APPENDIX B

CONCEPTUAL MODEL FOR THE DALLAS-FORT WORTH NONATTAINMENT AREA FOR THE 2015 EIGHT-HOUR OZONE NATIONAL AMBIENT AIR QUALITY STANDARD

Dallas-Fort Worth Moderate Area Attainment Demonstration
State Implementation Plan Revision for the 2015 Eight-Hour
Ozone National Ambient Air Quality Standard

Project Number 2022-021-SIP-NR
SFR-112/2022-021-SIP-NR

EXECUTIVE SUMMARY

This conceptual model provides a detailed examination of ozone formation in the Dallas-Fort Worth (DFW) area with a focus on ozone levels above 70 parts per billion (ppb). Ozone is not directly emitted into the atmosphere, but rather formed through a photochemical reaction with nitrogen oxides (NO_X) and volatile organic compounds (VOC). Most of the analyses in this conceptual model focus on the ozone season (March through October) data from 2012 through 2021 to show how, when, and where ozone forms in the DFW area.

Ozone concentrations in the DFW area have declined, with the eight-hour ozone design value decreasing by approximately 12.6% from 2012 through 2021. Median annual ambient NO_X concentrations at monitors operating during the entire ten year period decreased 10.4%, while 95th percentile values at those monitors decreased 13.0%. Median annual ambient VOC concentrations, as represented by total non-methane hydrocarbons (TNMHC), decreased 16.7%, while 95th percentile values decreased 27.2%. This suggests that efforts to control large sources of emissions have been successful at reducing the highest concentrations of ozone precursors.

This conceptual model supports the following conclusions regarding ozone formation in the DFW area:

- Ozone formation peaks from April through June and then again from August through October, with a mid-summer minimum occurring in July. This minimum is due to the location of the Bermuda High, a high-pressure system that brings clean air from the Gulf of Mexico into the DFW area in the mid-summer.

- High ozone typically occurs on hot sunny days with dry conditions and slow winds out of the southeast.

- Emissions located south and southeast of the DFW area combine with urban area emissions to create ozone, which is carried to monitors in the north and northwest portions of the DFW area.

- Ozone can be exacerbated by slow and variable winds that recirculate air on high ozone days.

- Meteorological conditions that create high local ozone formation potentially also create high regional background ozone, which combines with local emissions to produce eight-hour ozone levels above 70 ppb.

- Ozone chemistry in the DFW area appears to be NO_X limited to transitional. The dominant VOCs in the area are either naturally occurring isoprene from vegetation, or have low ozone formation potential; therefore, control of VOCs would have less effect on ozone concentrations in the DFW area compared to NO_X controls.

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

CHAPTER 1: INTRODUCTION

Ozone formation conceptual models characterize ozone trends, precursors, formation, and transport in a geographic area. This information provides a comprehensive picture of not only where and when ozone forms, but also how and why ozone forms in a geographic area. Conceptual models, also known as conceptual descriptions, are required by the United States (U.S.) Environmental Protection Agency (EPA) to accompany ozone photochemical modeling performed for State Implementation Plans (SIP) (EPA 2018). This conceptual model will focus on ozone formation for the nine-county Dallas-Fort Worth (DFW) non-attainment area for the 2015 eight-hour National Ambient Air Quality Standard (NAAQS) of 0.070 parts per million (ppm). This section discusses general ozone formation and includes a summary of previous conceptual models for the DFW area.

Conceptual models in previous DFW SIPs have thoroughly described the ozone formation process, meteorological dynamics, emissions sources, and ambient precursor levels in the DFW area (TCEQ 2011, TCEQ 2016, TCEQ 2020).

This conceptual model will touch briefly on the fundamentals of ozone formation and will focus on ozone and precursor concentrations measured in the DFW area from 2012 through 2021.

1.1 GENERAL DESCRIPTION OF OZONE FORMATION

Ozone is not directly emitted into the atmosphere; it is formed through a complex series of chemical reactions of oxides of nitrogen (NO_X) and volatile organic compounds (VOC) in the presence of sunlight. Ozone production is generally associated with relatively clear skies, light winds, abundant sunshine, and warm temperatures. These meteorological conditions are associated with high-pressure areas that migrate across the U.S. during the summer. 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 vertical mixing, further aggravating the situation by concentrating local emissions near the surface.

1.2 OZONE FORMATION IN THE DFW AREA

The DFW area, roughly comparable to what the U.S. Census Bureau defines as the Dallas-Fort Worth-Arlington Metropolitan Statistical Area (MSA), is located in north-central Texas and is the fourth largest MSA in the U.S., home to over 7.7 million residents as of 2021 (US Census Bureau, 2022). Ten counties in the DFW area were designated nonattainment for the 1997 eight-hour ozone NAAQS of 0.08 ppm and the 2008 eight-hour ozone NAAQS of 0.075 ppm. Nine of those counties were subsequently designated as nonattainment of the 2015 eight-hour ozone NAAQS of 0.070 ppm: Collin, Dallas, Denton, Ellis, Johnson, Kaufman, Parker, Tarrant, and Wise.

Residents, businesses, institutions, and other entities in these counties work, shop, and recreate at a multitude of commercial, industrial, educational, and recreational sites that contribute emissions from all manner of equipment. Despite recent increase in population, the area has observed improvements in air quality. The area is currently measuring attainment of the one-hour ozone NAAQS of 0.12 ppm and the 1997 eight-hour ozone NAAQS of 0.08 ppm. Work remains for the area to achieve attainment of the 2008 eight-hour NAAQS of 0.075 ppm and the 2015 eight-hour ozone NAAQS of 0.070 ppm.

Previous conceptual models for the DFW area were prepared as part of the serious (2020) and moderate (2016) classification attainment demonstration SIP revisions for the 2008 eight-hour ozone NAAQS (TCEQ 2016; TCEQ 2020). Those conceptual models, which focused on 2005 through 2014, established the following findings regarding ozone formation in the DFW area.

- Like many other Texas areas, the DFW area experiences two seasonal peaks in ozone concentrations. The first occurs from May through June and the second is from August through September. Both peaks have significant differences in meteorological conditions on high ozone days.

- Meteorological characteristics associated with high ozone in the DFW area include stagnated air, few frontal movements, lack of precipitation, clear skies, early morning surface winds from the northwest, upper-level winds from the northeast to the southeast, large diurnal temperature changes, and a low early morning mixing height followed by a rapid rise in the mixing height in the afternoon.

- During the May through June ozone-season peak, long-range transport has a greater effect on ozone in DFW. During the August through September ozone-season peak, monitors in DFW are most often impacted by local emissions and continental transport from the northeast.

- This and previous conceptual models conclude that, since transport causes most of the ozone recorded at local monitors, it is difficult for the DFW region to demonstrate attainment with only local emissions controls.

1.3 AIR MONITORS IN THE DALLAS-FORT WORTH AREA

The DFW area hosts an extensive network of surface monitors that sample and record concentrations of numerous chemical compounds in the ambient air, second only to the Houston-Galveston-Brazoria (HGB) area, and among the most thoroughly monitored regions in the US. This conceptual model will focus on monitors in operation in 2021 that measure ozone, ozone precursors, and meteorological parameters. The DFW area has twenty sites with ozone monitoring instruments that report to the EPA's Air Quality System (AQS) data mart; these twenty monitors are referred to as regulatory monitors and are used to determine compliance with the ozone NAAQS. Figure 1-1: *Map of Air Monitors in the DFW Area* shows the locations of these sites. Details of each monitor, including the parameters measured, are in Table 1-1: *Monitor Information for the DFW Area.* More details on monitors can be found on the Texas Commission on Environmental Quality (TCEQ) Air Monitoring Sites webpage (https://www.tceq.texas.gov/airquality/monops/sites/air-mon-sites).

