x concentrations from on-road sources during the morning rush hour. The lowest median ratio occurs at 08:00 local standard time (LST), but this ratio remains in the transitional regime and never enters the VOC limited regime. After 08:00 LST, ratios continuously increase throughout the day trending towards NO_x limited and they reenter the NO_x limited regime after 13:00 LST; however, the median remains just above the transitional boundary after 13:00 LST. Overall, the area around Camp Bullis appears to have mostly transitional to NO_x limited conditions.

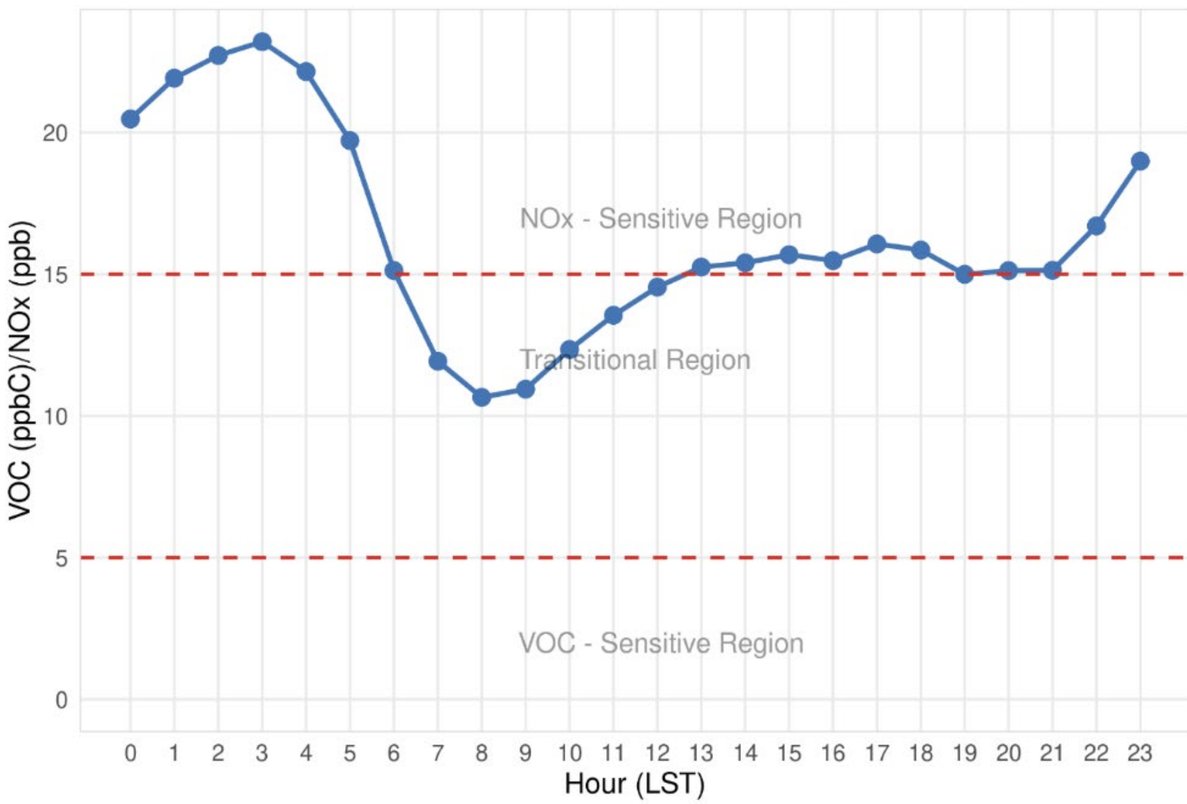

Figure 4-2: Median Hourly VOC-to-NO_x Ratios During the Ozone Season from 2016 through 2021 at Camp Bullis

Since morning hours are when peak VOC and NO_x concentrations are often observed, those hours were investigated more closely. The frequency that the VOC-to-NO_x ratio was either VOC limited, transitional, or NO_x limited was determined using the hours of 5:00 LST though 8:00 LST for the ozone season in Bexar County. Results are shown in Figure 4-3: *Frequency of VOC Sensitive, NO_X Sensitive, and Transitional Regimes During Ozone Season Mornings from 2016 through 2021 at Camp Bullis*. The results show that the morning hours are transitional most of the time, with a smaller number of hours measuring NO_x limited conditions in 2016 through 2018. After 2018 this trends reverses, with morning hours measuring more NO_x limited conditions and a smaller number of hours measuring transitional conditions. Very few hours from 2016 through 2021 measure VOC limited conditions. Due to the missing data in 2019 results may not be representative of the chemical regime for that year. Overall, these results indicate that ozone chemistry in Bexar County appears to be NO_x limited in recent years.

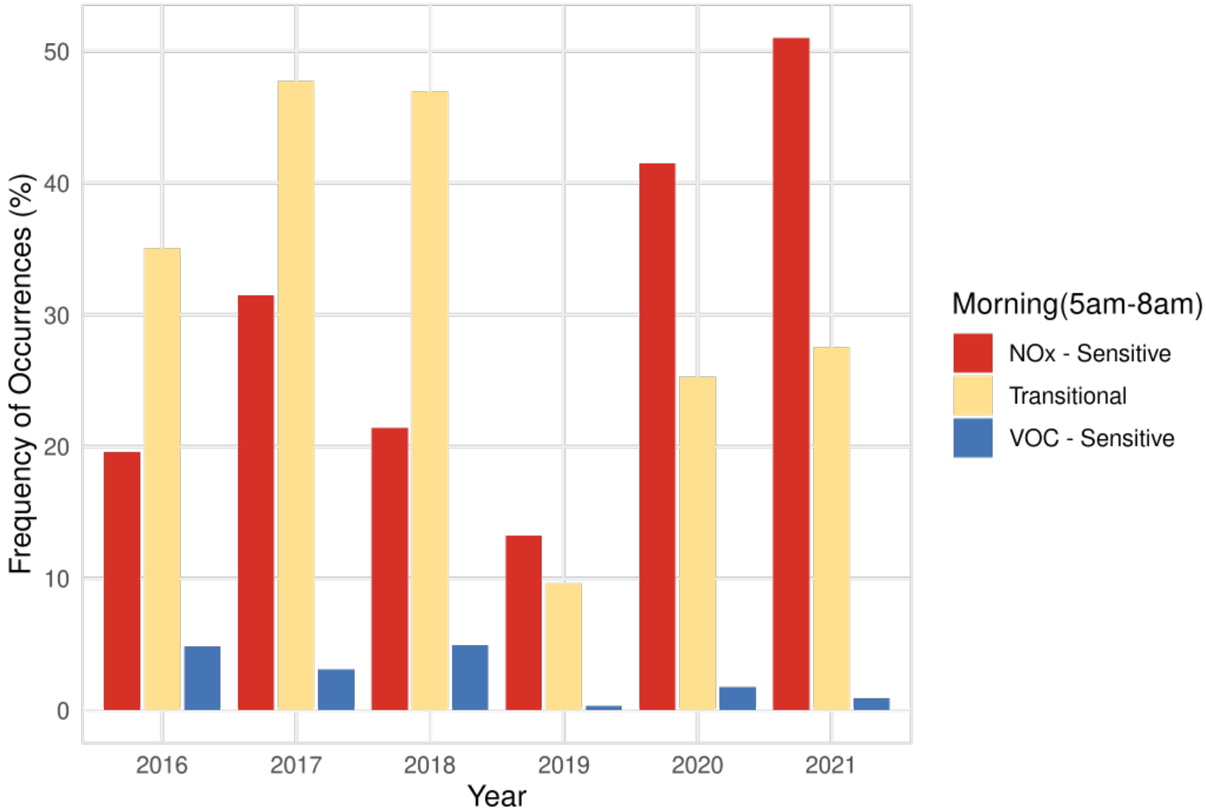

Figure 4-3: Frequency of VOC Sensitive, NO_x Sensitive, and Transitional Regimes During Ozone Season Mornings from 2016 through 2021 at Camp Bullis

VOC and NO_x limitations in the San Antonio area were studied extensively during the May 2017 San Antonio Field Study (SAFS). Researchers used modeled data, satellite data, and measured concentrations to determine that the San Antonio area exhibited mostly NO_x limited conditions (Flynn et al. 2018, Flynn et al. 2019, Anderson et al. 2019, Wood and Capps 2019). Higher ozone production rates in the San Antonio area tended to correspond to NO_x limited conditions (Yacovitch et al. 2017). Biogenic VOC were found to contribute the most to total hydroxyl radical (OH) reactivity, suggesting that even when San Antonio experiences VOC limited conditions, VOC controls may not be effective at reducing ozone concentrations compared to NO_x controls (Anderson et al. 2019).

4.2 WEEKDAY VERSUS WEEKEND ANALYSIS

Changes in ozone and its precursors by day of the week can be used to indicate an area's ozone chemistry as well as precursor emissions sources. Theoretically, if NO_x concentrations are lower on weekends, it would be due to lower mobile-source NO_x emissions in the absence of a morning rush hour. In addition, if ozone was also lower on weekends, it can be assumed that the changes are due to changes in NO_x, which supports the conclusion that the area is NO_x limited.

The weekday versus weekend effect on ozone was investigated in several different ways. First, the number of monitors that exceeded the 2015 eight-hour ozone standard of 70 parts per billion (ppb) on each day of the week was calculated. Since each exceeding monitor is counted, this analysis captures how widespread an exceedance event was, as opposed to counting ozone exceedance days. This analysis uses data from both regulatory and non-regulatory ozone monitors from 2012 through 2021.

Figure 4-4: *Number of Monitors Exceeding the 2015 Eight-Hour Ozone Standard by Day of the Week in the San Antonio Area from 2012 through 2021* shows that there is clearly a weekend effect, with the least number of exceedances recorded on both Saturday and Sunday. When patterns at individual monitors were examined, it was evident many, but not all, monitors experience a weekend effect, and it is most pronounced at Camp Bullis and Bulverde Elementary. There also appears to be an accumulation effect throughout the week, with the most exceedances occurring on Thursdays. The cause of this will be investigated in subsequent analyses.

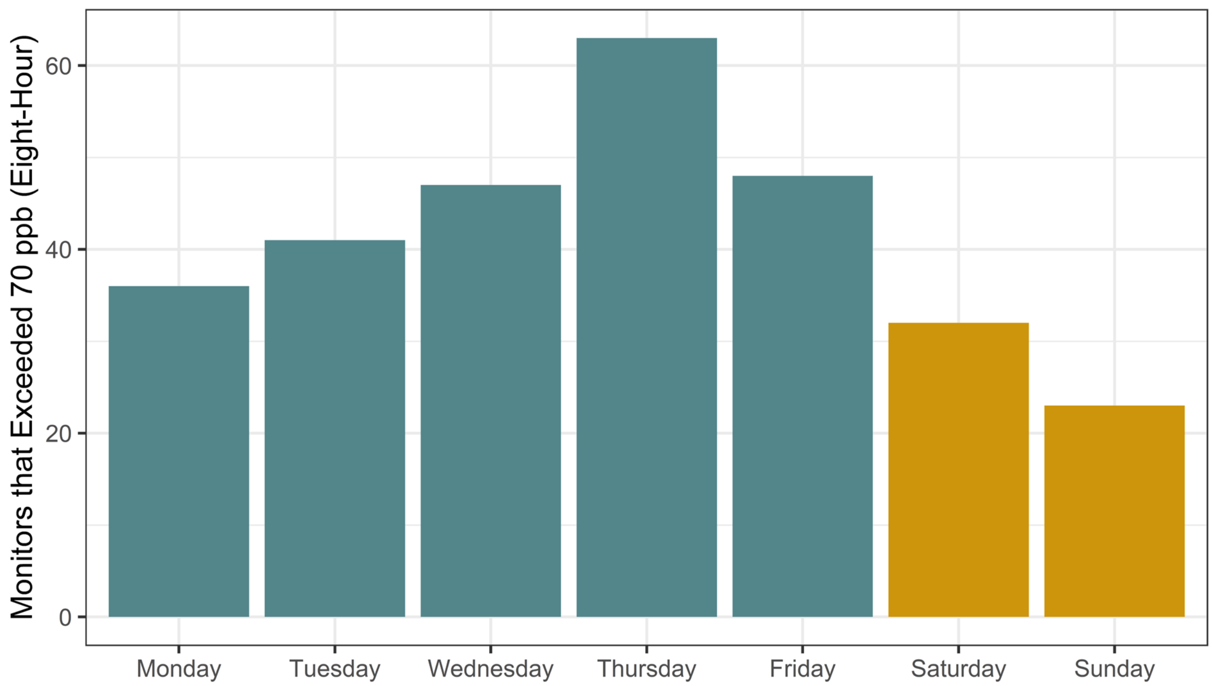

Figure 4-4: Number of Monitors Exceeding the 2015 Eight-Hour Ozone Standard by Day of the Week in the San Antonio Area from 2012 through 2021

These patterns in eight-hour ozone exceedance days by day of the week suggest changes in emissions from the weekdays relative to the weekends do influence ozone concentrations in the San Antonio area. To examine this further, one-hour ozone and NO_x concentrations were investigated by hour and day of the week for the ozone season at Calaveras Lake, San Antonio Northwest, and Camp Bullis. A line of best fit found using a generalized additive model (GAM and standard error ribbon are shown. Data from 2012 through 2021 was used for Calaveras Lake and Camp Bullis. Because San Antonio Northwest did not have NO_x data until 2013, data from 2013 through 2021 was used at that monitor. The figure is arranged roughly from upwind to downwind, typically air in the afternoon flows from southeast, where Calaveras Lake is located, to northwest, where San Antonio Northwest and Camp Bullis are located. Results are displayed in Figure 4-5: *One-Hour Ozone and Mean NO_x by Hour and Day of the Week for the Ozone Season at Calaveras Lake (top), San Antonio Northwest (middle), and Camp Bullis (bottom).* Scale in y-axis varies on each image for both NO_x and ozone.

