APPENDIX B

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

Bexar County Serious Reclassification Attainment Demonstration State Implementation Plan Revision for the Eight-Hour Ozone National Ambient Air Quality Standard

Project Number 2024-041-SIP-NR

EXECUTIVE SUMMARY

Ground-level ozone 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 data from March through October (hereafter referred to as the ozone season) from 2014 through 2023 and recent changes in how, when, and where ozone forms in the area.

Ozone concentrations in the Bexar County 2015 ozone NAAQS nonattainment area decreased from 2014 through 2023, with the eight-hour ozone design value decreasing 5%. However, in recent years, there was a 5% increase in eight-hour ozone design values from 2020 through 2023. From 2014 through 2023, the area's maximum daily VOC concentrations increased by 11%, but NO_x concentrations have not observed any significant change.

Ozone precursor emissions in the Bexar County 2015 ozone NAAQS nonattainment area declined from 2014 through 2023. 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 mid-summer 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 or 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 greater 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 which are then transported to the monitors located in the northwest portion 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 in the Bexar County 2015 ozone NAAQS nonattainment area.

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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 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 Antonio area for the 2015 eighthour 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, which includes Bexar, Comal, Guadalupe, Karnes, Kendall, Wilson, and Atascosa Counties.

1.1 GENERAL DESCRIPTION OF OZONE FORMATION

Ground-level ozone is primarily 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 in an urban area 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 air 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, county, and monitor type and parameters monitored at the site. Overall, this network of monitors allows for comprehensive spatial coverage and analysis of San Antonio area ozone formation.

Site Name	AIRS Number	CAMS Number	County	*Monitor Type	Parameters Measured
San Antonio Northwest	480290032	0023	Bexar	R	Ozone, PM _{2.5} , NO _x , Meteorology
Camp Bullis	480290052	0058	Bexar	R	Ozone, NO _x , VOC, Meteorology
Calaveras Lake	480290059	0059	Bexar	R	Ozone, PM _{2.5} , NO _x , Meteorology
Old Highway 90	480290677	0677	Bexar	NR	PM _{2.5} , VOC, Meteorology
City Public Service (CPS) Pecan Valley	480290055	0678	Bexar	NR	Ozone, Meteorology
Frank Wing Municipal Court	480290060	9999	Bexar	NR	PM ₁₀
Elm Creek Elementary	480290501	0501	Bexar	NR	Ozone, Meteorology
Fair Oaks Ranch	480290502	0502	Bexar	NR	Ozone, Meteorology
Heritage Middle School	480290622	0622	Bexar	NR	Ozone, PM _{2.5} , Meteorology
Gardner Rd. Gas Sub-Station	480290623	0623	Bexar	NR	Meteorology
Gate 9A CPS	480290625	0625	Bexar	NR	Meteorology
Gate 58 CPS	480290626	0626	Bexar	NR	Meteorology
San Antonio Interstate 35	480291069	1069	Bexar	NR	PM _{2.5} , NO _x , CO, Meteorology
San Antonio Gardner Road	480291080	1080	Bexar	NR	Meteorology
San Antonio Bulverde Parkway	480291087	1087	Bexar	NR	PM, Meteorology
San Antonio Red Hill Lane	480291091	1091	Bexar	NR	PM _{2.5} , Meteorology
Calaveras Lake Park	480291609	1609	Bexar	NR	РМ
Government Canyon	480291610	1610	Bexar	NR	Ozone, Meteorology
Bulverde Elementary	480910503	0503	Comal	NR	Ozone, NO _x Meteorology
City of Garden Ridge	480910505	0505	Comal	NR	Ozone, NO _x , VOC, Meteorology
New Braunfels Oak Run Parkway	480911088	1088	Comal	NR	PM, Meteorology
New Braunfels Airport	481870504	0504	Guadalupe	NR	Ozone, NO _x , Meteorology
Seguin Outdoor Learning Center	481870506	0506	Guadalupe	NR	Ozone, NO _x , Meteorology

 Table 1-1:
 Monitors in the San Antonio Area

Site Name	AIRS Number	CAMS Number	County	*Monitor Type	Parameters Measured
Karnes County	482551070	1070	Karnes	NR	NO _x , VOC, Meteorology
Floresville Hospital Boulevard	484931038	1038	Wilson	NR	NO _x , VOC, Meteorology
Von Ormy Highway 16	480131090	1090	Atascosa	NR	PM _{2.5} , Meteorology

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 2023 had a population of over 2 million, compared to a population of 1.7 million in 2010 (U.S. Census Bureau, 2023). Despite the increase in population, this area has observed modest improvements in air quality.

The previous conceptual model for the San Antonio area was prepared by the Texas Commission on Environmental Quality (TCEQ) in 2022 and focused on ozone concentrations over the 2015 ozone NAAQS of 70 ppb from 2012 through 2021 (TCEQ 2023). 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 dominates 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 there was no overall trend from 2012 through 2021.
- 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 are typically observed.
- 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 2014 through 2023 at regulatory and 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. This section will look at ozone data in various forms to characterize where, when, and how ozone forms in the area.

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 maximum daily eight-hour averaged ozone concentration (MDA8) 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 4 ppb, or 5%. From 2014 through 2018, the design value decreased roughly 1.4 ppb per year on average. In more recent years, progress has slowed and then saw an increase from 2020 through 2023 of 1 ppb per year on average. The lowest design value recorded for the Bexar County 2015 ozone NAAQS nonattainment area during the ten years reviewed was 72 ppb in 2018 and 2020.