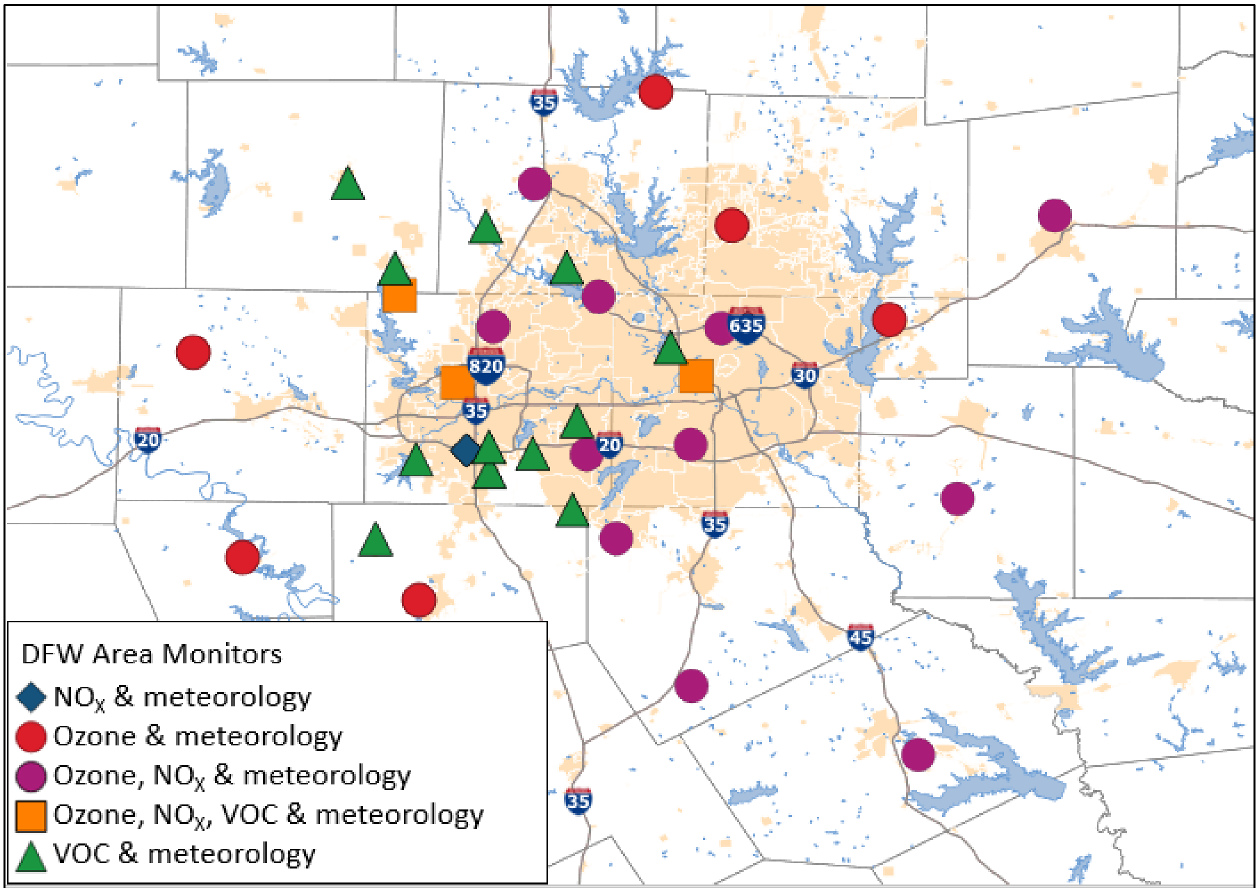


Figure 1-1: Map of Air Monitors in the DFW Area

Table 1-1: 2021 Monitor Information for the DFW Area

Monitor Name	AQS No.[1]	CAMS No.[2]	Compound or Parameter Measured
Frisco	480850005	0031, 0680	Ozone, meteorology
Dallas Hinton	481130069	0060, 0161, 0401, 3002	Ozone, meteorology, VOC, $PM_{2.5}$[3], NO2
Dallas North #2	481130075	0063, 0679	Ozone, meteorology, NOX
Dallas Redbird Airport Executive	481130087	0402	Ozone, NO_X, meteorology
Dallas LBJ Freeway	481131067	1067	NO_X, meteorology
Dallas Elm Fork	481131505	1505	VOC, meteorology
Denton Airport South	481210034	0056, 0157, 0163	Ozone, NO_X, $PM_{2.5}$, meteorology
Flower Mound Shiloh	481211007	1007	VOC, meteorology
DISH Airfield	481211013	1013	VOC, meteorology
Pilot Point	481211032	1032	Ozone, meteorology
Midlothian OFW	481390016	0052, 0137	Ozone, NO_X, $PM_{2.5}$, meteorology
Italy	481391044	1044	Ozone, NO_X, meteorology
Granbury	482210001	0073, 0681	Ozone, meteorology
Greenville	482311006	0198, 1006	Ozone, NO_X, meteorology
Cleburne Airport	482510003	0077, 0682	Ozone, meteorology
Mansfield Flying L Lane	482511063	1063	VOC, meteorology

Monitor Name	AQS No.[1]	CAMS No.[2]	Compound or Parameter Measured
Godley FM2331	482511501	1501	VOC, meteorology
Kaufman	482570005	0071	Ozone, NO_X, $PM_{2.5}$, meteorology
Corsicana Airport	483491051	1051	Ozone, NO_X, $PM_{2.5}$, meteorology
Parker County	483670081	0076	Ozone, meteorology
Rockwall Heath	483970001	0069	Ozone, meteorology
Eagle Mountain Lake	484390075	0075	Ozone, NO_X, VOC, meteorology
Fort Worth Northwest	484391002	0013	Ozone, NO_X, VOC, $PM_{2.5}$, meteorology
Everman Johnson Park	484391009	1009	VOC, meteorology
Arlington UT Campus	484391018	1018	VOC, meteorology
Fort Worth California Parkway North	484391053	1053	$PM_{2.5}$, NO_X, meteorology
Kennedale Treepoint Drive	484391062	1062	VOC, meteorology
Fort Worth Joe B. Rushing Road	484391065	1065	VOC, meteorology
Fort Worth Benbrook Lake	484391503	1503	VOC, meteorology
Keller	484392003	0017	Ozone, NO_X, meteorology
Grapevine Fairway	484393009	0070, 0182	Ozone, NO_X, meteorology
Arlington Municipal Airport	484393011	0061	Ozone, NO_X, meteorology
Decatur Thompson	484970088	0088	VOC, meteorology
Rhome Seven Hills Road	484971064	1064	VOC, meteorology

[1] AQS: EPA's Air Quality System.
[2] CAMS: Continuous Air Monitoring System.
[3]Particulate matter equal to or less than 2.5 microns (micrometers) in width.

CHAPTER 2: OZONE CONCENTRATIONS AND TRENDS

To characterize the current ozone situation in the Dallas-Fort Worth (DFW) area, this conceptual model will focus on ozone concentrations from 2012 through 2021. This section will examine ozone concentrations in various forms to characterize where, when, and how ozone forms in the DFW 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 federal ozone National Ambient Air Quality Standards (NAAQS) to make determinations for regulatory compliance. A design value for the 2015 eight-hour ozone NAAQS is calculated by averaging the annual fourth highest daily-peak eight-hour ozone concentration over three years. Ozone design values are calculated for each monitor, without combining monitors, and then the maximum design value from all monitors in the area is designated as the design value for the area. A monitor exceeds the level of the 2015 eight-hour ozone NAAQS when its design value exceeds 0.070 parts per million (ppm), or 70 parts per billion (ppb). This is different from an "exceedance," which occurs when any daily-maximum eight-hour average (MDA8) ozone exceeds the level of the NAAQS and is not a violation. Understanding exceedances can provide insight into non-attainment.

The eight-hour ozone design value trend for the DFW area is displayed in Figure 2-1: *Eight-Hour Ozone Design Values in the DFW Area*. The 2021 eight-hour ozone design value for the DFW nonattainment area is 76 ppb, which is the lowest eight-hour ozone design value ever recorded in the DFW area. This design value represents a 12.6% decrease from the 2012 design value of 87 ppb.

The largest decrease in design values occurred from 2013 through 2014, when the eight-hour ozone design value dropped by six ppb. After 2014, decreases in design values slowed, with the eight-hour ozone design value decreasing by only five ppb from 2014 through 2021. Decreases may be due to changes in meteorology or in background ozone, which will both be examined in later chapters.

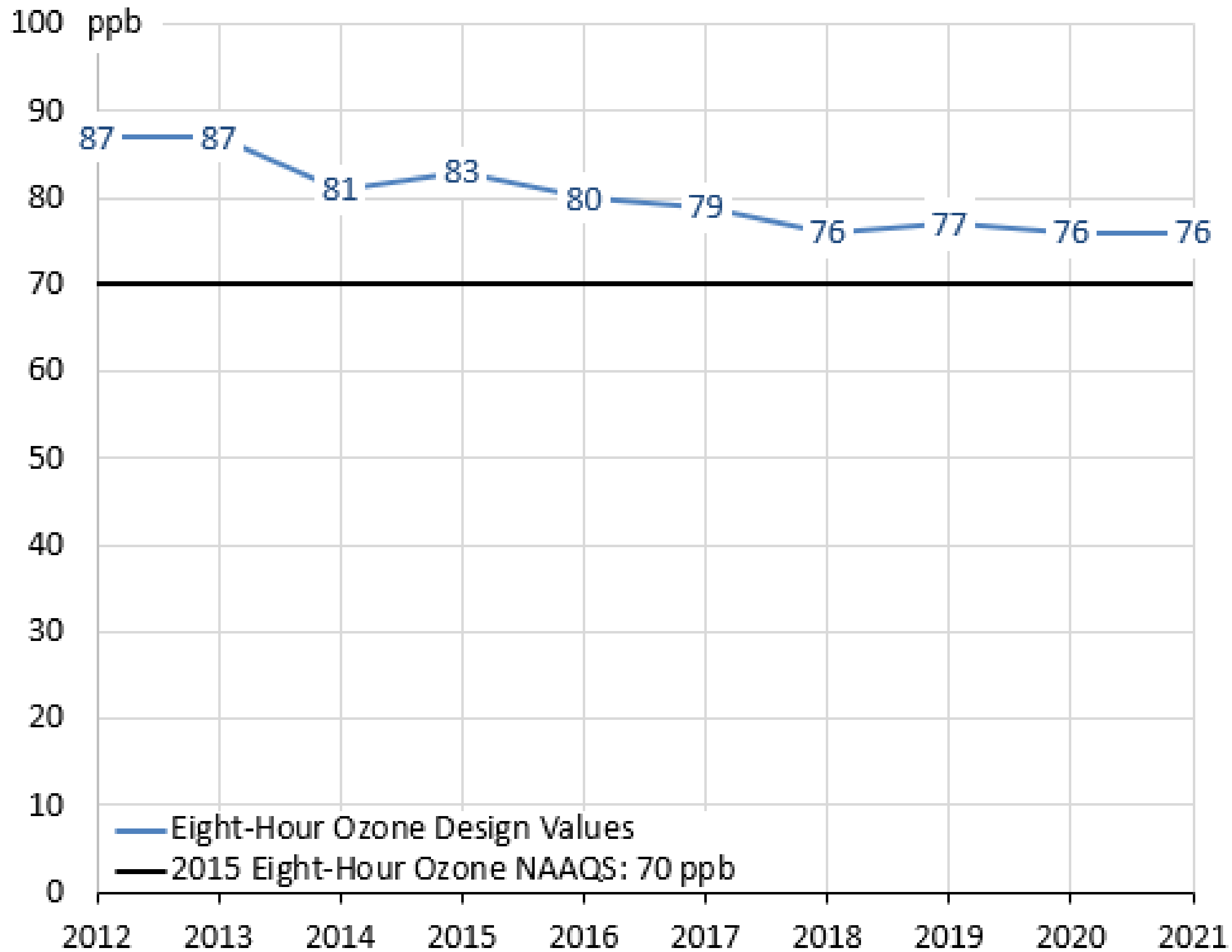


Figure 2-1: Eight-Hour Ozone Design Values in the DFW Area

Design values can vary substantially based on location within an area; therefore, examining individual design values computed for each monitor can provide more insight into how ozone is changing across a region. Figure 2-2: *Eight-Hour Ozone Design Values by Monitor in the DFW Area* shows that the range of design values has been decreasing across the entire DFW area. In 2015, eight monitors attained the 2015 NAAQS. By 2021, eleven monitors attained this standard. In 2021, only one monitor, Pilot Point, did not attain the 2008 NAAQS of 75 ppb.

The area-wide maximum design value each year is labeled on Figure 2-2. Five different monitors recorded the area-wide maximum design value over the ten-year period. In 2012, the monitor with the maximum design value was Keller. For the next five years, Denton Airport South recorded the maximum DFW design value. In 2018 and 2020, Grapevine Fairway recorded the maximum design value, 76 ppb. In the intervening year, Dallas North No.2 recorded the maximum design value. Finally, in 2021, Pilot Point recorded the maximum area-wide design value of 76 ppb.