Like the exceedance day study, results show that peak one-hour ozone is slightly lower on Saturdays and Sundays at Camp Bullis and San Antonio Northwest; however, the results for Calaveras Lake are less distinct. There is a clear enhancement in NO_x at all monitors in the early morning hours as rush hour is starting, and the boundary layer has not yet risen from surface warming. At all monitors, ozone is at a minimum in the early morning hours around 5:00 LST, this dip corresponds to the large NO_x enhancement seen in the morning. Because the NO_x enhancement is less pronounced on the weekend days, the dip in ozone is less pronounced due to lower rates of ozone titration by NO_x. These results support the conclusion that ozone is at least partially NO_x limited in Bexar County because days with lower NO_x concentrations tend to have lower peak ozone concentrations.

An interesting finding from this analysis was the spatial heterogeneity in the timing of the NO_x enhancement and ozone dip in the morning. At the Calaveras Lake monitor, the peak and valley of NO_x and ozone, respectively, line up almost exactly. However, at the San Antonio Northwest monitor, the peaks are slightly shifted, so the dip in ozone occurs before the NO_x peak. At the Camp Bullis monitor, even further downwind of most NO_x sources, the delay is even more pronounced, with a difference of three hours most mornings. This is likely caused by the locations of the monitors in relation to precursor emissions. Calaveras Lake is directly next to the Calaveras Power Plant, which is the largest NO_x emission source in the area. San Antonio Northwest is ten miles from downtown and near many mobile sources of NO_x, while Camp Bullis is further from downtown.

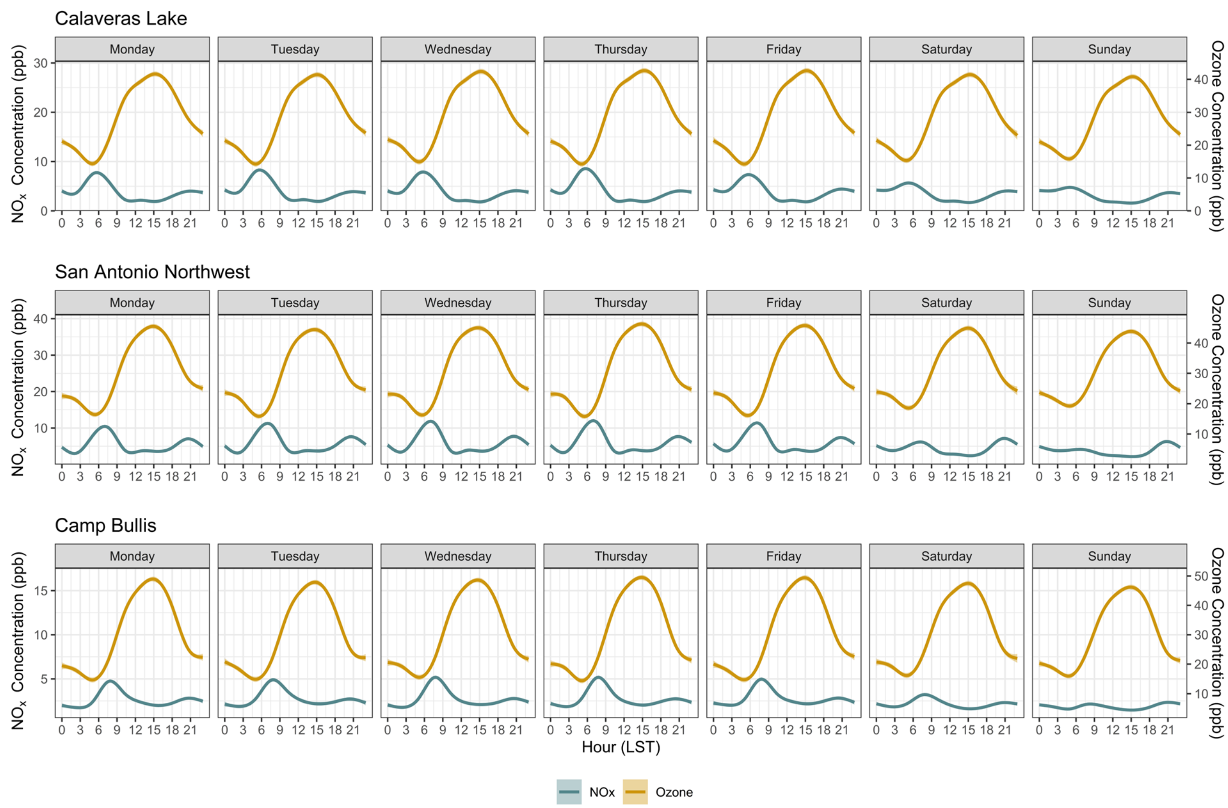

Figure 4-5: One-Hour Ozone and Mean NO_x by Hour and Day of the Week for the Ozone Season at Calaveras Lake (top), San Antonio Northwest (middle), and Camp Bullis (bottom)

To further investigate the weekday effect on NO_X concentrations at Camp Bullis, the diurnal patterns for NO_X were plotted together in Figure 4-6: *Hourly NO_X at Camp Bullis by Day of the Week for 2012 through 2021*. The day of week is indicated by the color of the line. For clarity, the standard error ribbon is not shown. The results show the clear distinction between weekday and weekend NO_X. There is also a distinct difference among weekdays. Monday, the forest green line, clearly has the lowest peak NO_X. Wednesday and Thursday track similarly and have the highest NO_X peaks. When compared to the frequency of exceedances in Figure 4-4, an interesting pattern emerges. The peak NO_X concentrations occur on days with the highest frequency of exceedances (Thursday) and the lowest NO_X concentrations align with the day with the least exceedances (Sunday). The observed patterns of increasing NO_X and ozone over the course of the work week (Monday to Thursday) and decreasing NO_X over the weekend (Friday to Sunday) may be indicative of carryover from one day to the next, both of precursors and ozone itself.

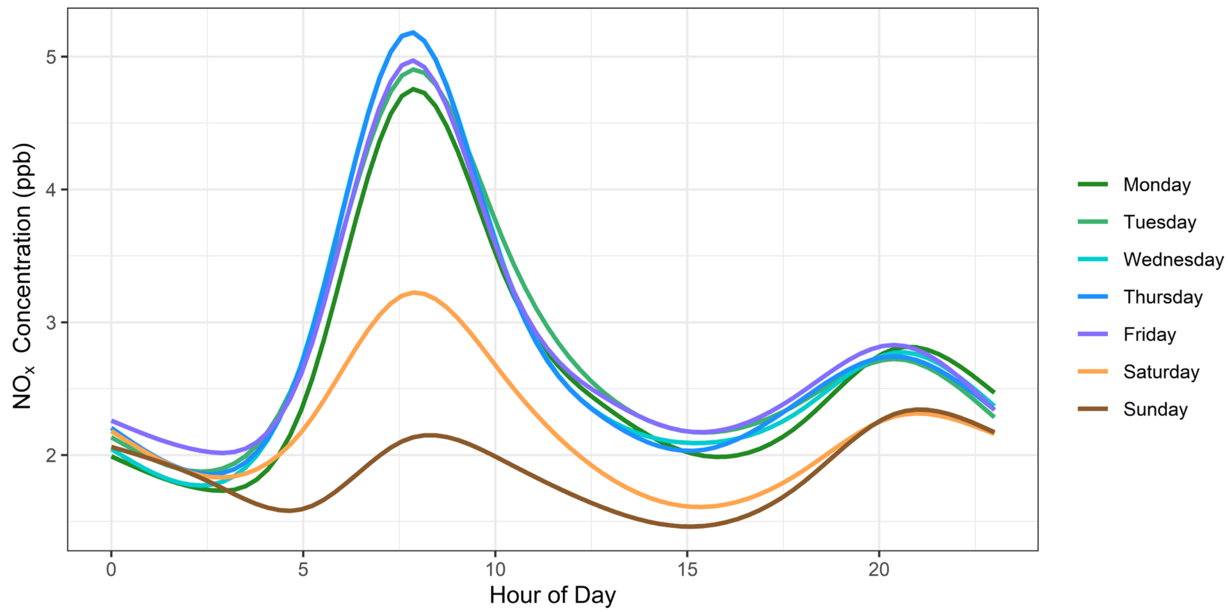

Figure 4-6: Hourly NO_x at Camp Bullis by Day of the Week for 2012 through 2021

VOC data by day of the week can also be useful in determining both the ozone chemistry and the type of VOC sources in the area. VOC emissions from point sources or oil and gas production activities should not change on weekdays versus weekends; whereas VOC emissions from on-road emission sources are likely to decrease on the weekends. First, the VOC groups described in Section 3.2.2 were evaluated by day of the week. At the Camp Bullis monitor, ethylene, propylene, styrene, toluene, and xylenes showed different concentrations on the weekend. At the Old Highway 90 canister site, only xylenes showed a substantial difference on the weekends. Next, a few key species were chosen to best exemplify the weekend effect seen on some, but not most, compounds. This analysis used auto-GC data from Camp Bullis from 2016 through 2021. Daily maximum VOC concentrations were calculated for six VOC: ethylene, toluene, styrene, m/p xylene, ethane, and 1,3-butadiene.

The results are shown in Figure 4-7: *Daily Maximum VOC Concentrations by Day of the Week for Ethylene, Toluene, Styrene, m/p Xylene, Ethane, and 1,3-Butadiene*. Ethylene, toluene, styrene, and m/p xylene all exhibit lower medians and maximum concentrations on weekends versus weekdays. These compounds are often associated with mobile sources, which are lower and more spread out on weekends versus weekdays. In contrast, ethane and 1,3-butadiene show day to day variability, but do not exhibit a difference on weekdays versus weekends. This indicates that these VOC are from sources that do not vary by the day of the week, such as oil and gas production. These results may be evidence of a transitional regime in the San Antonio area and that decreases in both mobile source VOC and NO_x lead to weekend ozone decreases.