The figure also indicates which monitor sets the design value in each year. Camp Bullis had the highest design value for the first three 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 value in 2016 and 2020. The other regulatory monitor, Calaveras Lake, was considered in this analysis, but it typically measures lower ozone concentrations and did not set the design value in 10 years of the 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 in addition to 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 a solid line. The non-regulatory monitors are marked with dashed lines. One of the non-regulatory monitors, Government Canyon, was activated mid-2017.

Overall, all monitors in the San Antonio area show a decreasing or stagnant trend in eight-hour ozone design values from 2014 through 2023. Some of the lowest design values ever recorded in the San Antonio area were observed from 2018 through 2021. CPS Pecan Valley showed a decrease of 23.9% from 2014 through 2023. Fair Oaks Ranch, New Braunfels Airport, and Seguin Outdoor Learning Center all saw decreases of over 10% from 2014 through 2023. For the three regulatory monitors located inside the Bexar County 2015 ozone NAAQS nonattainment area, there were two decreases and one small increase; San Antonio Northwest decreased 2.7%, Camp Bullis decreased 5%, and Calaveras Lake increased 3%.

The difference between the maximum design value and the minimum design value in the area increased by 8 ppb, from 14 ppb in 2014 to 22 ppb in 2023. 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 spatial ozone formation patterns. Eight-hour ozone design values from monitors in the San Antonio area from 2014, 2018, and 2023 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 area-wide design values from 2014, 2018, and 2023. 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 2023 compared to 2014. While values have changed, a consistent spatial pattern is observed across the study period. In 2014, 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 pattern 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 2014, it recorded a design value of 72 ppb which is on par with monitors north of town. However, in 2018 and 2023, its design value was considerably lower than the northern monitors. As discussed in Section 3.1: *Ambient* NO_x Trends, this may be evidence of the positive effects from lowered NO_x emissions from electric generating units (EGU) southeast of town.



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

2.2 FOURTH-HIGHEST EIGHT-HOUR OZONE

Ozone is more readily formed on warmer, sunny days when the air is stagnant. Meteorological variables like humidity, precipitation, and wind also affect ozone formation. Because of this, meteorology can play a big factor in yearly ozone concentrations. 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 MDA8 Ozone Values in the San Antonio Area* shows there is high year-to-year variability, but overall, the fourth-highest MDA8 ozone concentrations show a slight increase. The year-to-year variability is experienced by all monitors, indicating climatological influences. Two regulatory monitors, San Antonio Northwest and Camp Bullis, exhibited the highest values across the San Antonio area.

The Camp Bullis monitor saw a notable increase from 2020 through 2021, a pattern consistent with many other monitors. The third regulatory monitor, Calaveras Lake, exhibited lower ozone values compared to San Antonio Northwest and Camp Bullis for all years studied.

The largest of the fourth-high MDA8 values in the area occurred in 2015, 2021, and 2022, resulting in the elevated eight-hour ozone design values from 2015 through 2017 and from 2021 through 2023. The lowest values for the area were also higher during 2015, 2021, and 2022, indicating high background ozone during those years (aside from CPS Pecan Valley, which is missing 3 months of data for 2021 and 2022).

As noted, fourth-highest MDA8 trends can help determine which years may have been influenced by meteorology. When most or all monitors show either an increase or a decrease in fourth-highest MDA8 ozone values, climatological influence is possible. For example, years that are more hot, dry, and stagnant would be expected to show an increase in ozone values. Section 5.4: *Ozone Concentrations Adjusted for Meteorology* discusses more how meteorology plays a role in ozone formation. The fourth-highest MDA8 ozone values in San Antonio indicate that ozone in 2015, 2016, and 2018 may have been affected by unique meteorology. In 2016 there was an area-wide decrease in fourth-highest MDA8 ozone values, and in 2015 and 2018, there was an area-wide increase.



Figure 2-4: Fourth-Highest MDA8 Ozone Values in the San Antonio Area

2.3 EXCEEDANCE DAYS

An ozone exceedance day is defined as any day with at least one regulatory monitor in an area 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 the 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 exceeded 84 ppb. In

the past three years, there is an increase in the number of days exceeding 75 and 70 ppb. Overall, the frequency of exceedance days indicated slight progress towards lowering ozone concentrations in the Bexar County 2015 ozone NAAQS nonattainment area.



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 the ozone season 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 southern gulf waters 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). This pattern from the previous studies is the same pattern that is showing in studies from this conceptual model for the San Antonio area. The frequency of exceedance days by month was used to characterize the 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 2014 through 2023. This analysis is mostly corroborated by the findings in Houston and Dallas; the ozone season does exhibit two peaks but seems to have a mid-summer minimum occurring in July. Unlike Houston and Dallas, exceedances in the Bexar County 2015 ozone NAAQS nonattainment area during March are rare, and no such exceedances were from 2014 through 2023. It is also apparent that exceedance days occur more consistently in the latter half of the ozone season from August through October. The month with the most exceedances from 2014 through 2023 is August.



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 throughout each year's ozone season follows similar patterns, with some variation, like in August 2015 or all of 2019. This was likely due to fluctuations in meteorology, as discussed in Section 2.3: *Exceedance Days,* and Chapter 5, *Meteorology and its Effect on Ozone*.

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.



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

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 NAAOS nonattainment area investigated the spatial-temporal variation in peak ozone in the San Antonio area (TCEQ, 2023). 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 an area from outside the area or as ozone in the local air mass that has not been influenced by emissions from the area 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 of a particular area.