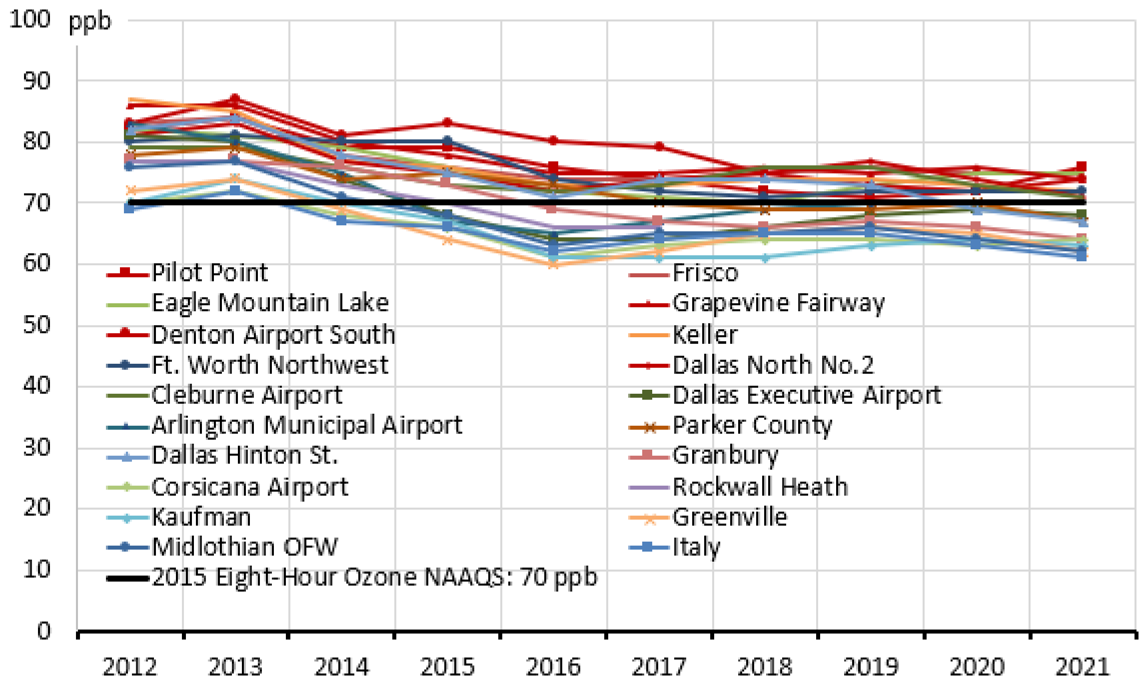


Figure 2-2: Eight-Hour Ozone Design Values by Monitor in the DFW Area

Table 2-1: *Eight-Hour Ozone Design Values in the DFW Area* reports design values for individual monitors. The design value at the Keller monitor dropped the most: 17%. It is in the northwest portion of the DFW region, which was typically where the highest DFW ozone concentrations and design values were recorded.

Other successes among north and northwest DFW monitors include reductions of 14% at Grapevine Fairway, 12% at Dallas North No. 2, and 11% at Denton Airport South. The monitor that determined the DFW design value in 2021, Pilot Point, has declined 7%.

Table 2-1: Eight-Hour Ozone Design Values in the DFW Area

Monitor / CAMS #	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021
Pilot Point C1032	82	84	79	79	76	74	72	71	72	76
Frisco C31	83	84	78	76	74	74	75	76	75	75
Eagle Mountain Lake C75	82	81	79	76	72	71	70	73	75	75
Grapevine Fairway C70	86	86	80	78	75	75	76	75	76	74
Denton Airport South C56	83	87	81	83	80	79	75	73	72	74
Keller C17	87	85	77	76	73	73	74	74	73	72
Ft. Worth Northwest C13	80	81	80	80	74	72	71	72	72	72
Dallas North No.2 C63	81	83	77	75	72	74	75	77	74	71
Cleburne Airport C77	79	79	76	73	72	73	76	76	73	71
Dallas Executive Airport C402	81	80	74	68	64	64	66	68	69	68
Arlington Municipal Airport C61	83	80	75	67	65	67	69	70	na	67
Parker County C76	78	79	74	75	73	70	69	69	70	67
Dallas Hinton St. C401/C60	82	84	78	75	71	74	74	73	69	67
Granbury C73	77	77	76	73	69	67	66	67	66	64
Corsicana Airport C1051	70	72	68	66	61	63	64	64	63	64

Monitor / CAMS #	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021
Rockwall Heath C69	77	77	73	70	66	66	na	na	na	63
Kaufman C71	70	74	70	67	61	61	61	63	64	63
Greenville C1006	72	74	69	64	60	62	65	66	65	62
Midlothian OFW C52/C137	76	77	71	68	63	65	65	66	64	62
Italy C1044	69	72	67	66	62	64	65	65	63	61

Source: EPA Air Quality System (AQS) data mart.

Displaying eight-hour ozone design values on a map can provide insight into ozone formation patterns. Eight-hour ozone design values in the DFW area from 2012, 2016, and 2021 were interpolated spatially using the kriging method. Maps of eight-hour ozone design values for the DFW area are shown in Figure 2-3: *Eight-Hour Ozone Design Value Maps for the DFW Area*. Figure 2-3 show substantial decreases in eight-hour ozone design values across the region and that the locations of high and low ozone are consistent throughout the years. The highest design values occur to the north and northwest of the DFW area at sites such as Keller, Grapevine Fairway, and Eagle Mountain Lake while the lowest design values are observed at monitors to the east and southeast of the DFW area. This suggests prevailing winds from the east or southeast carry background ozone and precursors across the most urbanized portions of DFW to the north/northwest of the metro area.

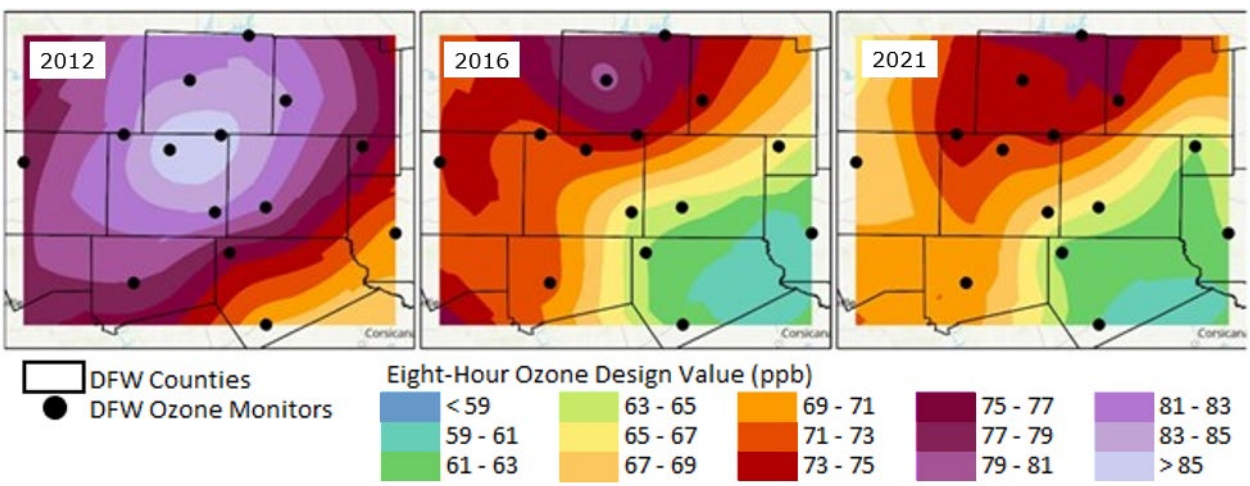


Figure 2-3: Eight-Hour Ozone Design Value Maps for the DFW Area

2.2 FOURTH-HIGHEST EIGHT-HOUR OZONE

Because design values incorporate annual fourth-highest values across three years, they obscure some of the variability across individual years. A single anomalous year with even just a small number of unfavorable, ozone-conducive meteorological events will impact design value computations for three consecutive years. Investigating trends in annual fourth-highest MDA8 ozone concentrations can provide more insight into each individual year. Variability in fourth-highest MDA8 ozone concentrations may indicate which years are more strongly affected by unusual episodes such as ozone conducive meteorology or variable precursor conditions such as transport from fire-generated precursors.

Area-wide fourth-highest MDA8 ozone trends are not particularly instructive because design values are calculated on a per monitor basis. Instead, fourth-highest MDA8 ozone trends are investigated at individual monitors. Figure 2-4: *Fourth-Highest Eight-Hour Ozone Concentration by Monitor in the DFW Area* spans 2010 through 2021 to encompass all years used in computations of design values over the ten-year period. A regression trend, displayed on this plot as a thick red line, confirms that overall trends in the fourth-highest eight-hour ozone concentrations are declining over the ten-year period, at a rate of just over 0.1 ppb per year.

The figure shows there is more variability in fourth-highest MDA8 ozone values compared to design values. Large increases in 2011, when only one monitor decreased and one was unchanged, were followed by consecutive years of mixed results, when either fourteen (2012) or thirteen (2013) monitors recorded decreases. All twenty monitors recorded decreases in 2014 and in 2018 all monitors recorded increases. This suggests that ozone concentrations in those years may be strongly influenced by non-local factors such as transport of ozone or precursors from outside the area or meteorology. Fourth-highest eight-hour ozone values suggest that meteorology may have caused higher ozone in 2011 and 2021 and lower ozone in 2014 and 2016.