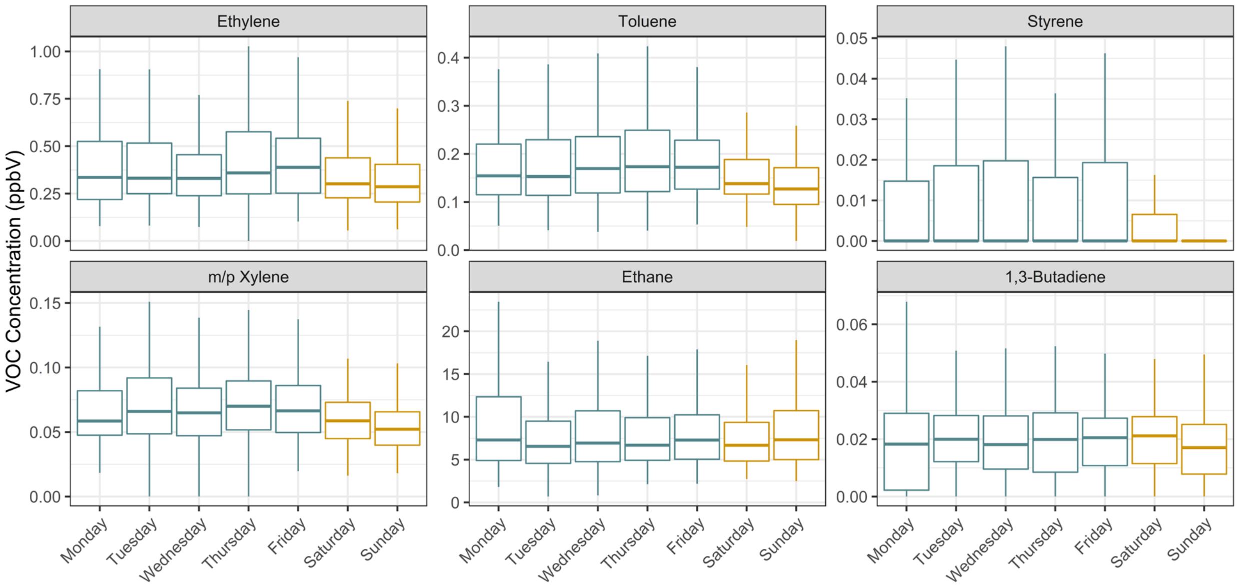

Figure 4-7: Daily Maximum VOC Concentrations by Day of the Week for Ethylene, Toluene, Styrene, m/p Xylene, Ethane, and 1,3-Butadiene

CHAPTER 5: METEOROLOGY AND ITS AFFECT ON OZONE

Meteorological factors play an important role in ozone formation. Meteorological conditions can affect how ozone precursors react, where ozone is formed, and how much ozone is accumulated in an area. The San Antonio area typically experiences high pressure in the summer months, resulting in daily high temperatures above 90° Fahrenheit (F) (NOAA, 2019). The wettest month in the San Antonio area is typically June, which averages 4.14 inches of rain, followed by October with 4.11 inches of rain, and May with 4.01 inches of rain. Surface winds during ozone season are typically out of the south-southeast with few winds out of the west. This section will look at these various meteorological factors at both the local-scale and the large-scale, or synoptic-scale, to determine their effects on ozone formation in the San Antonio area.

5.1 TEMPERATURE

Temperature can play an important part in the ozone formation process. Warmer temperatures often indicate sunny, cloudless days, which are ideal for ozone formation. To investigate the role of temperature on ozone formation in the San Antonio area, the area-wide daily maximum temperature was compared to the area-wide daily maximum eight-hour average (MDA8) ozone concentrations. This analysis used all monitors maintained by the Texas Commission on Environmental Quality (TCEQ), both regulatory and non-regulatory, and only used ozone season data from 2012 through 2021. All hours were used to find the daily-maximum temperature, and data completeness at each monitor was not assessed. Results are displayed in Figure 5-1: *Daily Maximum Temperature versus Daily Maximum Eight-Hour Ozone Concentrations in the San Antonio Area for the Ozone Season from 2012 through 2021*.

The results show that there is a positive relationship between temperature and ozone; however, at higher temperatures there is more variability in the data, with both high and low ozone levels recorded during days with high temperatures. In the graphic, days with a daily maximum eight-hour ozone concentrations greater than 70 parts per billion (ppb) are highlighted in red. Interestingly, no days with eight-hour ozone values above 70 ppb occurred with temperatures less than 75 degrees Fahrenheit (°F). This indicates that, while high ozone occurs during times with high temperatures, other conditions are needed for high ozone to form in the San Antonio area.

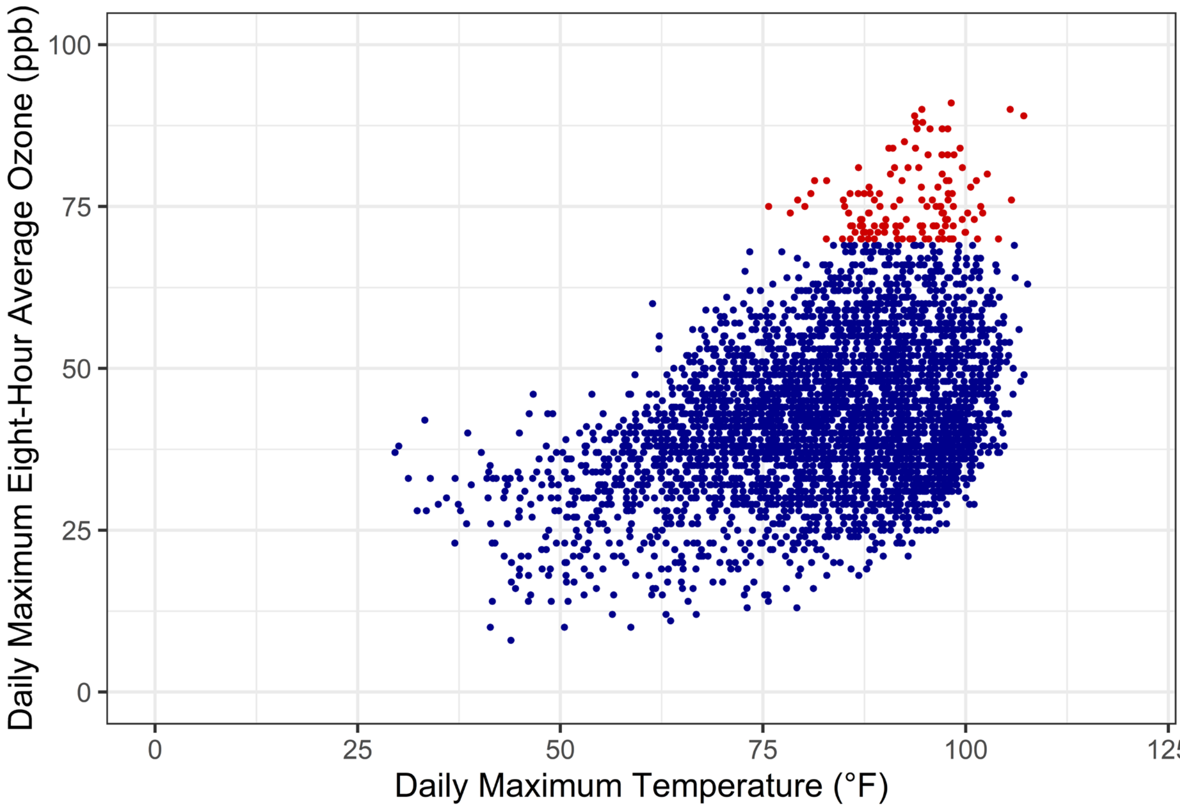

Figure 5-1: Daily Maximum Temperature versus Daily Maximum Eight-Hour Ozone Concentrations in the San Antonio Area for the Ozone Season from 2012 through 2021

5.2 RELATIVE HUMIDITY

Relative humidity is another meteorological factor that tends to correlate with ozone formation. Relative humidity measured at the New Braunfels Airport KBAZ site was compared to the MDA8 ozone for the San Antonio area. For this comparison, only daytime hours were used to calculate the daily-average relative humidity. Daytime hours are defined as the hours of 7:00 local standard time (LST) through 19:00 LST. The analysis used only days with at least 75% complete relative humidity data for the 13 hours investigated and used only ozone season data from 2012 through 2021. Both regulatory and non-regulatory monitors were used to find the MDA8 ozone concentration for the San Antonio area. Results are displayed in Figure 5-2: *Average Daytime Relative Humidity versus Daily Maximum Eight-Hour Ozone in the San Antonio Area for the Ozone Season from 2012 through 2021*.

Results show a negative correlation between average -daytime relative humidity and MDA8 ozone. Low relative humidity indicates less moisture in the air. The negative correlation suggests that as the air is more saturated with moisture, less ozone is formed. Days with MDA8 ozone concentrations greater than 70 ppb are highlighted in red. The general correlation but lack of causation indicate that low relative humidity does not cause high ozone but is among several contributing factors. Most likely, relative humidity is driven by synoptic scale conditions, such as post-frontal conditions. Typically, drier air follows cold fronts as they move through the San Antonio area. Several researchers have shown that post frontal conditions can be conducive to ozone formation in the HGB area (Lefer 2010; Rappenglueck 2008). The negative correlation of ozone and relative humidity for the San Antonio area indicates that these types of meteorological conditions may also lead to ozone formation in the San Antonio area.

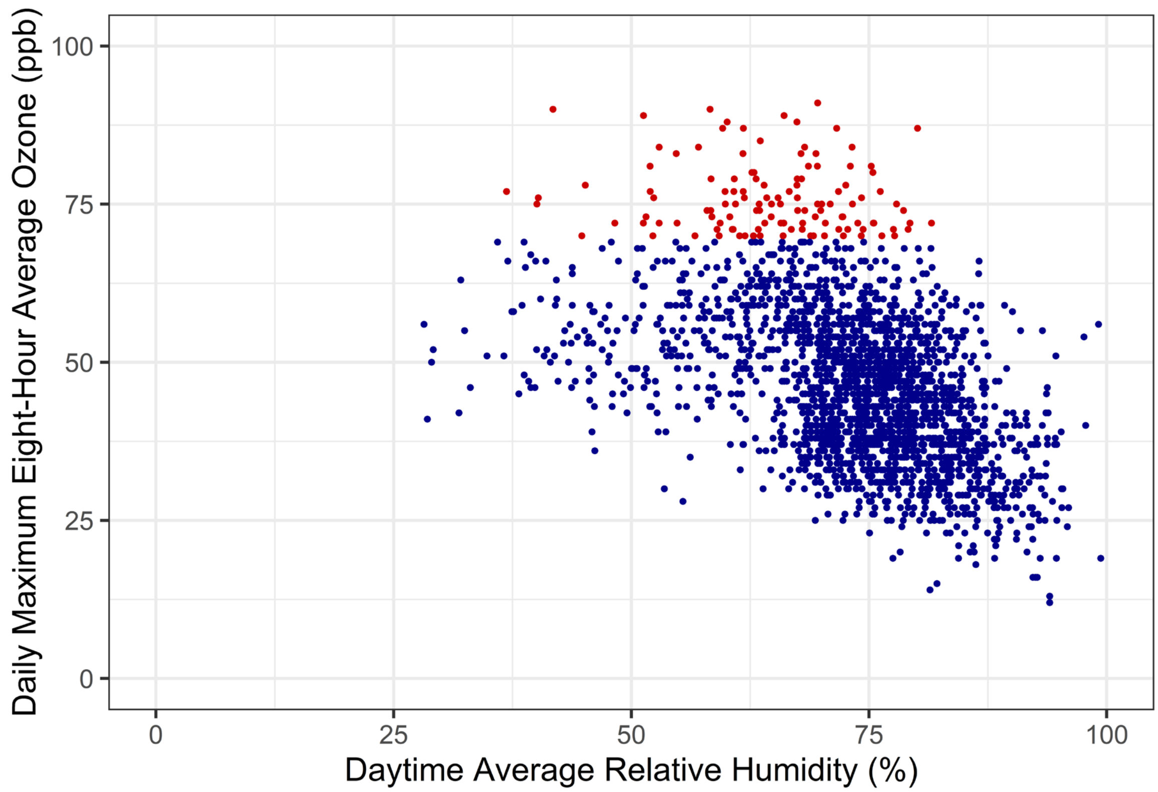

Figure 5-2: Average Daytime Relative Humidity versus Daily Maximum Eight-Hour Ozone in the San Antonio Area for the Ozone Season from 2012 through 2021

5.3 WINDS

Winds are characterized by wind speed and wind direction. Winds can play an important role in ozone formation. Low wind speeds can allow accumulation of ozone and its precursors, and high wind speeds can lead to increased dispersion. Changing wind directions can cause recirculation of pollutants in an area, bring about transported ozone from other areas, or bring precursor concentrations from sources upwind to areas downwind. This section will investigate the characteristics of the winds in the San Antonio area and determine how those winds affect ozone and its precursors in the San Antonio area.

5.3.1 Prevailing Wind Patterns

Examination of prevailing wind patterns in the San Antonio area will help determine if wind patterns observed on high ozone days are unique. One way to examine wind patterns in an area is with a wind rose. Wind roses show not only the direction of winds but also the speed at which they occur. Wind roses at three regulatory monitors in Bexar County 2015 ozone National Ambient Air Quality Standard (NAAQS) nonattainment area were examined for high ozone days from 2012 through 2021.

Wind Roses, overlaid on a map, are shown in Figure 5-3: *Wind Roses in the Bexar County 2015 Ozone NAAQS Nonattainment Area for High Ozone Days during the Ozone Season from 2012 through 2021*. For high ozone days, the wind roses show winds at Camp Bullis are generally out of either the northwest or southeast, with speeds generally from 0 to 10 miles per hour (mph). At the San Antonio Northwest and Calaveras Lake monitors, high ozone days generally have winds from the southeast, with speeds from 0 to 10 mph. During the ozone season, the prevailing wind direction for the San Antonio area is from the southeast. This meteorological feature is one reason most high ozone days have winds from the southeast. A noticeable difference between high and low ozone days (not shown) is that on high ozone days wind speeds at all three monitors are generally slower, from 0 to 10 mph, whereas on low ozone days wind speeds are faster, from 5 to 15 mph.