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 the San Antonio area, 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 2014 through 2023 in the San Antonio area were separated into high ozone days and low ozone days. Results are shown in Figure 2-8: Median *Background and Locally Produced Ozone During the Modified Ozone Season for Years 2014 through 2023 Separated by High and Low Ozone Days in the San Antonio Area.* In the ten years analyzed, 102 days were identified as high ozone days and 2,038 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 with no overall 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 the San Antonio area and throughout the South (EPA 2022). For high ozone days, estimated background ozone was the lowest in 2020. For low ozone days, estimated background ozone was the lowest in 2021. 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 16 ppb in 2018 up to 27 ppb in 2016 and 2022.

When investigating percent contributions, on average over the past ten years, background ozone has contributed about 71% to MDA8 ozone concentrations on low ozone days, meaning that locally produced ozone contributes roughly 29%. These contribution averages are similar for high ozone days, 69% and 31%, respectively. On low ozone days, the contribution of locally produced ozone ranges from 22% in 2015 to 35% in 2022. On high ozone days, it ranges from 21% in 2018 to 37% in 2016. 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: Median Background and Locally Produced Ozone During the Modified Ozone Season for Years 2014 through 2023 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* is a scatter plot of daily background contribution values, with those over 55 ppb in red (threshold selected based on AQI break points) and a line of best fit, fitted using a least squares polynomial fit, shown in green. The overall downward trend in background ozone is evident both from the downward trend of the fitted line (starting at around 35 ppb in 2014 and ending around 32 ppb in 2023) 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 contribution. Days with an estimated local contribution over 30 ppb are highlighted in red and a line of best fit, fitted using a least squares polynomial fit, shown in green. The upward trend of local ozone production is evident from the upward trend of the fitted line (starting at around 13 ppb in 2014 and ending around 20 ppb in 2023) and from an increasing frequency of days with locally produced ozone over 30 ppb. Another factor leading to the slight increasing trend in local ozone production is that the level of the lower values has increased.



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 by month. Results are shown in Figure 2-11: *Median Background and Locally Produced Ozone by Month for Years 2014 through 2023 Separated by High and Low Ozone Days in the San Antonio Area.* As previously discussed, the sample size for low ozone days was larger than for high ozone days for all months.

Background ozone exhibits a very different monthly pattern on high versus low days. On high ozone days, background ozone is highest in August, and lowest in September. For low ozone days background ozone is highest in April and May with a minimum in July. The evidence suggests that background ozone is more influenced by month-tomonth meteorological patterns. This is corroborated by the heuristic that ozone forms best under specific weather conditions such as high temperature and slow wind speed.

A mid-summer minimum is caused by a shift in the Bermuda High during July, which causes winds to prevail from the Gulf of Mexico on most days. This phenomenon explains the pattern observed in the low ozone days' background concentrations.

Locally produced ozone varies little across months, but it displays a slightly greater variation on the high ozone days. On high ozone days, locally produced ozone is slightly higher in June. On low ozone days, locally produced ozone is slightly higher in August. While these month-to-month differences are small, 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 more to ozone concentrations in the San Antonio area.



Figure 2-11: Median Background and Locally Produced Ozone by Month for Years 2014 through 2023 Separated by High and Low Ozone Days in the San Antonio Area

The findings of these analyses are further supported by the results of the 2017 San Antonio Field Study, which investigated ozone production rates in San Antonio (Flynn et al. 2019). Over the course of May 2017, ozone production rates were directly measured at sites upwind (Calaveras Lake) and downwind (San Antonio Northwest, Camp Bullis) of the city core and modeled using in situ data at a site near downtown. Rates at the outer city sites, upwind and downwind, 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). It 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 2014 through 2023*. Ozone season data from 2014 through 2023 show that background ozone is well correlated with daily-maximum ozone, with a correlation coefficient of 0.70. This may indicate that trends in ozone concentrations for the San Antonio area are driven by changes in the background ozone. The same study for locally produced ozone was completed but only saw a correlation coefficient of 0.31, indicating a poor correlation. The black, dashed line on Figure 2-12 represents the distinction of a high ozone day. High ozone days are more frequent on days where there are higher levels of background ozone.

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, a pattern emerges. The data show that points under 70 ppb that are below the red 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 MDA8 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 recorded in more distant years. The exceedance days that are associated with lower background concentrations are an almost equal mix of recent and distant years. Days with background concentrations over 60 ppb are rare in recent years. This 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 Modified Ozone Season in the San Antonio Area from 2014 through 2023

CHAPTER 3: OZONE PRECURSOR CONCENTRATIONS AND TRENDS

Ground-level ozone is primarily 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. This section will focus on NO_x and VOC concentration trends, emission trends, and the chemistry of 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 (NO₂). 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 area are mobile sources and large electric generation units (EGUs), especially in the area southeast of the city near Calaveras Lake, as shown in Figure 3-17: *Map of 2022 NO_x Point Source Emissions in the San Antonio Area.* Previous studies also observed that NO_x decreased from 2012 through 2021 (TCEQ, 2023).

There have been 12 NO_x monitors operated at some point from 2014 through 2023 in the San Antonio area; however, only three to eight NO_x monitors have 75% valid days in any given ozone season. In 2023, there were ten 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 2014 through 2023; however, several other monitors have at least seven years of data in that 10-year period. To focus on the monitors most affecting the Bexar County 2015 ozone NAAQS nonattainment area air quality, the Floresville and Karnes County monitors are not included in this analysis because they are further away from the San Antonio urban area than the other monitors and therefore not affected by the same local factors known to produce NO_x .