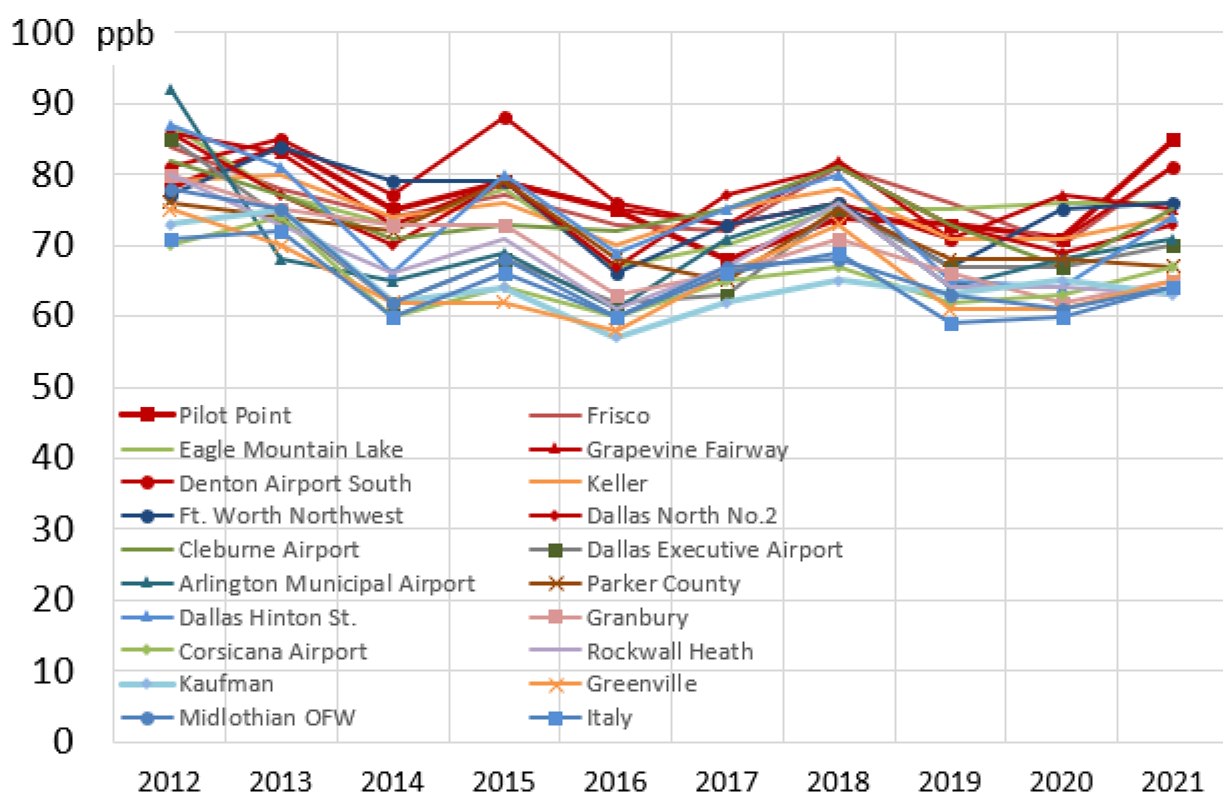


Figure 2-4: Fourth-Highest MDA8 Ozone Concentration by Monitor in the DFW Area

This variability at individual monitors suggests that controlling fourth-highest values is a difficult task, even with extensive control strategies. For example, the Pilot Point monitor currently sets the eight-hour ozone design value for the DFW area, 76 ppb in 2021. This value is the truncated average of fourth-highest values of 73 ppb in 2019, 70 ppb in 2020, and 85 ppb in 2021, as shown in Table 2-2: *Annual Fourth-Highest MDA8 Ozone Averages in the DFW Area.* This 2021 value, and several other 2021 fourth-highest MDA8 ozone values, was substantially higher than 2020, which will impact DFW design values through 2023.

Table 2-2: Annual Fourth-Highest MDA8 Ozone Averages in the DFW Area

Monitor / CAMS #	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021
Pilot Point	78	91	78	84	75	79	75	68	74	73	71	85
Frisco	74	91	84	78	74	77	73	72	81	76	70	81
Eagle Mountain Lake	80	80	87	77	73	78	67	70	75	75	76	76
Grapevine Fairway	83	91	86	83	73	79	75	73	82	71	73	75
Denton Airport South	74	95	81	85	77	88	76	73	76	71	71	81
Keller	85	97	79	80	74	76	70	75	78	71	71	74
Fort Worth Northwest	80	82	77	81	79	79	66	73	76	67	75	76
Dallas North #2	71	88	86	77	70	79	67	77	81	73	69	73
Cleburne Airport	78	79	82	77	71	73	72	74	81	73	66	75
Dallas Redbird Airport Executive	78	82	85	74	63	68	62	63	75	67	67	70
Arlington Municipal Airport	79	80	92	68	65	69	61	71	76	64	68	71
Parker County	70	88	76	74	72	78	68	65	75	68	68	67
Dallas Hinton	75	84	87	81	66	80	69	75	80	65	64	74
Granbury	77	76	80	75	73	73	63	66	71	66	62	65
Corsicana Airport	68	74	70	74	60	64	60	65	67	62	63	67
Rockwall Heath	73	80	80	73	66	71	61	64	76	64	64	63
Kaufman	64	74	73	75	62	64	57	62	65	63	65	63
Greenville	64	77	75	70	62	62	58	66	73	61	61	65
Midlothian OFW	72	80	78	75	62	68	60	67	68	63	61	64
Italy	63	75	71	72	60	66	60	66	69	60	60	64

Source: EPA Air Quality System data mart.
Note: Fourth-highest values included in computations of annual DFW area wide design values are shaded.

2.3 OZONE EXCEEDANCE DAYS

The number of days that MDA8 ozone concentrations are above the level of a NAAQS, termed an ozone exceedance day, provides a valuable measure of the severity of an area's ozone problem. The distribution of these days across the ozone season provides further insight into the unique characteristics driving ozone formation in an airshed. For the 2015 eight-hour ozone NAAQS, an eight-hour ozone exceedance day is considered any day that any monitor in the area measures an MDA8 ozone value greater than 70 ppb. A day when more than one monitor in an area exceeds the level of the standard is still considered to be only one exceedance day. This definition of ozone exceedance days will be used throughout this conceptual model when referring to high ozone days, unless otherwise noted.

The number of days that any MDA8 ozone concentration in the DFW area exceeded the level of the 2015 NAAQS each year is presented in Figure 2-5: *Eight-Hour Ozone Exceedance Days in the DFW Area*. The number of ozone exceedance days declined over the ten-year period from 60 days to 31 days, nearly 50%. There is substantial variability in the number of exceedance days per year over the ten-year period.

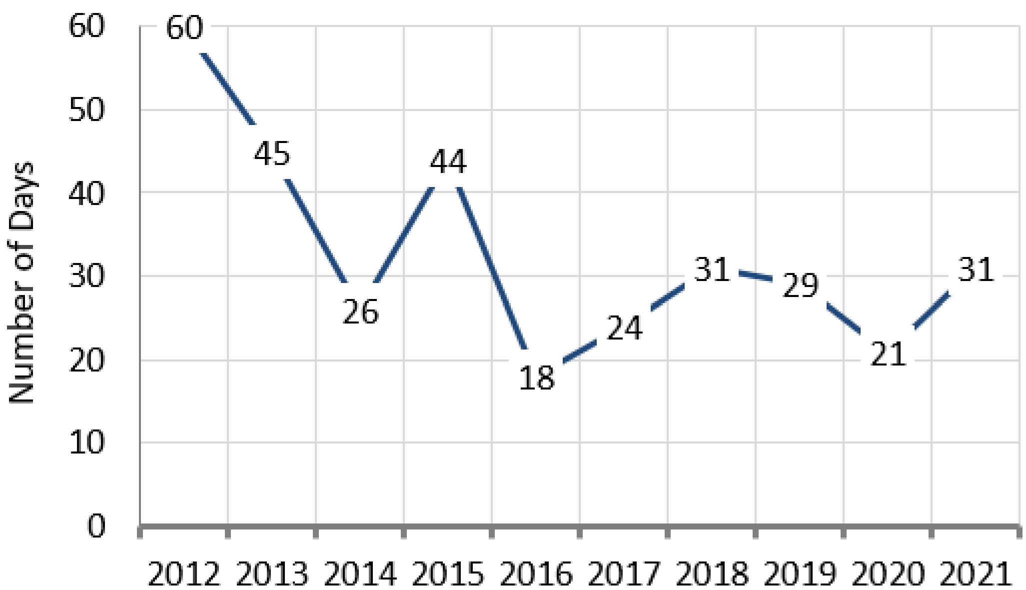


Figure 2-5: Eight-Hour Ozone Exceedance Days in the DFW Area

A simple statistical test was performed to investigate the possibility that the number of exceedance days per year is subject to greater variability than would be expected if exceedances were equally likely in every year. Pearson's chi-squared test was performed to test the null hypothesis that the observed number of exceedance days per year does not differ enough from the expected number of days. If the null hypothesis is rejected, the alternate hypothesis, that differences in the observed number of days from the expected number of days are large enough to suggest that years are different, can be accepted. The average number of exceedance days per year over the ten-year period 2012 through 2021, 33 days per year, is a reasonable expectation. This means that in any given year, we expect about 33 days to be exceedance days in the DFW area. This yields a chi-squared value of 46 which exceeds the critical value of chi-squared of 16.9 (p=0.05 with degrees of freedom=9). Because the computed value exceeds the critical value, the test rejects the null hypothesis, and the alternate hypothesis can be accepted. The decline in the number of exceedance days appears to be a true change and not merely year to year variability.

Further investigation of the number of exceedance days by month provides additional insight on how ozone formation has changed over the ten-year period. Table 2-3: *Ozone Exceedance Days by Month in the DFW Area* presents the number of exceedance days in the DFW area over the ten-year period by year and month. While ozone season is considered to begin in March, no exceedance days have been recorded in March in the DFW area since March 2012 when three days were recorded. Similarly, no exceedance days have been recorded in April since 2018, and six years over the decade recorded zero exceedance days in April. While October is included in ozone season, few exceedance days are recorded in October. The highest number of exceedance days occur in August and September.

Pooling multiple years can facilitate analysis when there are few observations in a particular year, as in this example. To this end, the decade was split into five-year groupings, known as pentads. The later pentad, 2017 through 2021, recorded 30% fewer exceedance days (136) than the earlier one (193). An even greater reduction was seen in the number of exceedance days recorded in August and September, dropping 44% from 98 in the earlier pentad to 55 in the later one. Roughly half (47%) of all exceedance days were recorded in August and September over the decade, but this shifted from 51% in the earlier pentad to 40% in the later one.

Table 2-3: Ozone Exceedance Days by Month in the DFW Area

Month	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2012-2016	2017-2021
March	3	0	0	0	0	0	0	0	0	0	3	0
April	3	0	1	1	0	0	2	0	0	0	5	2
May	8	3	3	2	0	5	8	5	4	2	16	24
June	12	6	2	7	8	4	2	5	5	6	35	22
July	11	8	5	2	2	3	11	7	0	7	28	28
August	14	10	10	20	2	3	8	5	10	5	56	31
September	9	16	4	9	4	8	0	7	0	9	42	24
October	0	2	1	3	2	1	0	0	2	2	8	5
Ozone season	**60**	**45**	**26**	**44**	**18**	**24**	**31**	**29**	**21**	**31**	**193**	**136**

Source: Texas Commission on Environmental Quality (TCEQ).

2.4 OZONE SEASON

Analysis of the temporal distribution of high ozone values across the DFW ozone season can provide useful insight into when, where, and why ozone forms in the DFW area. One way to delineate and characterize the ozone season is to examine the frequency with which individual months observe ozone exceedance days. This measure is a concise method of characterizing the severity of ozone across the season.

Previous conceptual models for the Houston-Galveston-Brazoria area (TCEQ, 2019a) and the DFW area (TCEQ, 2019b) have shown that ozone season in many areas of Texas, including the DFW area, has two peaks. The first peak occurs in April through June, and the second peak occurs in August through October. These areas also exhibit the mid-summer minimum, a short-term dip in ozone exceedance days in July and early August. This mid-summer minimum is likely caused by the dominance of high atmospheric pressure in the southeast US, which results in air flow from the Gulf of Mexico over eastern Texas, and hence low background ozone concentrations (Davis et al., 1998; Chan and Vet, 2010; Smith et al., 2013).