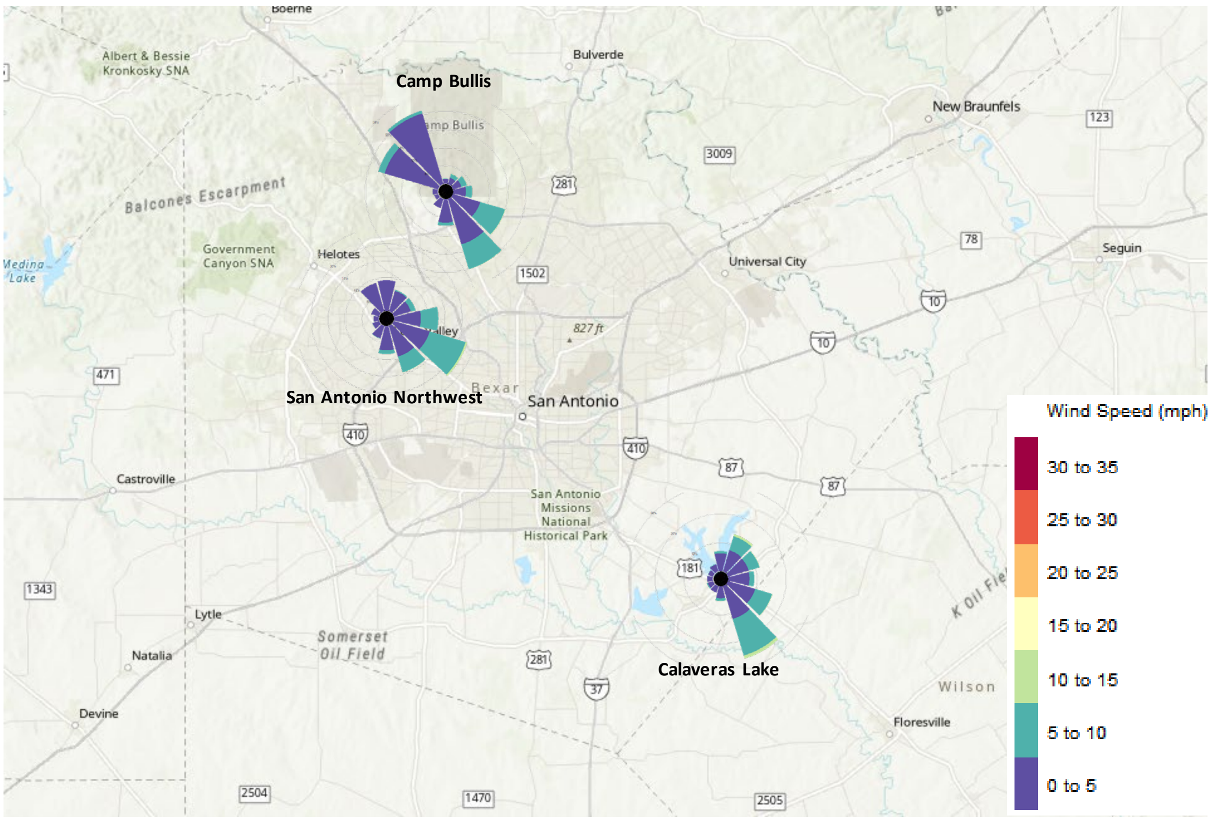

Figure 5-3: Wind Roses in the Bexar County 2015 Ozone NAAQS Nonattainment Area for High Ozone Days during Ozone Season from 2012 through 2021

5.3.2 Wind Speed

Typically, higher ozone concentrations are observed on days with lower winds speeds. Lower wind speeds, many times due to a surface-level high-pressure system in the area, give ozone precursors more time to mix and react, and ozone can quickly accumulate due to limited dispersion. High wind speeds ventilate an area, essentially diluting ozone and its precursors. To determine the effect of wind speeds on ozone formation, the average daytime (07:00 LST through 19:00 LST) resultant wind speeds at the Camp Bullis monitor were compared to the MDA8 ozone concentrations. Only ozone season months from 2012 through 2021 were used. To prevent biased data due to missing values, only days with at least 75% valid daytime hours of wind data were used.

Results are shows in Figure 5-4: *Average Daytime Resultant Wind Speed at Camp Bullis Versus Daily Maximum Eight-Hour Ozone for the Ozone Season from 2012 through 2021*. Days with an MDA8 ozone concentration greater than 70 ppb are highlighted in red. The results show that higher ozone is formed when average daytime resultant wind speeds are less than about eight mph; however, slower wind speeds don't always produce high ozone. This indicates that there are meteorological factors in addition to wind speed, such as wind direction, temperature, and relative humidity, that are involved in ozone formation in the San Antonio area.

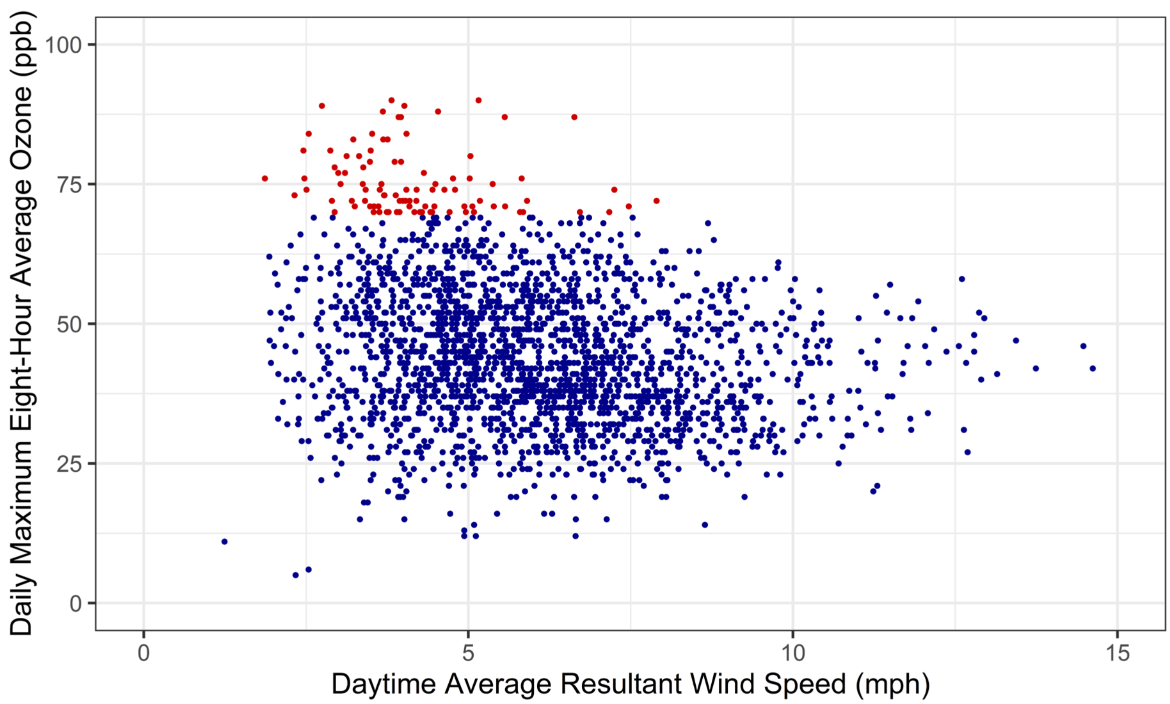

Figure 5-4: Average Daytime Resultant Wind Speed at Camp Bullis Versus Daily Maximum Eight-Hour Ozone for the Ozone Season from 2012 through 2021

5.3.3 Surface Winds on High Ozone Days

Surface-level back trajectories were used to examine the surface level wind patterns on high ozone days. These types of analysis are more informative because they consider both wind speed and wind direction. While a wind rose will show a summary of general wind patterns, a surface-level back trajectory can plot the location of an air parcel every five minutes, which can show of the path of surface winds on high ozone days. Surface-level back trajectories are calculated using a Lagrangian model that calculates the location of an air parcel using inverse distance square weighted wind speed and wind direction. This model uses no vertical mixing in the calculation of trajectories. The trajectory calculation uses five-minute resolution meteorological data from all TCEQ meteorological monitors in the San Antonio area.

For this analysis, surface-level back trajectories were calculated for every hour of each high ozone day in the Camp Bullis monitor from 2012 through 2021 and aggregated into figures for each hour of the day, which are shown in LST. For this analysis, only regulatory monitors were used to determine high ozone days. Trajectories were calculated starting at Camp Bullis and were run backwards in time for five hours. The results are shown below in Figure 5-5: *Surface Level Back Trajectories for Each Hour on High Ozone Days 2012 through 2021 Terminating at Camp Bullis.* Results show an evolution of wind speed and direction over the course of the day. On most high ozone days, there are two wind reversals over the 24-hour period. At midnight, southeastern winds prevail. By 8:00 LST, nearly all days show northwestern winds. Case studies show that this wind reversal usually takes place over the course of about four hours, but the exact start time fluctuates. Air flow does not remain northwesterly for long, starting a second reversal by 10:00 LST on most days. This second reversal also typically takes approximately four hours until winds are southeasterly or easterly. After this second reversal, winds tend to remain consistent for the rest of the day.

Most of the five-hour trajectories are short because slow wind speeds are prevalent on most high ozone days, as discussed in the previous section. Additionally, because of the slow wind speeds, most of the trajectories remain in the Bexar County 2015 ozone NAAQS nonattainment area. This further supports the conclusion that local emissions, discussed in Section 3.3.4, influence ozone formation in the Bexar County 2015 ozone NAAQS nonattainment area. Most of the trajectories show very slow wind flow from the northwest and faster wind flow from the southeast; however, the hours most conducive to ozone formation, 6:00 LST to 19:00 LST, often receive air masses from the northeast and eastern parts of San Antonio more than the southeastern part of San Antonio. This may indicate that emissions east and northeast of San Antonio have a greater impact on ozone formation at the Camp Bullis monitor than emissions in the southeast and west of the city. When compared to the emissions patterns maps in Section 3.3, the surface trajectories clearly travel through areas with several key sources of both volatile organic compounds (VOC) and nitrogen oxides (NO_X) such as mobile, cement kilns, electric generating units, etc.

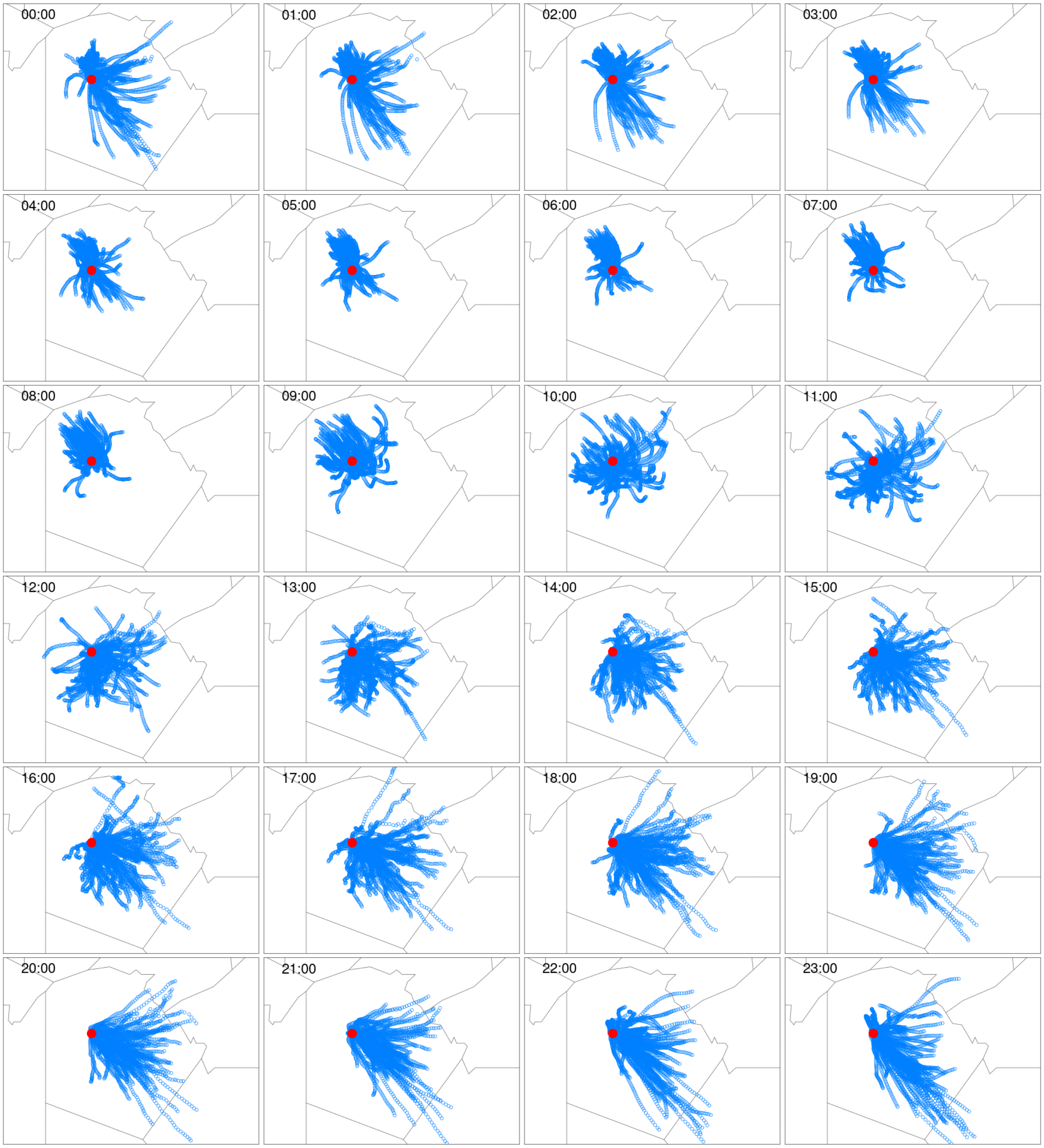

Figure 5-5: Surface Level Back Trajectories for Each Hour on High Ozone Days 2012 through 2021 Terminating at Camp Bullis