 NO_x trends are displayed in Figure 3-1: *Ozone Season Median Daily Maximum NO_x Trends for the San Antonio Urban Area.* For this analysis, the daily maximum one-hour NO_x concentration at each monitor was determined, and then, from this subset, the median value was calculated for all days in the ozone season. The figure shows that the NO_x monitor located near the interstate, San Antonio Interstate 35 (I-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, aside from 2022 when Calaveras Lake measured higher, and Camp Bullis measures the lowest NO_x .

Overall, there are not any strong trends in NO_x concentrations from 2014 through 2023. 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 San Antonio I-35 monitor. Because 2019 also saw lower NO_x values at the San Antonio I-35

monitor, 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 Urban Area

Area-wide NO_x trends of different types of monitors can also be examined to reveal more information about the distribution of NO_x concentrations and how they change over time. 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 (2016 through 2023).

The 98th percentile of non-roadside monitors has decreased about 10 ppb over the eight years studied. The roadside monitor's 98th percentile has also decreased significantly since 2016 but has been trending upward for the most recent five 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 area but may be trending up in recent years near sources of high vehicle traffic. It also shows that median NO_x concentrations have not changed over the past eight years at any monitors

in the city, though we do see that 2023 NO_x concentrations are lower in 2023 than they were in 2022.



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 2014 through 2023 were used for Calaveras Lake and San Antonio Northwest, but NO_x data at Camp Bullis were only available for 2015 through 2023. 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, and 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 Average* NO_x *and Ozone for Ozone Season at Calaveras Lake (left), Camp Bullis (center) and San Antonio Northwest (right).* 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. The results of these analyses may indicate that NO_x emissions age and react 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 Average NO_x and Ozone for Ozone Season at Calaveras Lake (left), Camp Bullis (center) and San Antonio Northwest (right)

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 the 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 the Floresville Hospital Boulevard (hereby Floresville) and Karnes County monitoring locations. Auto-GCs 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 the San Antonio area 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 the San Antonio area, 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 were analyzed, then data from monitors outside Bexar County were considered. For each of the four monitor locations, a figure with two plots is shown. Each figure includes a plot on the left that shows the median VOC concentrations for the top 20 species, ranked highest to lowest by magnitude at the monitor, and a plot on the right that shows the same median concentration weighted by MIR index, shown in the same order for comparison. This analysis considers data during ozone season from 2014 through 2023, aside from Camp Bullis, which only has available data from 2016 through 2023. Data are considered for all hours of the day, aside from Old Highway 90, which only has 24-hour samples.

The median VOC concentrations, in parts per billion by volume (ppbV), for the top 20 VOC species at Camp Bullis from mid-2016 through 2023 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 highest concentrations at Camp Bullis. Of the non-alkane compounds, isoprene is present in the greatest amount.

When considering the median concentrations weighted by MIR, a different pattern emerges. When weighted by MIR, isoprene is over two 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 being weighted by MIR. The last group of VOC species, alkenes and aromatic compounds such as ethylene, propylene, and toluene, 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 2014 through 2023. 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 n-butane, isopentane, and toluene. Toluene has a low concentration, but a larger MIR weighted concentration, meaning it is another highly reactive species. 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 is corroborated by 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 the 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 San Antonio 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.

Results for the Floresville monitor are shown in Figure 3-6: *Floresville VOC Species in ppbV (left) and Weighted by MIR Index (right).* 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. 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 g Ozone Produced/gVOC (gO₃/gVOC) for n-butane vs. 9.00 gO₃/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 farther from major roadways. Karnes County shows high MIR weighted concentrations of n-butane and propane that are near the levels of isoprene at the Camp Bullis monitor. This is an example of the

high concentration of low reactive VOC present in the Eagle Ford Shale area, indicative of oil and gas sources.



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 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, less relevant as a measure of precursor patterns, and is excluded from EPA's definition of VOC. 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 skewed towards values near zero with infrequent spikes of concentrations over 100 ppbV, 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 were 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 about ten times that at Camp Bullis.

At the Camp Bullis monitor, the TNMHC concentrations saw increases from 2016 through 2019, before decreasing until 2021. There was another slight increase from 2021 through 2023 at the monitor as well, with the 25th and 50th percentiles showing the largest jump, relatively. At the Floresville monitor, all percentiles saw a decrease from 2014 through 2016, an increase from 2016 through 2021, especially in the 95th and 75th percentiles, and then another decrease from 2021 through 2023. These trends were most noticeable at the 95th percentile. The data at Karnes County appear to be more variable year-to-year with a large increase in the 95th percentile from 2020 through 2022, before decreasing down to previous levels in 2023.