This analysis compares eight-hour ozone exceedance days at eight-hour ozone standards of 84 ppb, 75 ppb, and 70 ppb. Figure 2-6: *Ozone Exceedance Days by Month in the DFW Area* shows data from the twenty DFW area ozone monitors from 2012, 2016, and 2021.

In 2012, for all three standards, the ozone season exhibited two peaks with a mid-summer minimum. Days with eight-hour ozone values greater than 70 ppb were observed from March through September, while eight-hour ozone values greater than

84 ppb were observed only from May through September. High ozone occurred most frequently in June or August. By 2017, this pattern shifted to later in the year, with no exceedances of any standards recorded in March or April of 2017, and with no exceedances of the 1997 level recorded at all. The number of 70 ppb exceedances has dropped 45%. While the multi-modal nature of seasonal exceedances is still apparent in 2021, it is much attenuated.

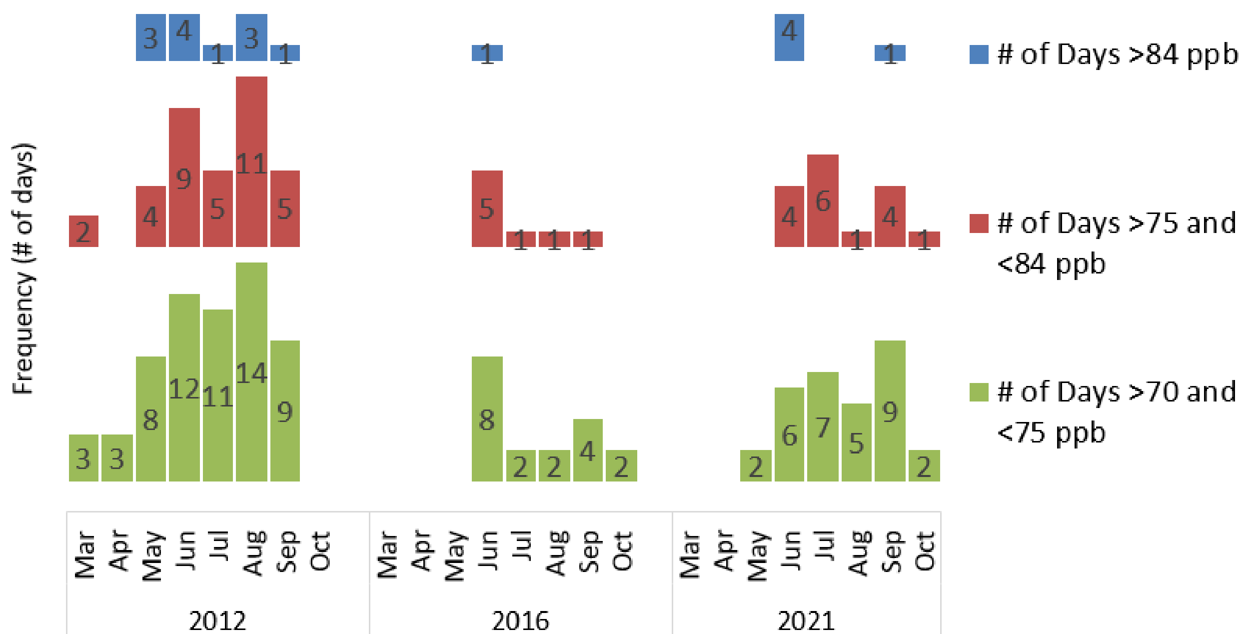


Figure 2-6: Ozone Exceedance Days by Month in the DFW Area

2.5 TIME OF PEAK OZONE

The time of day when peak ozone occurs, including differences in time of peak ozone across monitors, can provide insight into ozone formation dynamics in an area. Later peak times suggest that ozone was formed from precursors that are transported to downwind receptors, usually passing over portions of the area with large numbers of emitting sources. Differences in time of day of peak ozone between high ozone days and low ozone days was also investigated.

Figure 2-7: *Time of Day of Peak Ozone in the DFW Area* shows that the hour of the day with the highest frequency of one-hour daily maximum ozone concentration is 16:00 local standard time (LST), which is 4:00 p.m. LST. This hour accounts for 26% of all daily maxima, with 62% of all daily maxima occurring within one hour of 16:00, either before or after. Note that all sampling times are reported in LST even though the DFW area uses local daylight time (LDT) during most of ozone season.

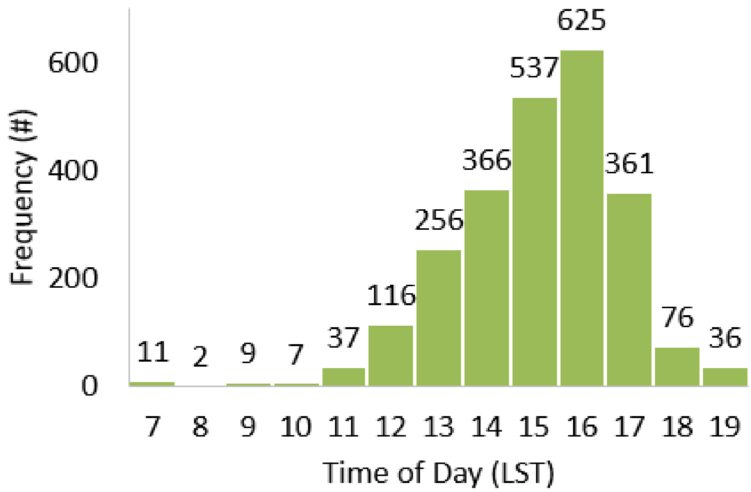


Figure 2-7: Time of Day of Peak Ozone in the DFW Area

While roughly the same pattern emerges when days are grouped according to whether the day recorded an exceedance of the 2015 ozone NAAQS, as shown in Figure 2-8: *Time of Day of Peak Ozone in the DFW Area by Exceedance Status*, there are several notable features. First, the hour that most frequently recorded the peak one-hour ozone concentration was 16:00 LST, whether the day was an exceedance day or not. On days that did not exceed the 2015 NAAQS, peak one-hour ozone occurred anywhere from 7:00 LST to 19:00 LST, although only very infrequently did it occur before 12:00 LST (8%) or after 17:00 LST (3%). For the 704 exceedance days over the period, these figures were 0% and 4%. On exceedance days, the peak hour was limited to 10:00 LST to 19:00 LST, with two-thirds (67%) of days observing peak during the three-hour window of 15:00 LST through 17:00 LST. This suggests that exceedances typically occur after a long period of ozone conducive conditions in the morning.

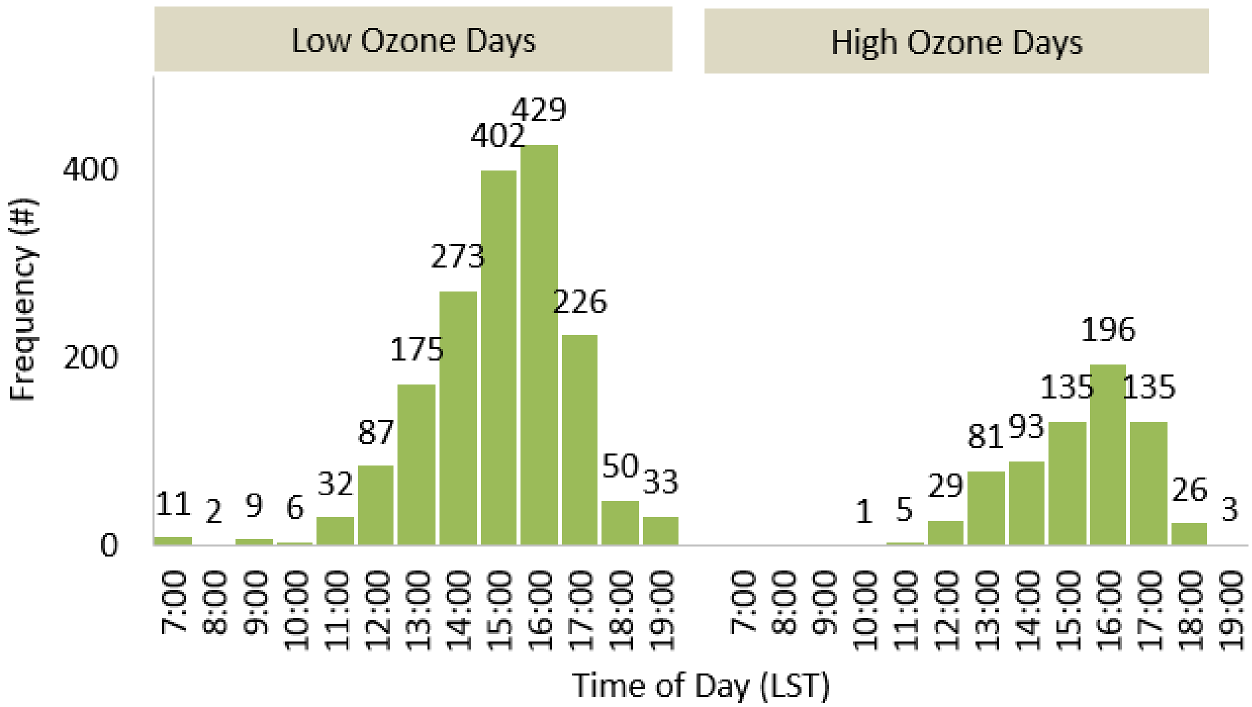


Figure 2-8: Time of Day of Peak Ozone in the DFW Area by Exceedance Status

Dividing these totals by year, as in Figure 2-9: *Time of Day of Peak Ozone in the DFW Area by Year*, the occurrence of these hours as peak hours is stable over the period. The percentage of days when the peak was recorded at 16:00 LST is roughly 26%, ranging from 21% in 2015 to 31% in 2022. The three-hour period from 15:00 LST to 17:00 LST accounts for about 63% of all peak hours, ranging from 56% in 2020 to 65% in 2022. This suggests that exceedance days typically occur when ozone has had sufficient time to form over the course of an afternoon.