In addition to an hourly analysis of surface level winds, an annual analysis was conducted. The results are shown in Figure 5-6: *Surface Level Five-Hour Back Trajectories for Every Hour on High Ozone Days 2012 through 2021 Terminating at Camp Bullis*. This analysis shows substantial year-to-year variations, with some years sharing a very similar pattern. The variation in wind patterns may be a partial driver in variability to ozone levels due to meteorology, as is discussed in Section 5.4.

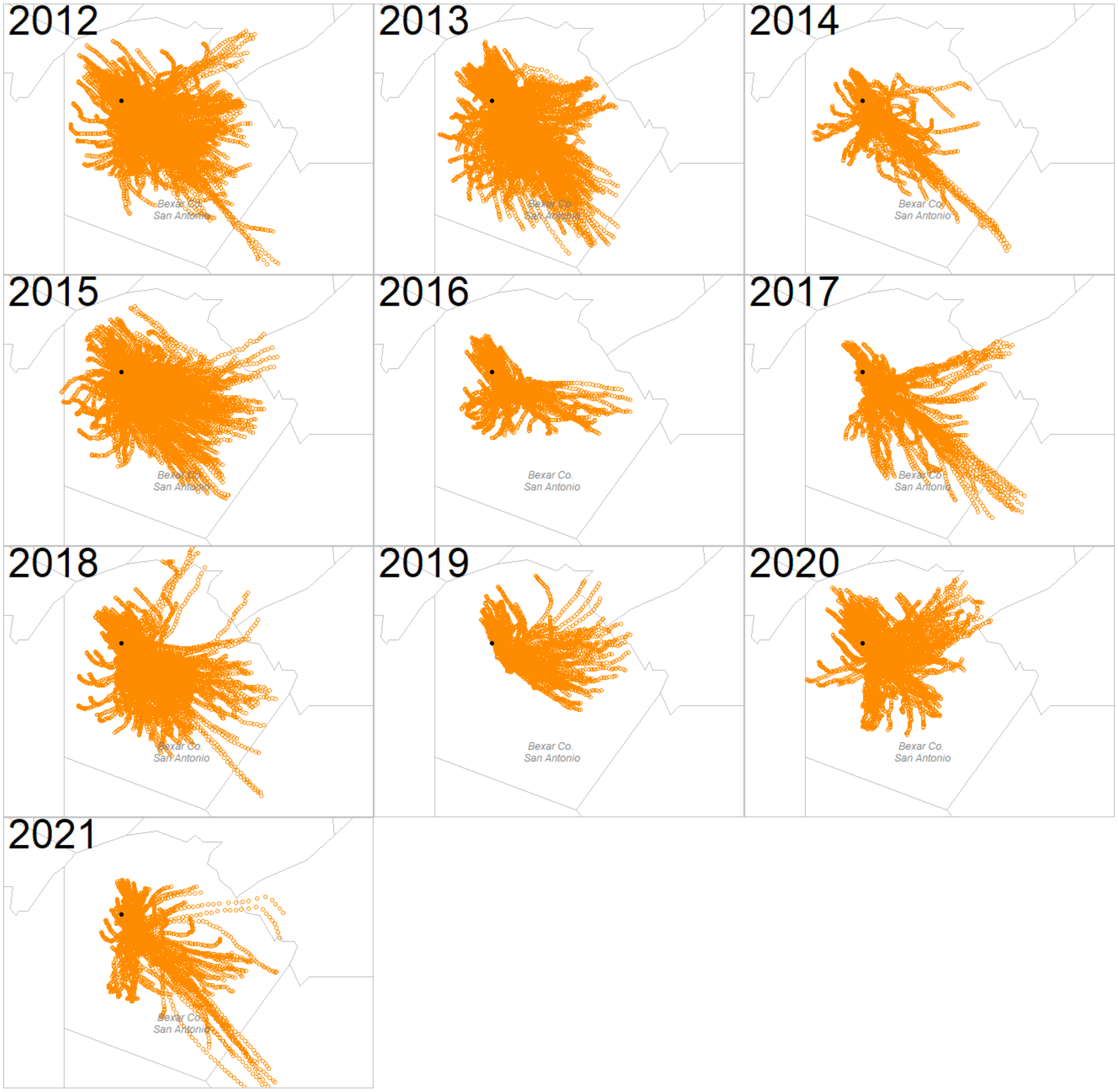

Figure 5-6: Surface Level Five-Hour Back Trajectories for Every Hour on High Ozone Days 2012 through 2021 Terminating at Camp Bullis

5.3.4 Upper-Level Winds

While surface winds can show how ozone is formed locally, upper-level wind characterization can indicate potential sources that transport ozone into the area from other regions. Upper-level winds are examined using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by the National Oceanic and Atmospheric Administration's (NOAAS's) Air Resources Laboratory (ARL) and using North American Mesoscale (NAM) Forecast System 12 kilometer (km) input files (Stein et al. 2015, Rolph et al. 2017). Upper-level back trajectories were computed for each day of the modified ozone season, which is defined as April through October, from 2012 through 2021. The 36-hour back trajectories end at 18:00 LST at the Camp Bullis monitor at an altitude of 500 meters above ground level (mAGL).

Trajectories with similar patterns can be combined based on their size and shape to discern common transport patterns more easily, a process called clustering. Clustering can also help distinguish between paths that lead to higher or lower than average ozone concentrations. The first set contains trajectories for each day in April through October in 2012 through 2021, this modified ozone season was used since only one exceedance day has occurred in March for the past ten years, which may skew the low ozone results. The low ozone dataset includes 1955 trajectories that were successfully clustered. The second set contains trajectories for only high ozone days in the San Antonio area from 2012 through 2021. The high ozone days dataset includes 91 days, all of which were successfully clustered. Background ozone was estimated for each trajectory as described in Section 2.6 and statistics were calculated based on the cluster of each trajectory. The area's MDA8 ozone was calculated as the highest MDA8 ozone of both regulatory and non-regulatory ozone monitors in the San Antonio area on each day.

Results of the cluster analysis for low days and the ozone statistics for each cluster are displayed in Figure 5-7: *Mean of 36-Hour Back Trajectory Clusters for All Low Ozone Days 2012 through 2021* and Figure 5-8: *Estimated Eight-Hour Background Ozone (right) and Area Wide Daily-Maximum Eight-Hour Ozone Concentrations (left) by Cluster for All Low Ozone Days 2012 through 2021*. The y-axis scales in the two images in Figure 5-8 are different. These trajectories are grouped into six clusters, three clusters are coastal and account for 85% of days and three clusters are land-based which account for 15% of days. Generally, the pattern in background ozone values follows the pattern in area MDA8 ozone for each cluster. This corroborates with the analysis presented in Section 2.6 that shows a strong correlation between background ozone and area MDA8 ozone. The continental West cluster, cluster 6, has the largest relative difference between its background ozone and area MDA8 ozone medians, with a much higher relative median in the area MDA8 ozone than background ozone. Because this cluster only contains 24 trajectories its statistics are less normalized relative to the other clusters. The box plots of estimated background ozone and MDA8 ozone indicate the highest median background ozone is associated with the continental Texas cluster, cluster, and the continental Midwest cluster, cluster. Looking at the coastal clusters, it is evident that the clusters passing through the Corpus Christi and Houston areas bring in much higher background zone than the cluster from southern Texas. This may be partially influenced by the slower wind flow, indicated by the shorter trajectory lines, but this also indicates that higher background ozone is being partially driven by pollution from other Texas cities.

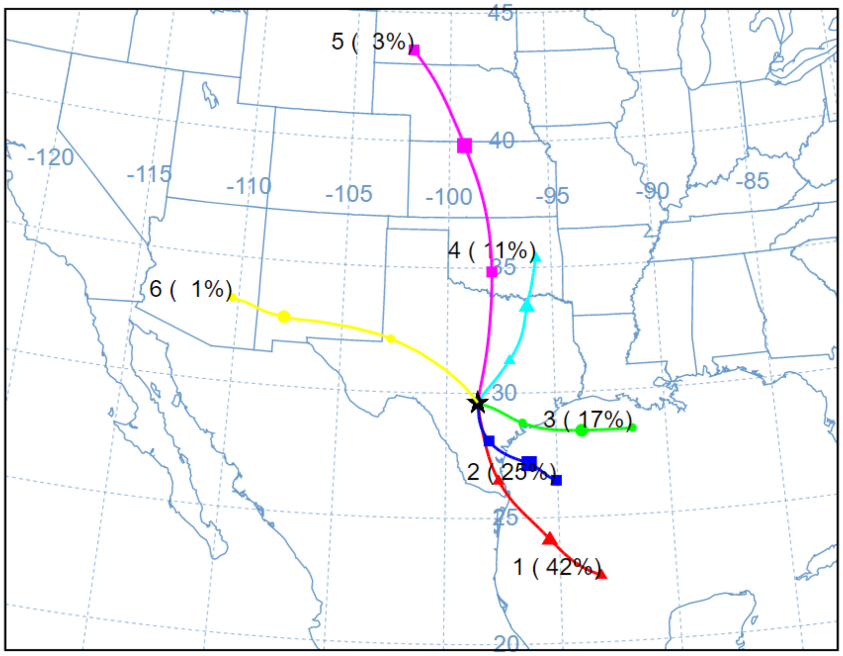

Figure 5-7: Mean of 36-Hour Back Trajectory Clusters for All Low Ozone Days 2012 through 2021 Terminating at Camp Bullis

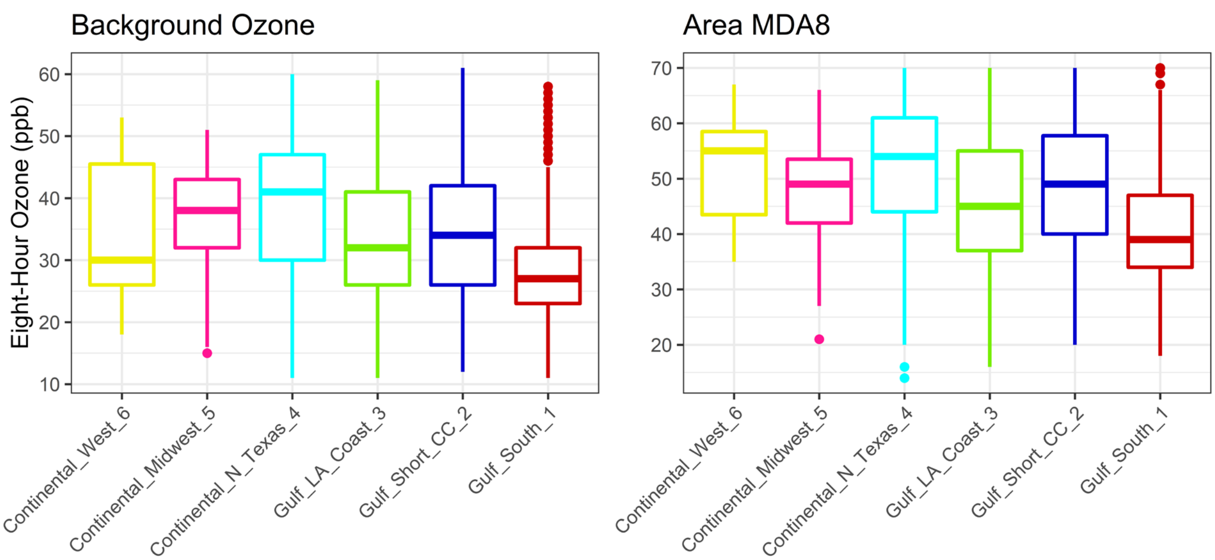

Figure 5-8: Estimated Eight-Hour Background Ozone (right) and Area Wide Daily-Maximum Eight-Hour Ozone Concentrations (left) by Cluster for All Low Ozone Days 2012 through 2021