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, shown in Table 3-1: *VOC Group Definitions*, that share chemical characteristics and often source categories as well. A few species, such as isoprene, propylene, ethylene, and 1,3-butatdiene, are distinct enough in their chemical properties, including their ozone formation potential, that they have their own groups.
VOC Group	VOC Species
1,3-Butadiene	1,3-Butadiene
Alkanes	2,2,4-Trimethylpentane, 2,2-Dimethylbutane, 2,3,4-Trimethylpentane, 2,3-Dimethylpentane, 2,4-Dimethylpentane, 2-Methylheptane, 3-Methylheptane, 3-Methylhexane, n-Decane, n-Heptane, n-Hexane, n-Nonane, n-Octane
Aromatics	Benzene, Ethylbenzene, Isopropylbenzene, n-Propylbenzene
Butanes	Isobutane, n-Butane
C2C3	Acetylene, Ethane, Propane
Cyclos	Cyclohexane, Methylcyclohexane, Methylcyclopentane
Ethylene	Ethylene
Isoprene	Isoprene
Other	2-Methyl-2-Butene, Cyclopentane, n-Undecane
Pentanes	Isopentane, n-Pentane
Pentenes	1-Pentene, cis-2-Pentene, trans-2-Pentene
Propylene	Propylene
Styrene	Styrene
Toluene	Toluene
Trimethylbenzenes	1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene
Xylenes	m/p Xylene, o-Xylene

 Table 3-1:
 VOC Group Definitions

For this analysis, hourly concentrations of each species in each group were added together to reach a group total concentration in ppbV. 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 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. It should be noted that the Old Highway 90 canister site measures a 24-hour sample every 6 days, where the other sites measure continuously, taking hourly averages. This means that the sample size at Old Highway 90 is much smaller than that of the other sites.

Figure 3-9 shows that there are no strong trends in the data for Camp Bullis. Of the 16 VOC groups, most of them seem to show a slight increase from 2021 through 2023.



Figure 3-10 shows that, at the Old Highway 90 canister VOC monitor, most species exhibit a flat trend over the ten-year period. There is a slight upward trend in isoprene, toluene, and xylenes, with most of the increase coming from 2018 through 2020. Across most species, 2020 seems to have a larger spread between the third and fourth quartile, represented by the top of the box and the highest whisker, and most medians are higher than the prior and following years. This indicates that there was more frequent high to extreme values for the year. Comparing 2023 to 2020, most medians are at similar levels, if not decreased, and the interquartile ranges are smaller, indicating fewer high values.



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

Figure 3-11 shows that propylene exhibits the most consistent trend, steadily increasing from 2017 through 2023. Xylenes, toluene, trimethylbenzenes, and carbon compounds appear to follow a similar year-to-year pattern. They each exhibited stagnation for the first few years, increases around 2018 to 2020, and decreases since. Butenes have one anomalous 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: *Point Source Emission Trends* also shows the presence of these VOC sources in the San Antonio area. Pentenes have had an average of zero concentration until 2020, but have started measuring small amounts, indicating a possible new source.



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

Figure 3-12 shows that, at the monitor the farthest 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. Also showing a similar trend at this monitor are aromatics, propylene, and pentanes. Karnes County also shows 1,3-butadiene levels consistently higher over the last 4 years, similar to Floresville.



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 all sites, but a slight one at the two monitors southeast of San Antonio, Karnes and Floresville.

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 a 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-weight 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 (TCEQ, 2020).

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*. Factor one and two show nearly identical patterns, increasing from 2016 through 2019, decreasing until 2021, and then increasing again in 2022 and 2023. Factor three shows a similar patter, but not quite the same. Factor three also shows a large jump from 2021 through 2022, with the median nearly doubling and staying there for 2023. Factor two's medians are about seven times higher than factor one's and 100 times larger than factor three's median. When weighted by MIR, however, factors 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 slight downward trend in factor one VOC is evident from 2014 through 2023. From 2018 through 2021 there appears to be an increase, but it decreases again in 2022 and 2023. 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 VOC from vehicle emissions are present nearer to the city center. Factor two shows a similar pattern to factor two as it did at Camp Bullis. However, the concentrations of factor two are comparable to the concentrations seen at Camp Bullis. Factor three shows a varying, but overall stagnant trend in total factor concentration. 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 indicate 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 the 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 the San Antonio area are from area sources, oil and gas production sources, and on-road sources.

TCEQ funded a study by the Texas Transportation Institute (TTI) to estimate on-road emissions trends throughout Texas from 1999 through 2060 using the 2020 version of the Motor Vehicle Emission Simulator (MOVES3) model (TTI, 2023). On-road NO_x and VOC emissions in the San Antonio area decreased from 1999 through 2023 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.

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 2023 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 a previous Bexar County nonattainment area conceptual model (TCEQ, 2020)

The rest of this section focuses 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. This analysis uses data in tons per year (tpy) from 2014 through 2022. Emissions from 2023 were not yet available to be included in this analysis. Figure 3-15: NO_x Point Source Emissions from 2014 through 2022 in the Bexar *County 2015 Ozone NAAOS Nonattainment Area* shows the recent trend in NO_x emissions. Based on 2022 emissions, this six named point sources make up 97% of NO_x emissions, with the top three making up 88%. The largest and third-largest NO_x emission sources each year are two power plants, the Calaveras Lake plant and the VH Braunig plant. Their 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, like seen in the Calaveras plant, they have been increasing from 2020 to 2022. Calaveras Plant has seen the greatest decrease in NO_x emissions over the ten-year period. Compared to 2014 emissions, Calaveras Plant 2022 NO_x emissions decreased by 34%.