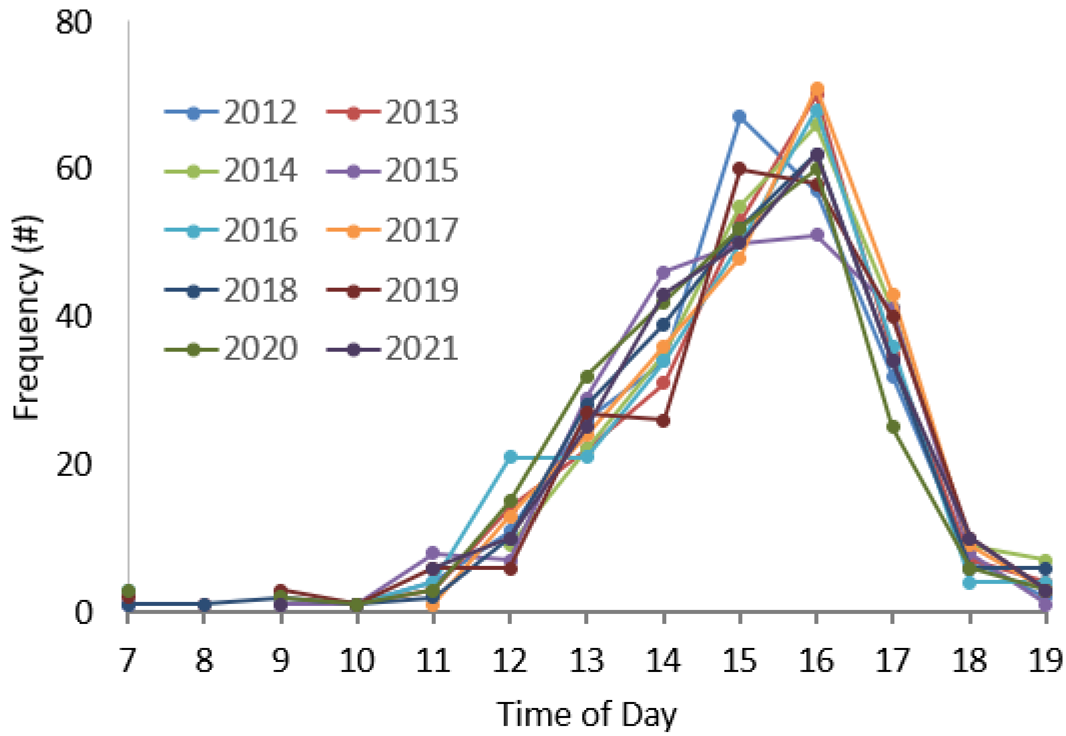


Figure 2-9: Time of Day of Peak Ozone in the DFW Area by Year

Figure 2-10: *Time of Day of Peak Ozone on Exceedance Days in the DFW Area by Month* shows that the time of day of peak ozone on exceedance days varies little by month, with peaks occurring almost exclusively after noon on exceedance days, typically late in the afternoon. As expected, most exceedances occur in August, followed by September and July.

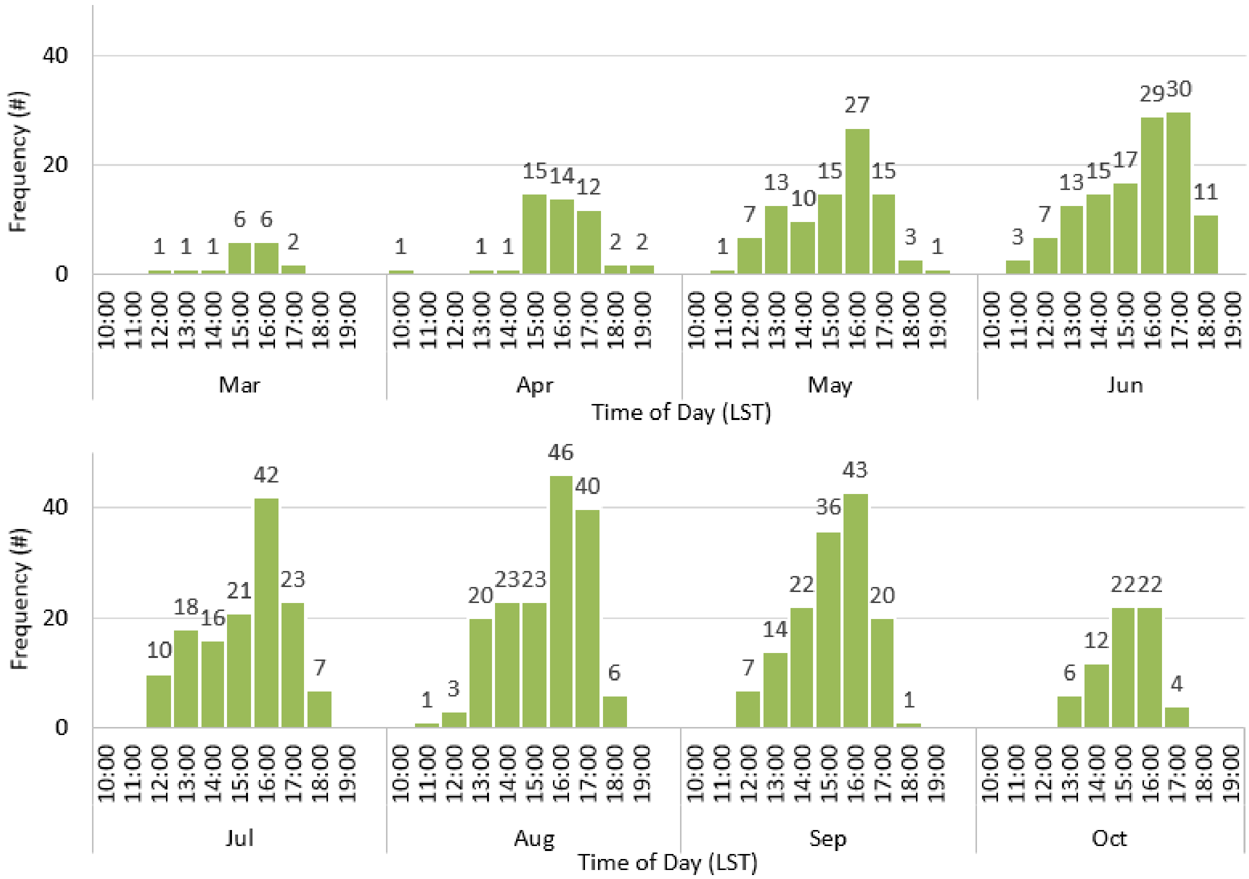


Figure 2-10: Time of Day of Peak Ozone on Exceedance Days in the DFW Area by Month

2.6 BACKGROUND OZONE

Regional background ozone is defined as ozone present in the air entering a city from outside the city limits, or as ozone in the local air mass that has not been influenced by emissions from the city of interest. There are several ways to estimate regional background ozone, but none of these techniques is a perfectly accurate measure of 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 control of state and local authorities. Since background ozone concentrations are not easily controlled, the local component of ozone formation is the amount of ozone that the area could potentially control.

The technique used here for estimating regional background ozone concentrations is similar to methods used by Nielsen-Gammon et al. (2005) and described by Berlin et al. (2013). Monitoring sites capable of measuring regional background ozone were selected based on their distance from local emissions sources in the urban core and industrial areas of the DFW area. Each selected site is expected to receive air with regional background ozone when it is upwind, or at least not downwind, of the urban and industrial areas. 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, background ozone cannot be lower than the estimated value. Eight-hour average background ozone was then estimated as the lowest MDA8 ozone value observed at the selected background sites for each ozone season day from 2012 through 2021.

For this analysis, selected sites included ten monitors on the periphery of the DFW metro area, chosen because they are likely to record regional background ozone: Cleburne Airport, Eagle Mountain Lake, Frisco, Granbury, Greenville, Kaufman, Italy, Parker County, Pilot Point, and Rockwall Heath. Monitor locations are displayed in Figure 2-11: *Map of Selected Background Monitors in the DFW Area*. These perimeter monitors were selected to avoid low biased ozone concentrations found in the urban core as a result of high NO_x emissions, which scavenge ozone through NO_x titration. NO_x-influenced low urban ozone concentrations can underestimate background ozone concentrations.

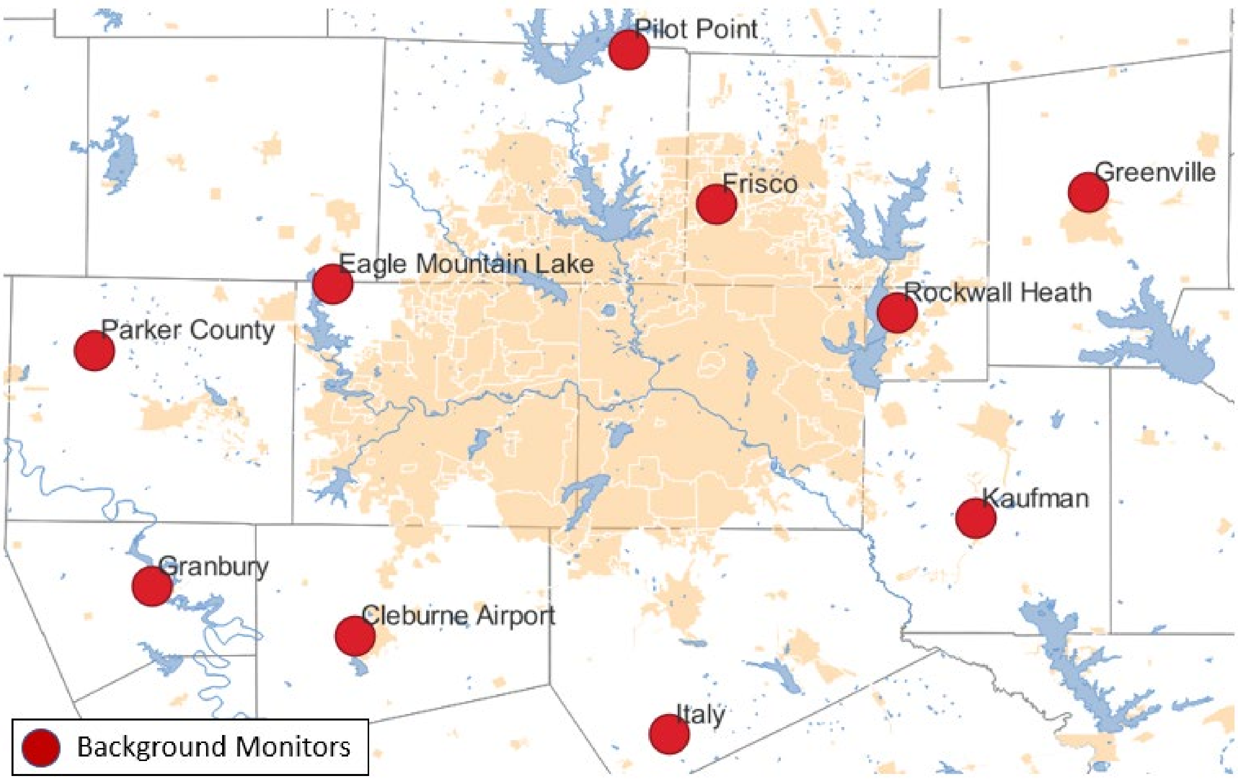


Figure 2-11: Map of Selected Background Monitors in the DFW Area

In addition to daily background ozone, daily locally produced ozone was also calculated by subtracting the computed daily background ozone concentration from the highest MDA8 ozone value for the area. Results were then separated into low ozone days and high ozone days to investigate possible changes in background ozone that may occur on days with high ozone.