The results of the high ozone days cluster analysis are shown in Figure 5-9: *Mean of 36-Hour Back Trajectory Clusters for All High Ozone Days 2012 through 2021* and Figure 5-10: *Estimated Eight-Hour Background Ozone (right) and Area Wide Daily-Maximum Eight-Hour Ozone Concentrations (left) by Cluster for All High Ozone Days 2012 through 2021*. Y-axis scales on the images in Figure 5-10 are different. The trajectories are grouped into four clusters; 54 high ozone days originated from the gulf area, clusters 1 and 3, 10 originated from the north, cluster 4, and 27 days had long-term recirculating flow in the immediate area, cluster 2. Compared to the low ozone days, these trajectories are much shorter, indicating slower wind speeds. Half of the individual trajectories that comprise the continental cluster are short enough to be contained within Texas. This corroborates the analyses presented in Section 5.3.2 that shows slower wind speeds are conducive to ozone formation. Additionally, this dataset differs greatly from the low ozone dataset in that the background ozone and area MDA8 ozone do not follow similar patterns among clusters. The continental cluster, cluster 4, has the lowest median background ozone, perhaps because of the longer transport path, but among the highest area MDA8 ozone medians. This may indicate that higher levels of precursors are transported into the city and react locally to form ozone. Meanwhile, the central Texas cluster, cluster 2, that shows circulation in the immediate area has background ozone similar to other clusters but the highest area MDA8 ozone. This aligns with the general understanding of ozone formation, slow recirculating wind flows allow local emissions and secondary products such as ozone to accumulate, often over several days. Overall, this analysis shows that most high ozone days result from slow upper wind flow from within Texas or just offshore over the gulf.

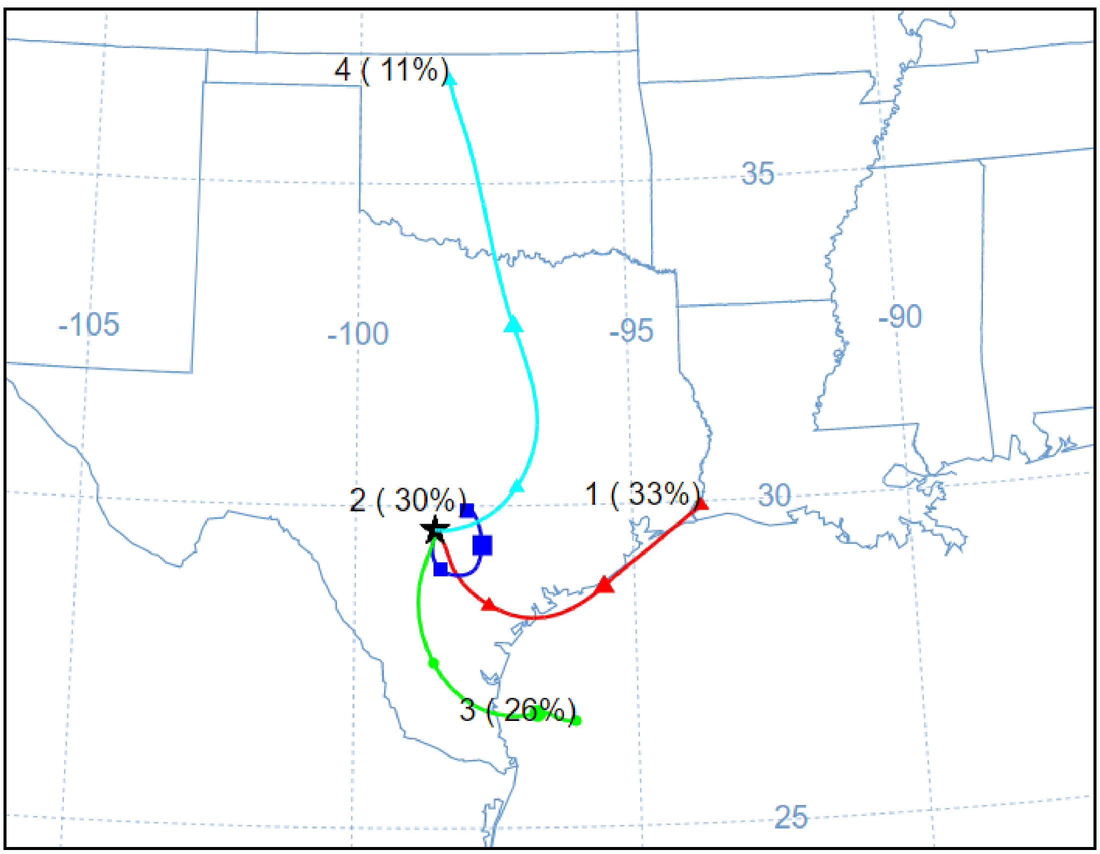

Figure 5-9: Mean of 36-Hour Back Trajectory Clusters for All High Ozone Days 2012 through 2021 Terminating at Camp Bullis

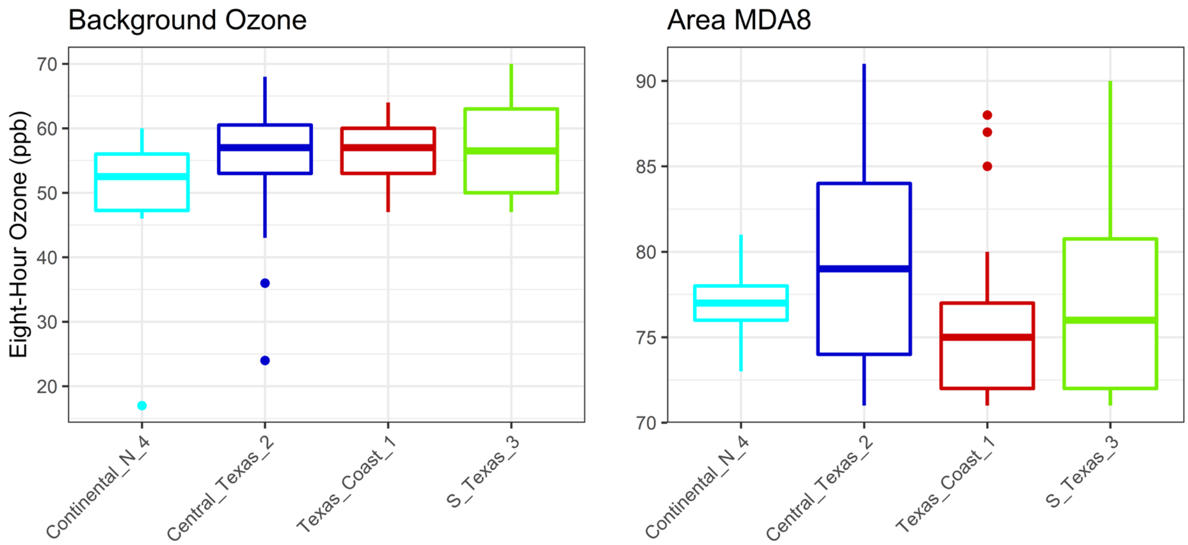

Figure 5-10: Estimated Eight-Hour Background Ozone (right) and Area Wide Daily-Maximum Eight-Hour Ozone Concentrations (left) by Cluster for All High Ozone Days 2012 through 2021

The findings from these analyses corroborate with those of the San Antonio Field Study (Flynn et al. 2019). Using the supplementary data collected during the field study, ozone in San Antonio was modeled for May 2017. Flynn et al. (2019) found that ozone variability was mostly associated with continental winds. This suggested that high background levels were transported into the city from continental winds and then combined with local emissions, resulting in high ozone concentrations observed in the San Antonio area.

5.3.5 Ozone and NO_x Concentrations versus Winds

Wind speed and direction are also used to determine potential sources for both ozone and NO_x. One method to perform this type of source attribution involves the use of bivariate polar plots (Uria-Tellaetxe and Carslaw 2014). An R package called openair (Carslaw and Ropkins 2012) is used to create the plots. Bivariate polar plots show how pollutant concentrations vary with wind speed and wind direction at certain receptor location. These types of plots help to figure out the type of source based on wind-speed dependence analysis. Bivariate polar plots use the conditional probability function (CPF) to identify potential sources. CPF calculates the probability that, for a particular wind direction, the concentration of species is greater than a specified value. The value specified is usually expressed as a percentile of the species of interest. Bivariate polar plots are constructed by partitioning wind speed, wind direction, and pollutant concentration data into wind speed and wind direction bins. Mean pollutant concentration is then calculated for each bin. CPF is the ratio of number of samples in a given bin having some defined high concentration, to the total number of samples in that bin. The CPF analysis shows which wind direction and wind speed intervals are dominated by high concentrations.

This analysis used NO_x, one-hour ozone, resultant wind speed, and resultant wind direction data for the ozone season from 2012 through 2021 at the Calaveras Lake monitor, and Camp Bullis monitor. According to the prevailing wind directions in the

San Antonio area, the Calaveras Lake monitor is considered a monitor upwind of the San Antonio area, while the Camp Bullis monitor is considered a monitor downwind of the San Antonio area. All hours were used in this analysis.

For NO_x, the conditional probability was calculated for the 95th percentile for high ozone days using hourly data. This value corresponds to NO_x concentrations greater than or equal to 21 ppb at Calaveras Lake and greater than or equal to 7.2 ppb at Camp Bullis. The results for NO_x are shown in Figure 5-11: *Bivariate Polar Plots, based on a CPF at the 95th Percentile, for NO_x during the Ozone Season from 2012 through 2021 at Calaveras Lake (upwind) and Camp Bullis (downwind).* Note that the plots for Camp Bullis and Calaveras Lake are not the same scale. In the plots, the warmer (redder) colors represent wind direction and speeds that are more likely to have high NO_x concentrations. The higher wind speeds are further from the center of the plots, with each light gray ring representing a wind speed increment of 5 mph.

The bivariate polar plots for NO_x show that the highest NO_x concentrations at both monitors occur at the slower wind speeds, typically less than 5 mph. At the Calaveras Lake monitor, the highest NO_x concentrations are most likely to be from the west to northwest. These concentrations may indicate emissions from the Calaveras Lake power plant. At Camp Bullis, the highest NO_x concentrations are likely from the south, southwest, and southeast; these high NO_x concentrations with slow wind speeds may indicate mobile emissions or a source at that monitor.