Figure 3-15: NO_x Point Source Emissions from 2014 through 2022 in the Bexar County 2015 Ozone NAAQS Nonattainment Area

To further understand how emissions have changed over time, the percent change in NO_x point source emissions was 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 2014 through 2022.* There is an 18% decrease in NO_x emissions over the nine

years studied, mainly from point sources inside Bexar County. Based on the 2022 emissions inventory, emission sources in Bexar County make up roughly 52% of NO_x emissions in the San Antonio area and the adjacent counties makes up roughly 48% 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 2014 through 2022

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 2022 NO_x Point Source Emissions in the San Antonio Area*. Each facility's 2022 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: *Prevailing Wind Patterns*, 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 2022 NO_x Point Source Emissions in the San Antonio Area

There have been a few small sources to the southeast and southwest of the Camp Bullis monitor that increased NO_x emissions from 2014 through 2022, but these changes are minor compared to the decreases seen at other facilities throughout the area. The largest NO_x emissions increases were from entities to the northwest and northeast of the city, just outside of Bexar County.

Emissions of VOC from point sources in the Bexar County 2015 ozone NAAQS nonattainment area were also investigated. The total VOC emissions inventory for 2014 through 2023 in the Bexar County 2015 ozone NAAQS nonattainment area is shown in Figure 3-18: *VOC Point Source Emissions from 2014 through 2023 in the Bexar County 2015 Ozone NAAQS Nonattainment Area.* Compared to NO_x sources, there are less VOC sources of substantial size. The six named point sources make up approximately 53% of the total VOC emissions. The largest VOC point source is the Toyota Vehicle Assembly Plant with 240 tons per year (tpy) of VOC emissions in 2022. The second largest VOC source is the San Antonio Petroleum Refinery, with 161 tons of VOC emissions in 2022. Other point sources include power plants, cement plants, oil and gas infrastructure, and other industrial, manufacturing, and research facilities. Compared to NO_x emissions are less affected by electricity demands that fluctuate

with weather conditions. There seems to be no trend in total emissions, but the emission levels of the largest point sources are decreasing.



Figure 3-18: VOC Point Source Emissions from 2014 through 2022 in the Bexar County 2015 Ozone NAAQS Nonattainment Area

Year-to-year variability in VOC emissions is also seen in the Bexar County 2015 ozone NAAQS nonattainment area VOC sources. The largest VOC emissions source shows a decrease of 45% from 2014 through 2022.

To further understand how emissions have changed over time, the percent change in VOC emissions from 2014 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 2014 through 2022*. From 2014 through 2022, the San Antonio area saw a 15% increase in total VOC, with Bexar County having a less than 1% increase, and adjacent counties showing a 34% increase. All the increase in the adjacent counties seems to be recent, as VOC levels were lower in 2019 than they were in 2014. As will be discussed in Section 4.1: *VOC and NO_x Limitations*, 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 2014 through 2022

As mentioned for NO_x emissions, understanding the spatial distribution of precursor 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 2022 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 (another larger VOC point source in the area in 2022); 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 2022 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 are 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 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 nonmethane 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 a 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 gaschromatograph (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 the 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 from March through October (referred to as 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 2023, 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 2023 at Camp Bullis are shown in Figure 4-2: *Median Hourly VOC-to-NO_x Ratios During the Ozone Season from 2016 through 2023 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 11:00 LST; however, the median remains just above the transitional boundary after 11:00 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 2023 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 05:00 LST though 08:00 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 2023 at Camp Bullis.* The results show that, from 2016 through 2019, morning hours at Camp Bullis were transitional. After 2019 this trend 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 2023 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 2023 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 2014 through 2023.

Figure 4-4: *Number of Monitors Exceeding the 2015 Eight-Hour Ozone Standard by Day of the Week in the San Antonio Area from 2014 through 2023* indicates a possible weekend effect, with the least number of exceedances recorded on Sunday. There also appears to be an accumulation effect throughout the week, with the most exceedances occurring on Thursdays.



Figure 4-4: Number of Monitors Exceeding the 2015 Eight-Hour Ozone Standard by Day of the Week in the San Antonio Area from 2014 through 2023

These patterns in eight-hour ozone exceedances 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 is found by taking the average of all values at each hour. 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: *Mean One-Hour Ozone and 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 exceedances 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 06:00 LST, and 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.

Another 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 farther 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. This may be part of the reason why the NO_x values at Camp Bullis are lower during that morning spike.



Figure 4-5: Mean One-Hour Ozone and 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 2014 through 2023.* 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 blue 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, a pattern emerges. 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 through Friday) and decreasing NO_x over the weekend (Saturday and 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 2014 through 2023

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: *Ambient VOC Trends in the San Antonio Area,* 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 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 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 Concentrations at Camp Bullis by Day of the Week for Ethylene, Toluene, Styrene, m/p Xylene, Ethane, and 1,3-Butadiene

CHAPTER 5: METEOROLOGY AND ITS EFFECT 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 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 2014 through 2023. 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 MDA8 Ozone Concentrations in the San Antonio Area for the Ozone Season from 2014 through 2023*.

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 MDA8 concentrations greater than 70 parts per billion (ppb) are highlighted in red. There were no days with eight-hour ozone values above 70 ppb when temperatures were 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 MDA8 Ozone Concentrations in the San Antonio Area for the Ozone Season from 2014 through 2023

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 07:00 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 2014 through 2023. 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 MDA8 Ozone in the San Antonio Area for the Ozone Season from 2014 through 2023*. Days with MDA8 ozone concentrations greater than 70 ppb are highlighted in red.

Results show a negative correlation between average daytime relative humidity and MDA8 ozone. Lower 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 in Figure 5-2 and indicates that low relative humidity is one among several contributing factors that cause high ozone. Typically, cold fronts bring more humid air

to the San Antonio area and leave drier air as the cold fronts move away. Several studies 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 MDA8 Ozone in the San Antonio Area for the Ozone Season from 2014 through 2023

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 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 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 the Bexar County 2015 ozone National Ambient Air Quality Standard (NAAQS) nonattainment area were examined for high ozone days in the months of March through October from 2014 through 2023.