Median MDA8 ozone, background ozone, and locally produced ozone were calculated for the ozone season of each year. Because ozone concentrations are skewed, with many low values and few high ones, the median is a better statistic to use to investigate the central tendency of background ozone. Results are displayed in Figure

2-12: *Ozone Season Trends in MDA8 Ozone, Background Ozone, and Locally Produced Ozone for High versus Low Ozone Days in the DFW Area*.

Over the entire decade, median background ozone was 34 ppb on low ozone days, increasing to 51 ppb on high ozone days. Although median background ozone was higher on high ozone days, the median local ozone contribution also increased at a greater than proportional rate on these days. On high ozone days, background ozone accounted for approximately 68% of the MDA8 ozone and on low ozone days, it accounted for roughly 72%. Locally produced ozone accounted for approximately 28% to 32% of MDA8 ozone, regardless of whether the day was a high ozone day or not.

Because it is difficult to identify trends visually in Figure 2-13, simple linear ordinary least squares regressions were run. Annual average background ozone appeared to be declining by -0.79 ppb per year on high ozone days, but the slope on low ozone days was not statistically significant, suggesting this method cannot identify a trend. Annual median local ozone was found to be increasing by 0.73 ppb per year on high ozone days and by 0.27 ppb per year on low ozone days. Both of these results were statistically significant; however, caution should be used when interpreting these results because of the low number of observations available.

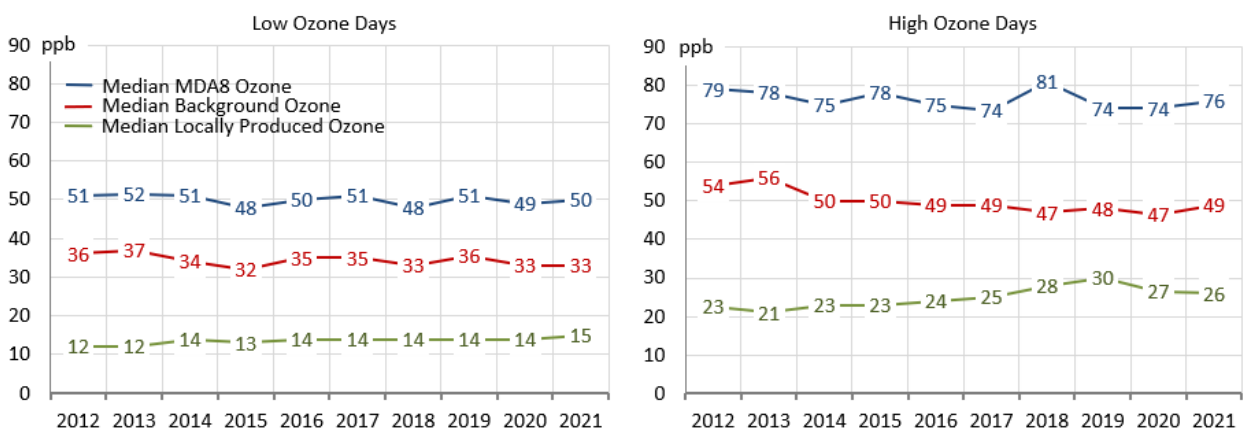
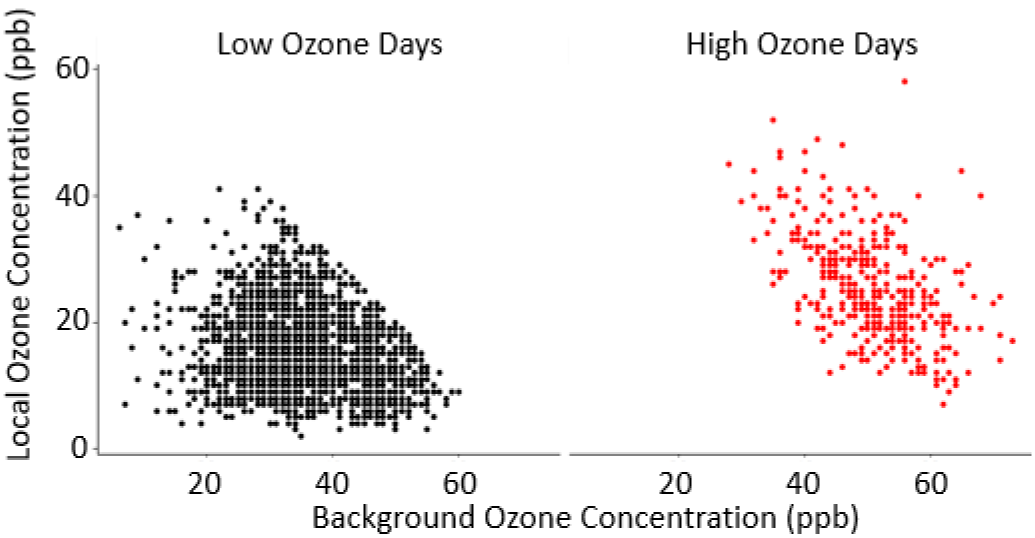


Figure 2-12: Ozone Season Trends in MDA8 Ozone, Background Ozone, and Locally Produced Ozone for High versus Low Ozone Days in the DFW Area

Annual averages obscure much of the variation in background and local ozone contributions, especially higher values that determine compliance. Daily values of these measures are presented in Figure 2-13: *Daily Background and Local Ozone Concentrations in the DFW Area*. This figure plots high ozone days in red on the left, and all other days in black on the right. Substantial variability in background ozone is apparent, even on days with high MDA8 ozone, ranging from 29 to 74 ppb on those days. Background ozone accounted for 28 to 84% of total ozone on these days. On low ozone days, background ozone ranged from 3 to 62 ppb, contributing from 10% to 94% of total ozone on these days. An exceedance could have been recorded at a non-periphery monitor, so exceedance cannot be determined solely by summing the horizontal and vertical values of the plotted points, which are all based on values computed from periphery monitors.



Source: Texas Air Monitoring Information System.

Figure 2-13: Daily Background and Local Ozone Concentrations in the DFW Area

Background ozone on both high and low ozone days very closely correlates with daily maximum ozone. This is seen in Figure 2-14: *Background Ozone versus MDA8 Ozone for the Ozone Season in the DFW Area from 2012 to 2021*. This indicates that ozone concentrations in the DFW area are driven more by background ozone rather than locally produced ozone. This also indicates that conditions that lead to high ozone within DFW also enhance ozone formation regionally.

Pearson's correlation coefficient is a useful measure of the strength of the relationship between two variables, the extent to which they move in tandem, though it does not indicate causality. It can range between negative one, that is, perfectly negatively correlated, and positive one, perfectly positively correlated. Zero indicates no correlation in either direction. Pearson's correlation coefficient between background ozone and MDA8 ozone is 0.80, which is a strong positive correlation. Pearson's correlation coefficient between local ozone and MDA8 ozone is less, 0.61, while the correlation between background and local ozone is only 0.04. This suggests that background ozone is the dominant factor determining an exceedance and that background and local ozone are only weakly positively correlated.

Different patterns emerge in these correlations when days are grouped by high or low MDA8 ozone. The correlation between background ozone and MDA8 ozone remains fairly strong at 0.76 on low ozone days, but is only 0.35 on high ozone days, though still a moderately positive correlation. The correlation between local ozone and MDA8 ozone differs little between high and low ozone days: 0.40 and 0.47, respectively.

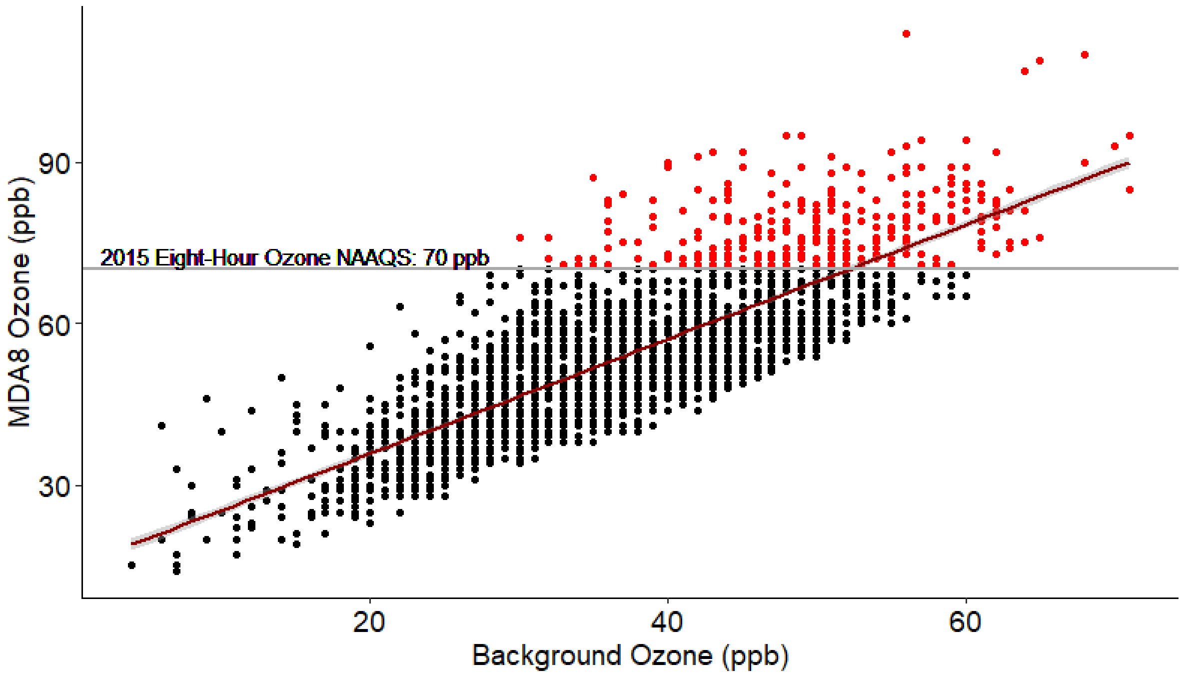


Figure 2-14: Background Ozone versus MDA8 Ozone for the Ozone Season in the DFW Area from 2012 to 2021

Background ozone concentrations also change throughout ozone season. Average background ozone and local ozone contribution in the DFW area were calculated for each month from 2012 through 2022. Results displayed in Figure 2-15: *Estimated Background Ozone and Local Ozone Contribution by Month in the DFW Area* show that for the ozone season, the highest background ozone occurs in the spring (March, April, and May), when average background eight-hour ozone averages around 40 ppb. The lowest background ozone occurs in July. In the late summer (August, September, and October), background increases to an average around 34 ppb. The local contribution to eight-hour ozone starts at the lowest in March and steadily increases until August. This indicates that the early spring ozone season in DFW is likely caused by high regional background ozone while the late summer ozone season is characterized by more local ozone production.