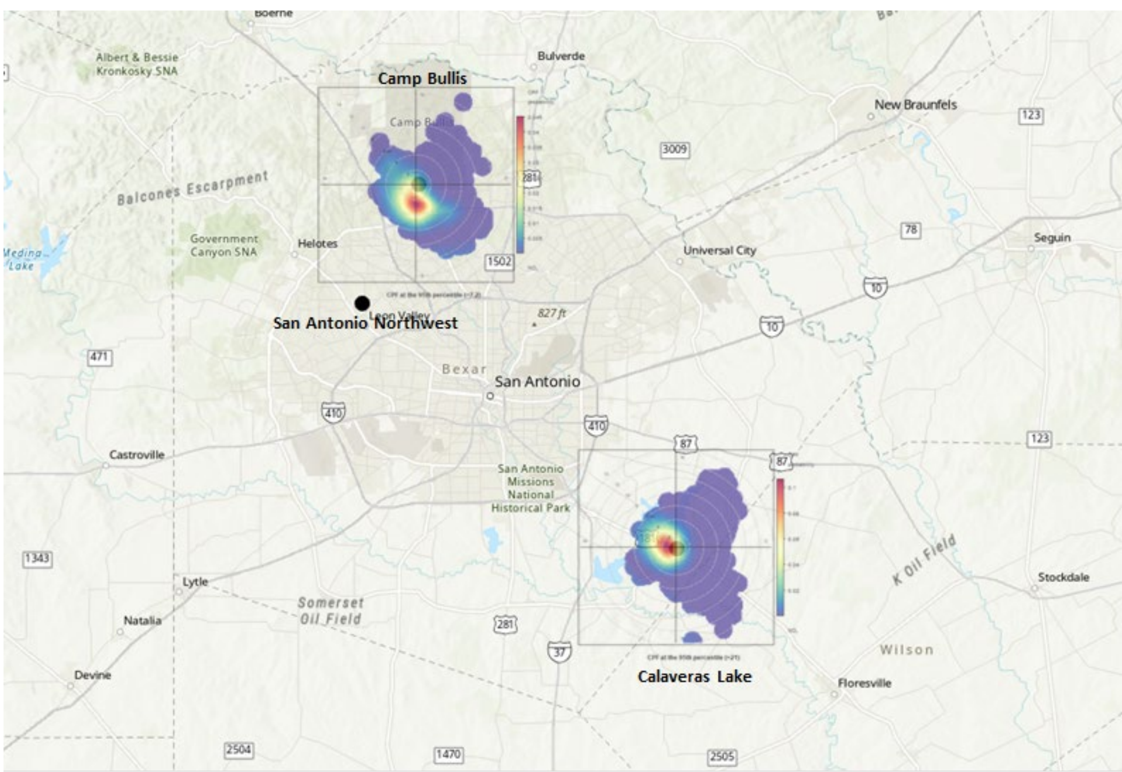

Figure 5-11: Bivariate Polar Plots, based on a CPF at the 95th Percentile, for NO_x Corresponds to the Days having Daily Maximum Eight-Hour Ozone over 70 ppb, During the Ozone Season from 2012 through 2021 at Calaveras Lake (upwind) and Camp Bullis (downwind)

For ozone, the conditional probability was also calculated at 95th percentile for high ozone days using hourly data. This value corresponds to ozone concentrations greater than or equal to 72 ppb at Calaveras Lake and greater than or equal to 86 ppb at Camp Bullis. The bivariate polar plots for one-hour ozone are displayed in Figure 5-12: *Bivariate Polar Plots, based on a CPF that Corresponds to the Days having Daily Maximum Eight-Hour Ozone over 70 ppb, for the Ozone Season from 2012 through 2021 at Calaveras Lake and Camp Bullis*. As with the NO_x plots, the bivariate polar plots for ozone are not to the same scale.

Like with NO_x, the highest one-hour ozone values are most likely to occur with wind speeds less than 5 mph. At the Calaveras Lake monitor, the highest one-hour ozone values are most likely from the north, although there is some probability of high ozone to the northeast. With prevailing winds in the San Antonio area out of the southeast, Calaveras Lake is usually an upwind monitor for the San Antonio area. It appears that Calaveras Lake observes high ozone concentrations in situations where winds from the north bring urban-area San Antonio emissions and Calaveras Lake Power Plant emissions to the monitor.

At the Camp Bullis monitor, the highest one-hour ozone concentrations occur when winds are slow and from the southeast. This matches the prevailing wind patterns for the San Antonio area. When winds are from the southeast, it appears that emissions from the Calaveras Lake power plant combine with mobile emissions from the urban core of the San Antonio area to create high ozone downwind at Camp Bullis.

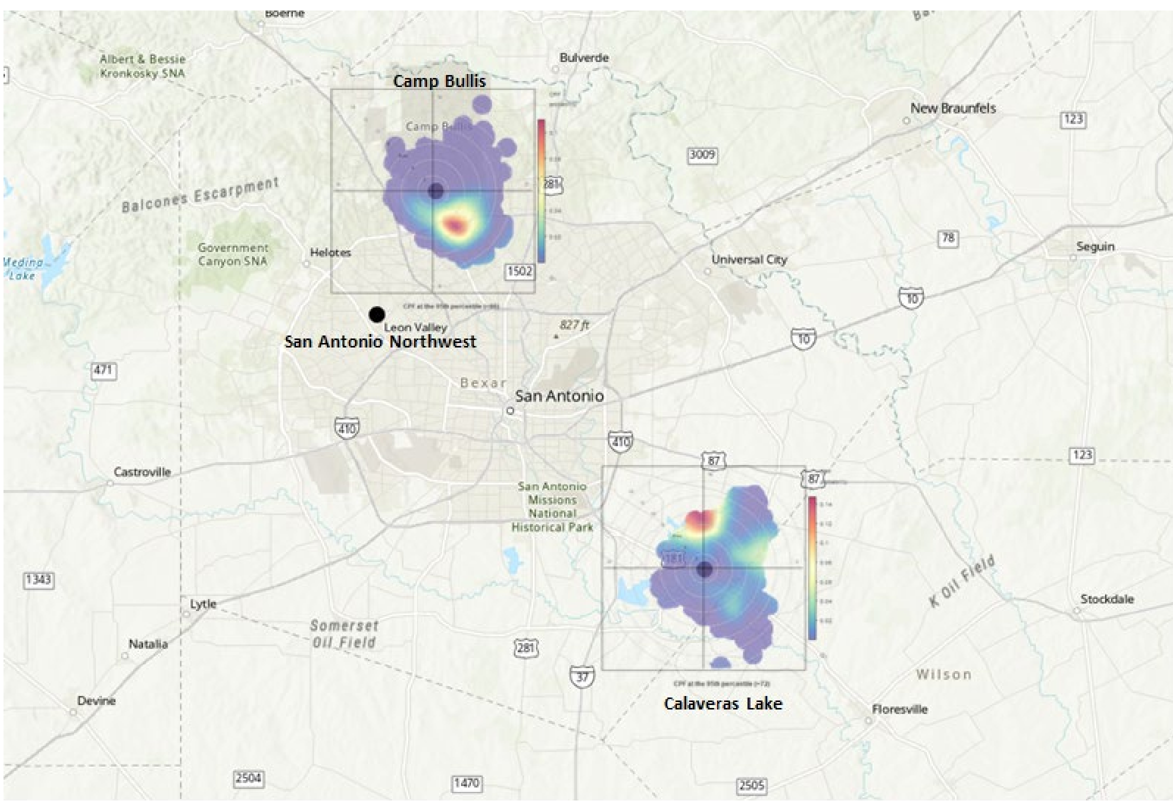

Figure 5-12: Bivariate Polar Plots, based on a CPF that Corresponds to the Days having Daily Maximum Eight-Hour Ozone over 70 ppb, for the Ozone Season from 2012 through 2021 at Calaveras Lake and Camp Bullis

5.4 OZONE CONCENTRATIONS ADJUSTED FOR METEOROLOGY

Meteorological conditions play an important role in ozone formation. Year-to-year variability in meteorological conditions in turn cause variability in ozone concentration trends. Although design values consider this variability by averaging the fourth-highest MDA8 ozone over three-years, this is often not enough to account for years with extreme meteorological conditions such as low winds speeds, drought, or extremely high temperatures. Investigating meteorological influences on ozone trends allows analysis of how ozone concentrations respond to changes in emissions rather than changes in the meteorology.

Meteorologically adjusted MDA8 ozone values represent what the ozone would have been if meteorological effects on ozone concentrations are removed. Without the influence of meteorology, changes observed in ozone concentrations are more likely due to emission changes rather than extreme meteorological events. The Environmental Protection Agency (EPA) has developed a statistical model (Wells et al. 2021) that uses local weather data to adjust the ozone trends according to the meteorology for that year. These trends compare the average, 90th percentile, and 98th percentile MDA8 ozone from May through September to the meteorologically adjusted average, 90th percentile, and 98th percentile MDA8 ozone from May through September. The EPA calculated these trends for each regulatory ozone monitor in Bexar County (EPA 2022) from 2012 through 2021. Although results for all statistics were examined, only the 98th percentile trends will be discussed in this document since it most closely relates with the ozone values that are used in the design value calculations. The 98th percentile is approximately the eight-largest MDA8 value for the year. Figure 5-13: *Measured 98th Percentile Ozone Values in the Bexar County 2015 Ozone NAAQS Nonattainment Area* and Figure 5-14: *98th Percentile Ozone Values Adjusted for Meteorology in the Bexar County 2015 Ozone NAAQS Nonattainment Area* shows the trends in the measured 98th percentile and the trends in the 98th percentile when adjusted for meteorology for the three regulatory monitors in Bexar County.

Generally, the adjusted ozone concentrations experience less year-to-year variability. This confirms the hypothesis that much of the large swings are due to fluctuations in meteorological patterns. A clearer downward trend is observed in the adjusted data set compared to the measured data set for the two highest monitors, Camp Bullis and San Antonio Northwest; however, it does appear that Calaveras Lake has been experiencing an upward trend.

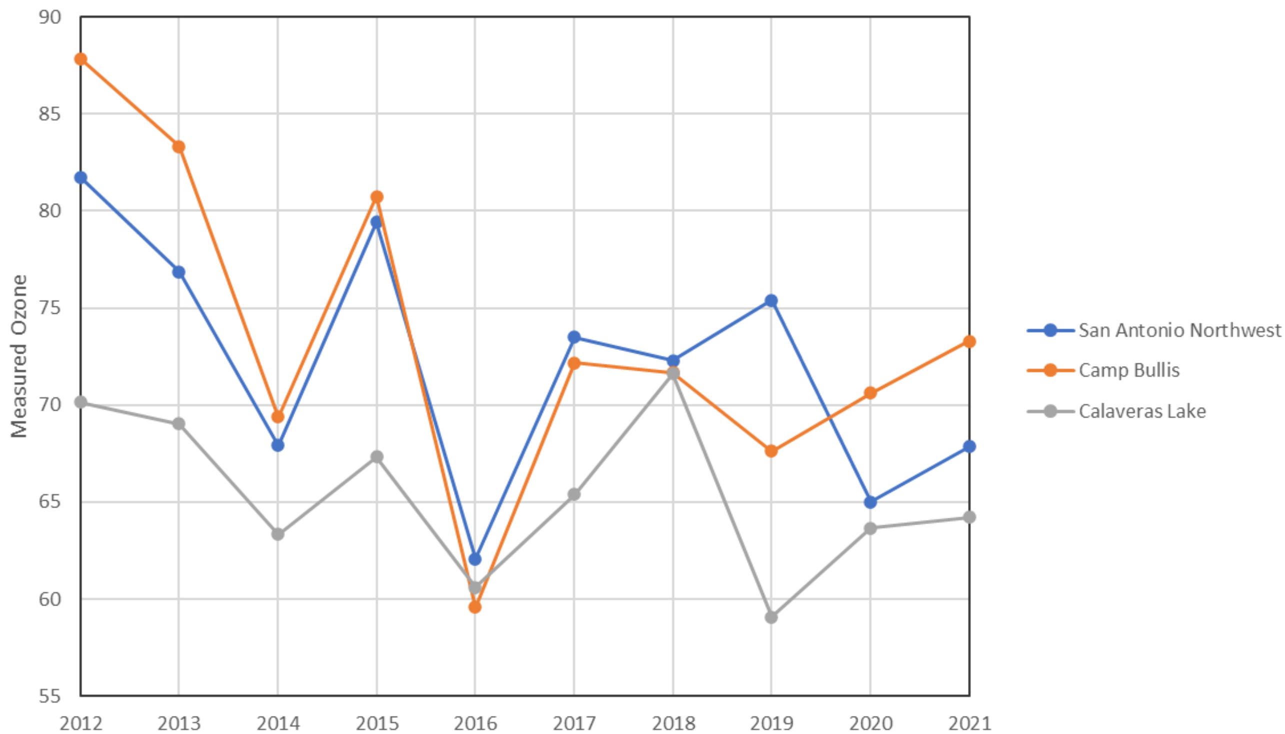

Figure 5-13: Measured 98th Percentile Ozone Values in the Bexar County 2015 Ozone NAAQS Nonattainment Area