Wind Roses, overlaid on two maps, are shown in Figure 5-3: *Wind Roses in the Bexar County 2015 Ozone NAAQS Nonattainment Area for High Ozone and Low Ozone Days during the Ozone Season from 2014 through 2023.* 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 monitor, high ozone days generally have winds from the southeast or the north, with speeds from 0 to 10 mph. At the Calaveras Lake monitor, high ozone days generally have winds from the southeast, with speeds from 0 to 15 mph, or winds from the northeast, with speeds from 5 to 25 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 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 and Low Ozone Days during Ozone Season from 2014 through 2023

5.3.2 Wind Speed

Typically, higher ozone concentrations are observed on days with lower winds speeds. Lower wind speeds, often due to a surface-level high-pressure system in the area, give ozone precursors more time to mix and react, and 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 at the monitor. Only ozone season months from 2014 through 2023 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 shown in Figure 5-4: *Average Daytime Resultant Wind Speed Versus MDA8 Ozone at Camp Bullis for the Ozone Season from 2014 through 2023*. 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 other 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 Versus MDA8 Ozone at Camp Bullis for the Ozone Season from 2014 through 2023

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 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 2014 through 2023 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 2014 through 2023 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 08:00 LST, nearly all days show northwestern winds. 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 3.1: Ambient NO_x Trends, 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 that are most conducive to ozone formation, 06:00 LST through 19:00 LST, often receive air masses from the northeast and eastern parts of San Antonio, more frequently than from 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 3.1: Ambient NO_x Trends, 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 sources, cement kilns, electric generating units, etc.



Figure 5-5: Surface Level Back Trajectories for Each Hour on High Ozone Days 2014 through 2023 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 2014 through 2023 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: *Ozone Concentrations Adjusted for Meteorology.*



Figure 5-6: Surface Level Five-Hour Back Trajectories for Every Hour on High Ozone Days 2014 through 2023 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 (NOAA'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 from 2014 through 2023. The 36-hour back trajectories end at the time of the max hourly value at the Camp Bullis monitor and are 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 low ozone day from

2014 through 2023. The low ozone dataset includes 3314 days that were successfully clustered. The second set contains trajectories for only high ozone days in the San Antonio area from 2014 through 2023. The high ozone days dataset includes 130 days, all of which were successfully clustered. Background ozone was estimated for each trajectory as described in Section 2.6: *Background Ozone* 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 2014 through 2023 and Figure 5-8: Estimated Eight-Hour Background Ozone (right) and Area Wide MDA8 Ozone Concentrations (left) by Cluster for All Low Ozone *Days 2014 through 2023.* The y-axis scales in the two images in Figure 5-8 are different. These trajectories are grouped into five clusters. Two of these clusters are coastal and account for 67% of days, and three clusters are land-based which account for 33% of days. Generally, the pattern in background ozone values follows the pattern in area MDA8 ozone for each cluster. This corroborates the analysis presented in Section 2.6: *Backaround Ozone* that shows a strong correlation between background ozone and area MDA8 ozone. The southern Gulf of Mexico cluster, cluster 4, has the largest relative difference between its background ozone and area MDA8 ozone medians, with a lower relative median in the area MDA8 ozone than background ozone. The box plots of estimated background ozone and MDA8 indicate that all clusters besides cluster 4, the southern Gulf of Mexico cluster, have similar median background ozone. Cluster 1, the shorter Gulf of Mexico cluster, has the highest associated MDA8 ozone median. 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 transport from the Corpus Christi and Rockport area, the endpoint of Cluster 1.



Figure 5-7: Mean of 36-Hour Back Trajectory Clusters for All Low Ozone Days 2014 through 2023 Terminating at Camp Bullis



Figure 5-8: Estimated Eight-Hour Background Ozone (right) and Area Wide MDA8 Ozone Concentrations (left) by Cluster for All Low Ozone Days 2014 through 2023

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 2014 through 2023* and Figure 5-10: *Estimated Eight-Hour Background Ozone (right) and Area Wide MDA8 Ozone Concentrations (left) by Cluster for All High Ozone Days 2014 through 2023*. Y-axis scales on the images in Figure 5-10 are different. The trajectories are grouped into

five clusters: 78 high ozone days originated from the gulf area, clusters 1 and 3, 18 originated from the continental north, cluster 5, 7 days originated from south towards Mexico, cluster 4, and 27 days had long-term recirculating flow in the San Antonio area, cluster 2. Compared to the low ozone days, these trajectories are much shorter, indicating slower wind speeds. Half of the individual trajectories from the continental north, cluster 5, are short enough to be contained within Texas. This corroborates the analyses presented in Section 5.3.2: *Wind Speed* 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 5, 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 includes the highest area MDA8 values, including a day with a 91ppb MDA8. This aligns with the general understanding of ozone formation, which involves slow recirculating wind flows allowing 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 2014 through 2023 Terminating at Camp Bullis



Figure 5-10: Estimated Eight-Hour Background Ozone (right) and Area Wide MDA8 Ozone Concentrations (left) by Cluster for All High Ozone Days 2014 through 2023

The findings from these analyses are corroborated by results from 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). Bivariate polar plots show how pollutant concentrations vary with wind speed and wind direction at a certain receptor location. These types of plots help to determine the type of source based on windspeed 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 2014 through 2023 at the design value setting monitor, Camp Bullis. According to the prevailing wind directions in the San Antonio area, the Camp Bullis monitor is considered 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 6.0 ppb at the Camp Bullis monitor. The results for NO_x are shown in Figure 5-11: *Bivariate Polar Plot, based on a CPF at the 95th Percentile, for NO_x Corresponding to the Days having MDA8 Ozone over 70 ppb, during the Ozone Season from 2014 through 2023 at Camp Bullis (downwind).* In the plot, 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 plot, with each light gray ring representing a wind speed increment of 5 mph.