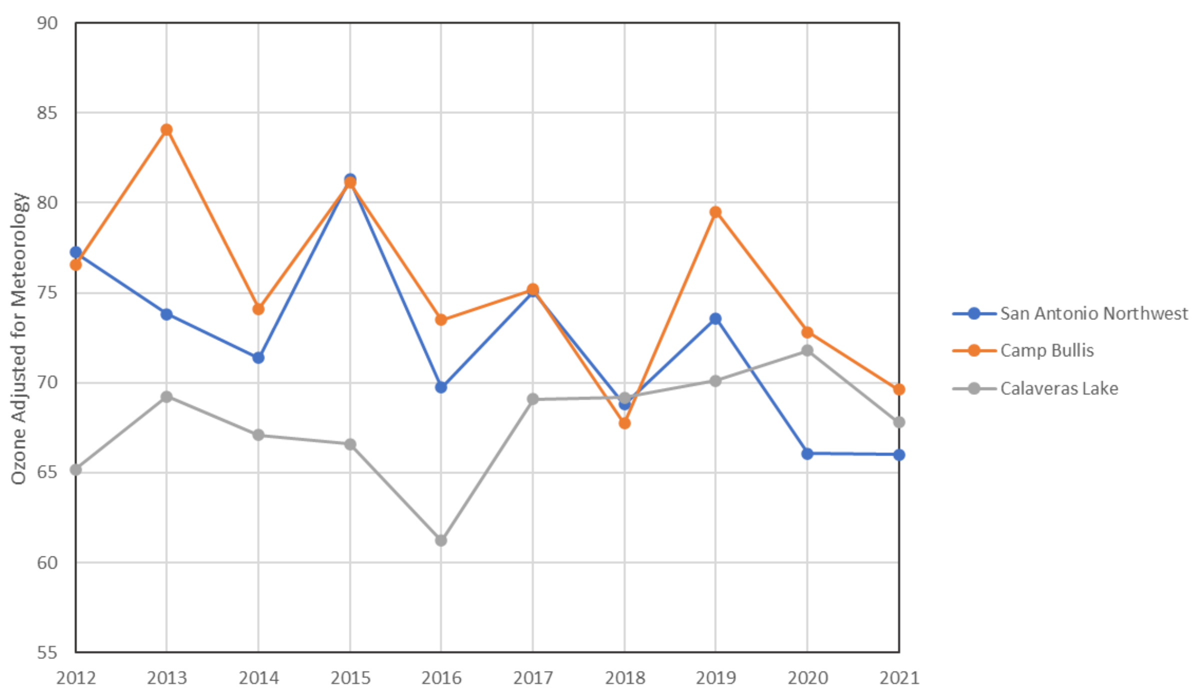

Figure 5-12: 98th Percentile Ozone Values Adjusted for Meteorology in the Bexar County 2015 Ozone NAAQS Nonattainment Area

Figure 5-15: *Difference Between Measured and Adjusted for Meteorology 98th Percentile Ozone in the Bexar County 2015 Ozone NAAQS Nonattainment Area* below shows the difference between the actual measured 98th percentile MDA8 ozone at each monitor and the 98th percentile MDA8 ozone adjusted for meteorology. Points above the x-axis indicate years that meteorology caused measured ozone to be higher and points below the x-axis indicate years that meteorology caused measured ozone to be lower.

In the ten-year period studied, four years were not impacted strongly by meteorology, three years experienced higher ozone from meteorology, and three years experienced lower ozone from meteorology. Of these, the strongest impacts were in 2012, 2016, and 2019. In 2012, the 98th percentile MDA8 ozone was estimated to be 4 to 12 ppb higher due to meteorological patterns. In 2016, it was estimated to be 1 to 14 ppb lower due to meteorological patterns, with the highest impacts at Camp Bullis and San Antonio Northwest. In 2019 meteorology is estimated to have decreased the 98th percentile MDA8 ozone values at Camp Bullis and Calaveras Lake by about 12 ppb but increased the 98th percentile ozone value at San Antonio Northwest by 2 ppb. Upon comparison with Figure 5-6, there seems to be somewhat atypical surface level wind patterns in 2016 and 2019. In 2016, high ozone only occurred on days with very short trajectories, which corresponds to very slow winds speeds, and there were no trajectories from the northeast. Conversely, in 2019, most high ozone days had trajectories that passed through the northeast part of Bexar County, but again only short trajectories occurred on high ozone days.

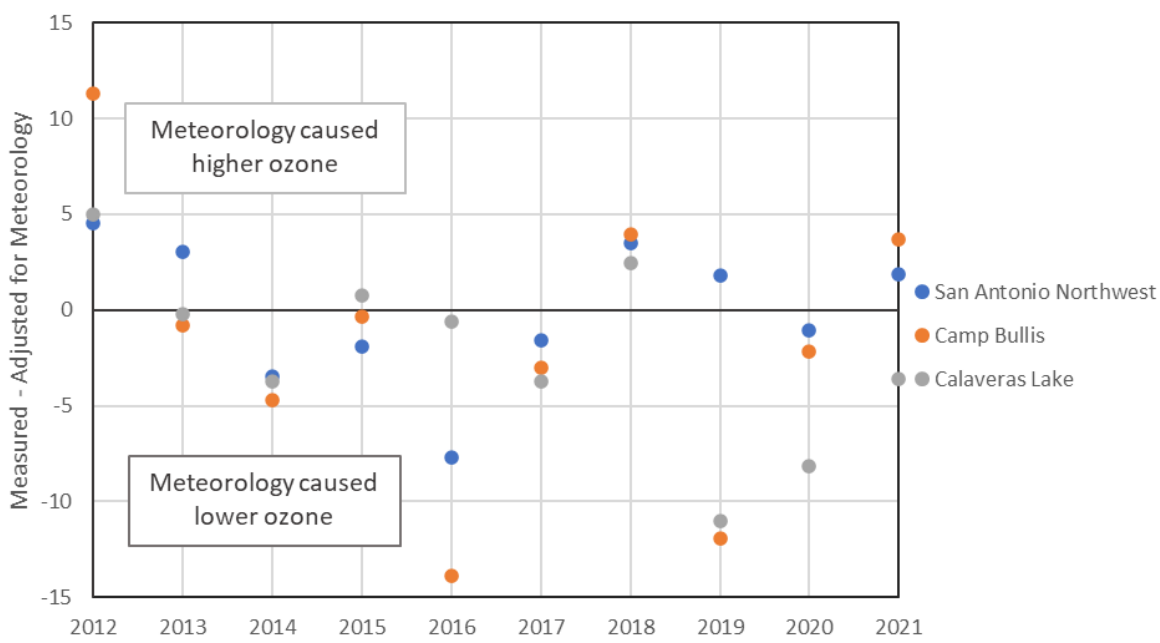

Figure 5-13: Difference Between Measured and Adjusted for Meteorology 98th Percentile Ozone in the Bexar County 2015 Ozone NAAQS Nonattainment Area

Overall, variation in meteorological patterns causes some amount of variation in ozone levels. It is seen from meteorology adjusted trends observed at the design value setting monitors in the Bexar County 2015 ozone NAAQS nonattainment area.

CHAPTER 6: CONCLUSIONS

This conceptual model provides a detailed examination of ozone formation in the Bexar County 2015 ozone National Ambient Air Quality Standard (NAAQS) nonattainment area with a focus on ozone levels above 70 parts per billion (ppb). Most of the analyses in this conceptual model focus on ozone season data, from March through October, in 2012 through 2021 to assess how, when, and where ozone forms in the Bexar County 2015 ozone NAAQS nonattainment area.

From 2012 through 2021, eight-hour ozone design values in the Bexar County 2015 ozone NAAQS nonattainment area have decreased by about 9%, or 7 ppb, but trends remained mostly flat after 2016. The area monitors attainment of both the 1997 and the 2008 eight-hour ozone NAAQS of 84 ppb and 75 ppb, respectively, but remains above 2015 eight-hour ozone NAAQS of 70 ppb. Maximum eight-hour ozone design values occur in northwest Bexar County, with lower ozone observed in southeast Bexar County. Fourth-highest eight-hour ozone values, which are used to calculate the design values, have decreased from 2012 but have remained mostly flat since 2016. Notably the design value setting monitor, Camp Bullis, showed sharp increases in fourth-highest eight-hour ozone values in 2020 and 2021.

The ozone season in the San Antonio area lasts from March through October, with most exceedances occurring after April. The second half of the ozone season, August through October, experiences more high ozone episodes compared to the first half. There is a minimum in July, that breaks the season up into halves.

Ozone is not directly emitted into the atmosphere, but rather formed through a photochemical reaction with nitrogen oxides (NO_x) and volatile organic compounds (VOC). From 2012 through 2021, peak NO_x concentrations decreased across the Bexar County 2015 ozone NAAQS nonattainment area, especially at non-roadside monitors. Low percentile value of NO_x concentrations have decreased at all monitors as well, although the downward trend has stagnated and possibly turned upward since 2018.

From 2012 through 2021, the VOC species associated with mobile sources show a slight downward trend in Bexar County 2015 ozone NAAQS nonattainment area. Species associated with oil and gas activity have had year-to-year variability, but overall show flat or slightly downward trends. Ethane, propane, and n-butane, VOC with low ozone formation potential, contribute the most to the total VOC concentrations observed in the Bexar County 2015 ozone NAAQS nonattainment area. When weighted by reactivity, isoprene, ethylene, n-butane, and toluene contribute the most to total VOC in the Bexar County 2015 ozone NAAQS nonattainment area. The VOC with lower reactivities have such large concentrations in the Bexar County 2015 ozone NAAQS nonattainment area that they still contribute a large portion to total VOC composition even when weighted by reactivity.

Point source NO_x emissions have decreased 13% from 2012 through 2021. VOC point source emissions have had little change of 4% decrease over the analysis years in San Antonio area. The largest NO_x and VOC point sources are in southeast and south of Bexar County and to the northeast outside of Bexar County.

On high ozone days, ozone first peaks near the center of the city of San Antonio and then peaks later in the day on the outskirts of the city to the northwest. This indicates that ozone is first formed in the center of the city and then transported to the northwest, where the highest ozone concentrations typically occur.

Regional background ozone coming into the Bexar County 2015 ozone NAAQS nonattainment area is well correlated with the daily-maximum eight-hour averaged ozone concentrations recorded in the Bexar County 2015 ozone NAAQS nonattainment area. The local production of ozone and background ozone increase proportionally from low ozone days to high ozone days, indicating strong synoptic scale effects on the ozone concentrations in the Bexar County 2015 ozone NAAQS nonattainment area. Overall, background ozone is decreasing, and local production is increasing slightly on both high and low ozone days. Background ozone on low ozone days peaks during the beginning and end of ozone season, but on high ozone days peaks during June and August. This indicates that the high ozone days during the beginning and end of the ozone season are characterized by high regional ozone and those experienced in the middle of ozone season are characterized by elevated local production.

The VOC or NO_x limitation of an air mass can determine decreasing NO_x or VOC would have been more effective on decreasing ozone concentrations. The automated gas-chromatograph (auto-GC) data at Camp Bullis shows the area is trending from transitional to NO_x limited. In recent years, during the morning rush hour, the air mass has become more NO_x limited meaning decreasing NO_x is more effective to decrease ozone concentrations.

Analysis of ozone and precursors on the weekdays versus the weekends shows that there are less ozone exceedances and slightly lower mean ozone on weekends versus weekdays. There is lower peak and median NO_x across the city and lower VOC that are associated with mobile sources on the weekends, this indicates that the weekend effects are due to lower mobile source activity. The relative reductions in ozone, NO_x and VOC on weekends support the conclusion that the ozone formation may be more NO_x limited than VOC limited in Bexar County.

Meteorological conditions linked to high ozone in the Bexar County 2015 ozone NAAQS nonattainment area include high temperatures, lower relative humidity, and slow wind speeds. Ozone season winds are generally from the southeast. On high ozone days, surface winds indicate slow winds with two reversals in wind direction, from the southeast to the northwest, and then from the northwest back to the southeast. These reversals cause higher accumulation of emissions and increased ozone production. Upper-level winds also show that the highest ozone concentrations occur with the slowest wind speeds. Overall, high ozone in the Bexar County 2015 ozone NAAQS nonattainment area occurs when upper-level winds are slow and there is recirculation of the wind direction, when winds are slow from coastal regions, or when winds are continental in origin.

Investigation of NO_x and ozone by wind speed and direction show high NO_x from downtown San Antonio and the area near the Calaveras Lake power plant. At the Camp Bullis monitor, located to the northwest of the San Antonio urban core, the highest ozone concentrations originate from the southeast. At the Calaveras Lake monitor, located to the southeast of the San Antonio urban core, the highest ozone originates from the north. The location of high ozone at Camp Bullis combined with the location of high ozone at Calaveras Lake indicate that ozone is first produced from emissions from the urban area of San Antonio and is then transported downwind.

Overall, it appears that high ozone in the Bexar County 2015 ozone NAAQS nonattainment area mostly occurs from April through June and from August through October. High ozone typically occurs on hot sunny days with dry conditions and slow wind speeds out of the southeast. Emissions located south, southeast, and east of the San Antonio area combine with urban area mobile-source emissions to create ozone and transport it to the monitors located in the northwest of the Bexar County 2015 ozone NAAQS nonattainment area. Ozone accumulation is further exacerbated by shifting wind directions that occur throughout the day. In addition, these conditions also create high levels of regional background ozone, which combines with the local ozone and emissions to produce eight-hour ozone levels more than 70 ppb. Ozone chemistry on these days appears to be mostly NO_X limited. Because of this, NO_X controls would be expected to be more effective in decreasing ozone in the Bexar County 2015 ozone NAAQS nonattainment area when compared to VOC controls.

CHAPTER 7: REFERENCES

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