The bivariate polar plot for NO_x shows that the highest NO_x concentrations occur at the slower wind speeds, typically less than 5 mph. 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 near source.



Figure 5-11: Bivariate Polar Plot, based on a CPF at the 95th Percentile, for NO_x Corresponding to the Days having MDA8 Ozone over 70 ppb, During the Ozone Season from 2014 through 2023 at 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 84 ppb at the Camp Bullis monitor. The bivariate polar plot for one-hour ozone is displayed in Figure 5-12: *Bivariate Polar Plot, based on a CPF that Corresponds to the Days having MDA8 Ozone over 70 ppb, for the Ozone Season from 2014 through 2023 at Camp Bullis*.

The bivariate polar plot shows that the highest one-hour ozone values are most likely to occur with wind speeds between 5 and 10 mph. 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 east and 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 the Camp Bullis monitor.



Figure 5-12: Bivariate Polar Plot, based on a CPF that Corresponds to the Days having MDA8 Ozone over 70 ppb, for the Ozone Season from 2014 through 2023 at 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 eight-hour design value calculations 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 2024) from 2014 through 2023. 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 eighth-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 stagnant trend is observed in the adjusted data set compared to the upward trend in 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 in both the measured and adjusted data set.



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



Figure 5-14: 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, three years were not impacted strongly by meteorology, two years experienced higher ozone from meteorology, four years experienced lower ozone from meteorology, and one year showed inconclusive results from meteorology adjustment. Of these, the strongest impacts were in 2016, 2018, and 2019. In 2016, it was estimated to be 2.5 to 12.0 ppb lower due to meteorological patterns, with the highest impacts at Camp Bullis and San Antonio Northwest. In 2018, meteorology is estimated to have increased the 98th percentile MDA8 ozone values by 4 to 7 ppb. In 2019, meteorology is estimated to have decreased the 98th percentile MDA8 ozone values at Camp Bullis and Calaveras Lake by about 2 and 14 ppb, respectively, but increased the 98th percentile ozone value at San Antonio Northwest by 6 ppb.



Figure 5-15: 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 as 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 data from March through October in 2014 through 2023 to assess how, when, and where ozone forms in the Bexar County 2015 ozone NAAQS nonattainment area as well as the greater San Antonio area.

From 2014 through 2023, eight-hour ozone design values in the Bexar County 2015 ozone NAAQS nonattainment area have decreased by 5%, or 4 ppb, but trends turned slightly upward after 2020. In 2023, the area monitors attainment of the 1997 eight-hour ozone NAAQS of 84 ppb, but the 2023 eight-hour design value is now above the 2015 and 2008 eight-hour ozone NAAQS of 70 ppb and 75ppb, respectively. Maximum eight-hour ozone design values occur in northwest Bexar County, with lower ozone observed in southeast Bexar County. Fourth-highest MDA8 ozone values, which are used to calculate eight-hour ozone design values, have slightly increased from 2014 through 2023. Notably, the design value setting monitor for 2023, 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 mid-summer minimum in July, that breaks the season up into halves.

From 2014 through 2023, peak nitrogen oxides (NO_x) concentrations decreased across the Bexar County 2015 ozone NAAQS nonattainment area, especially at non-roadside monitors. The bottom 75% of hourly NO_x concentrations have been stagnant at all monitors as well.

From 2014 through 2023, the volatile organic compounds (VOC) species associated with mobile sources show a slight upward trend in the 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 upward 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. In the greater San Antonio area, some VOC with lower reactivities, such as n-butane, ethane, propane, isopentane, have such large concentrations in the that they contribute to ozone formation when weighted by reactivity.

From 2014 through 2022, point source NO_x emissions have decreased by 18%, and point source VOC emissions have increased 1% in the Bexar County 2015 ozone NAAQS Nonattainment Area. The largest NO_x and VOC point sources are in southeast and south 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 if decreasing NO_x or VOC would be more effective to decrease ozone concentrations. The automated gaschromatograph (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 recorded on weekdays versus weekends shows that there are less ozone exceedances and slightly lower mean ozone concentrations on weekends versus weekdays, specifically on Sundays. There is lower peak and median NO_x across the city and lower VOC that are associated with mobile sources on the weekends, and this indicates that the weekend effects are due to lower mobile source activity. The relative reductions in ozone and NO_x 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 wind speeds 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 from the continental north 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 are recorded when winds are from the southeast. At the Calaveras Lake monitor, located to the southeast of the San Antonio urban core, the highest ozone concentrations are recorded when winds are from the north and northeast. At the San Antonio Northwest monitor, located in the northwest part of urban San Antonio, the highest ozone concentrations are recorded when winds are from the east, while the high NO_x concentrations are recorded when winds are 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 primarily 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 greater than 70 ppb. Ozone chemistry on these days appears to be primarily NO_x limited.

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CHAPTER 8: DATA SOURCES

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