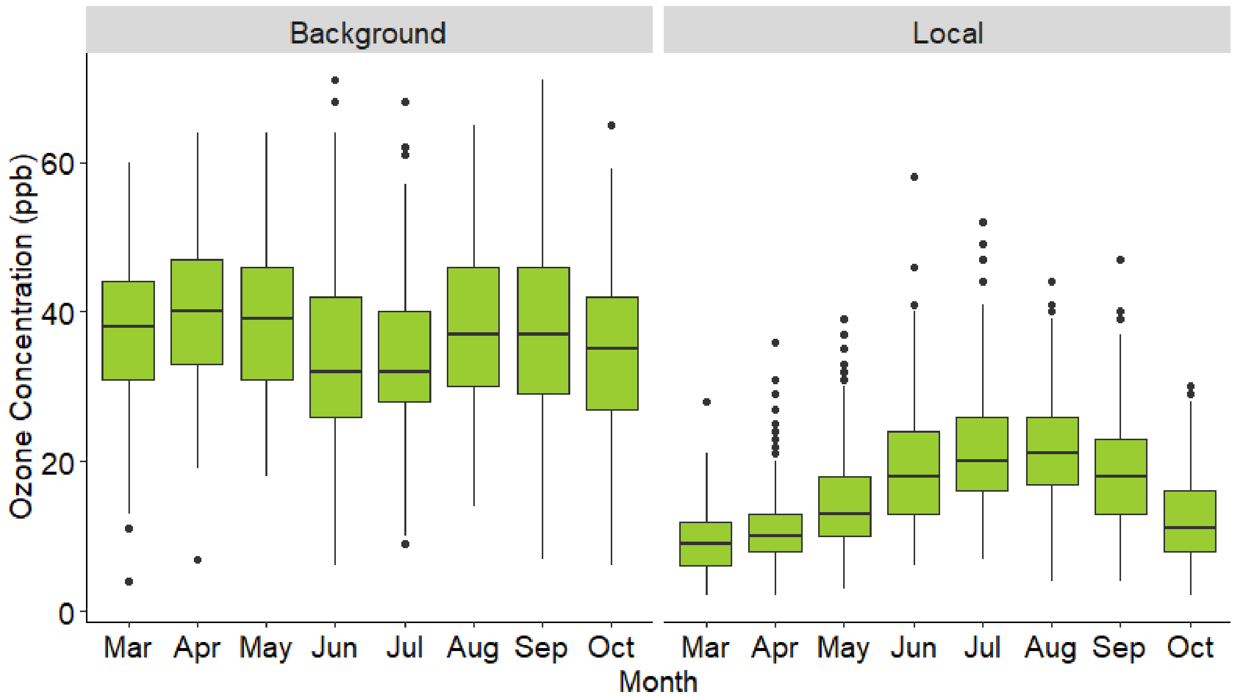


Figure 2-15: Estimated Background Ozone and Local Ozone Contribution by Month in the DFW Area

CHAPTER 3: OZONE PRECURSOR CONCENTRATIONS AND TRENDS

As a secondary pollutant, ozone is not directly emitted into the atmosphere but formed through photochemical reactions with nitrogen oxides (NO_X) and volatile organic compounds (VOC). The complexity of ozone formation requires a comprehensive examination of these precursors to ozone formation. This section will focus on NO_X and VOC concentration and emissions trends in the Dallas-Fort Worth (DFW) area.

3.1 AMBIENT NO_X TRENDS

NO_X, a precursor to ozone formation, is a variable mixture of nitric oxide (NO) and nitrogen dioxide (NO_2). NO_X is primarily emitted by fossil fuel combustion, lightning, biomass burning, and soil. Examples of common NO_X emissions 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 DFW area are mobile sources, large electric generation units (EGU), and industrial processes. These sources can produce large, concentrated plumes of emissions that can enhance ozone generation.

Ambient NO_X concentrations follow diurnal and seasonal patterns, typically exhibiting the highest values at night and in winter months. These values are excluded here because they do not coincide with times of ozone formation, which is daylight hours during ozone season. Further, because of substantial variability in NO_X concentrations, it is helpful to distinguish between days when NO_X concentrations reached very high levels and those when they did not.

Since 2012, there have been at least 15 NO_X monitors operating in the DFW area, all of which report to the Environmental Protection Agency (EPA). In 2014 and 2015, as part of an EPA program to expand NO_X monitoring of on-road mobile sources, two new monitors were installed near two highly trafficked roadways in the DFW area: Dallas LBJ Freeway, which began operation April 2014, and Fort Worth California Parkway North, which began operation in March 2015. These near-road monitors provide valuable information about on-road mobile sources, but because of their proximity to sources, they tend to record among the highest NO_X concentrations observed, which must be considered in comparisons across time periods.

All valid hours and years of NO_X concentrations during ozone season were used to calculate yearly median and 95th percentile NO_X trends. The 95th percentile was examined to show the upper end of the NO_X distribution while the median was examined to show the central tendency of NO_X concentrations in the DFW area. Figure 3-1: *Ozone Season NO_X Trends in the DFW Area* shows the 95th percentile ozone season NO_X concentration rose 19.5% from 20.0 parts per billion (ppb) to 23.9 ppb, while the median remained roughly the same at 4.0 ppb. However, these trends are biased by inclusion of near-road monitors in 2021 values but not in 2012 values. Excluding near-road monitors, 95th percentile and median NO_X concentrations fell 13.0% and 10.4%, respectively. Beginning in 2016, the first full year of measurements from both near-road monitors, 95th percentile concentrations barely changed, dropping 1.7%, while median NO_x concentrations rose 8.3%.

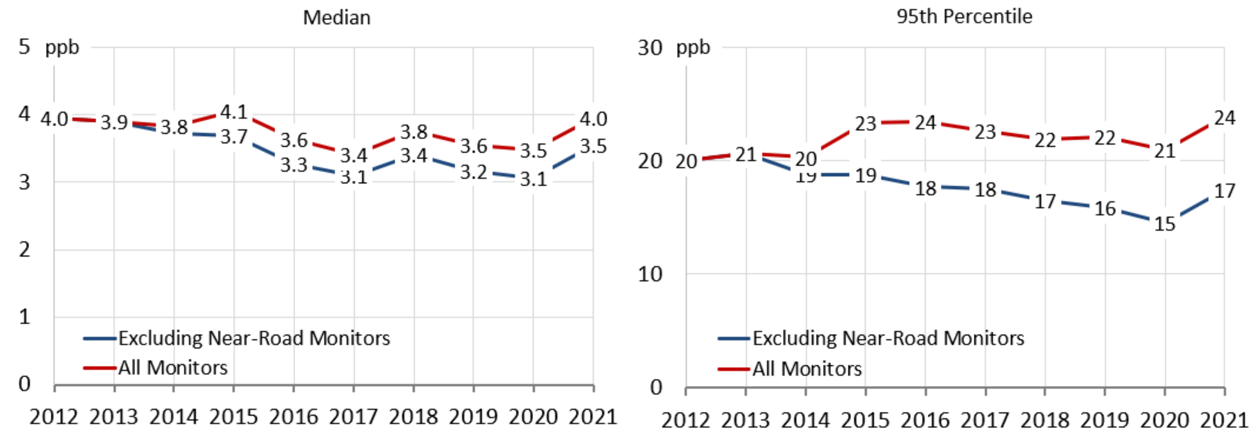


Figure 3-1: Ozone Season NO_x Trends in the DFW Area

Median and 95th percentile NO_x concentrations for the DFW area were also investigated on a monthly time scale. Figure 3-2: *Monthly NO_x Trends in the DFW Area* shows the seasonality in NO_x concentrations, with high concentrations typically recorded in cooler months. This occurs because cooler months have less sunlight, which causes less NO_x to react to form ozone. Patterns within each month are similar across years. The 95th percentiles rose over the decade, with substantial variability within each month. Large increases in 95th percentile values in all months beginning in about 2015 are likely associated with deployment of new near-road NO_x monitors in April 2014 (Dallas LBJ Freeway) and March 2015 (Fort Worth California Parkway North).

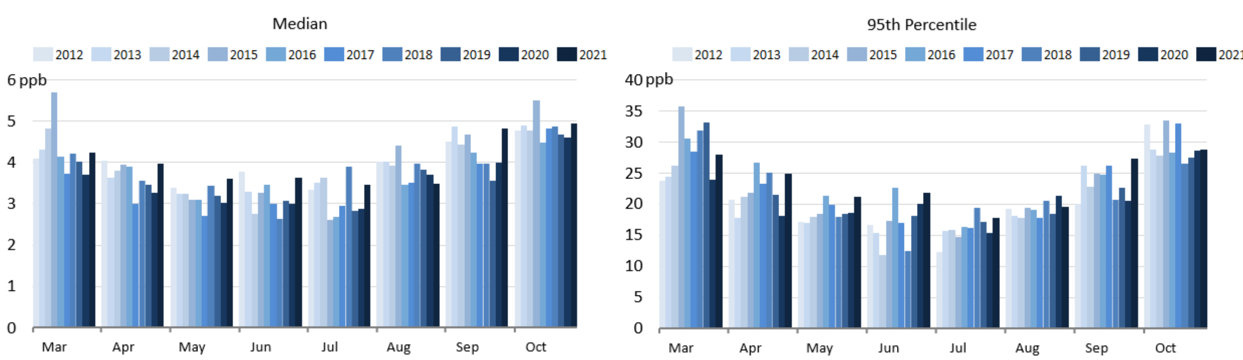


Figure 3-2: Monthly NO_x Trends in the DFW Area

Diurnal trends in ozone season NO_x for the DFW area are displayed in Figure 3-3: *Ozone Season Hourly NO_x Trends in the DFW Area*. Hourly trends for both the median and 95th percentile ozone season NO_x show that, for the daylight hours considered, the highest NO_x concentrations occur in the morning around 7:00 a.m. local standard time (LST), which is 6:00 a.m. local daylight time (LDT). This coincides with morning rush hour. Hours before 7:00 a.m. were also examined but the morning peak in all years was 7:00 a.m. LST. There is a smaller peak in the afternoon for the evening rush hour. The lower afternoon peak is due to higher mixing layer heights, which allow more volume for NO_x to mix, causing monitors to measure lower concentrations of NO_x.

This figure also clearly shows the impact of deploying two near-road NO_x monitors. In the top panels which include all monitors, years 2012 through 2014 are lower for both statistics, and median values are much lower. Once those monitors were fully operational in 2015, medians and 95th percentiles increased. By early evening, these monitors no longer record high NO_x concentrations divergent from other monitors.

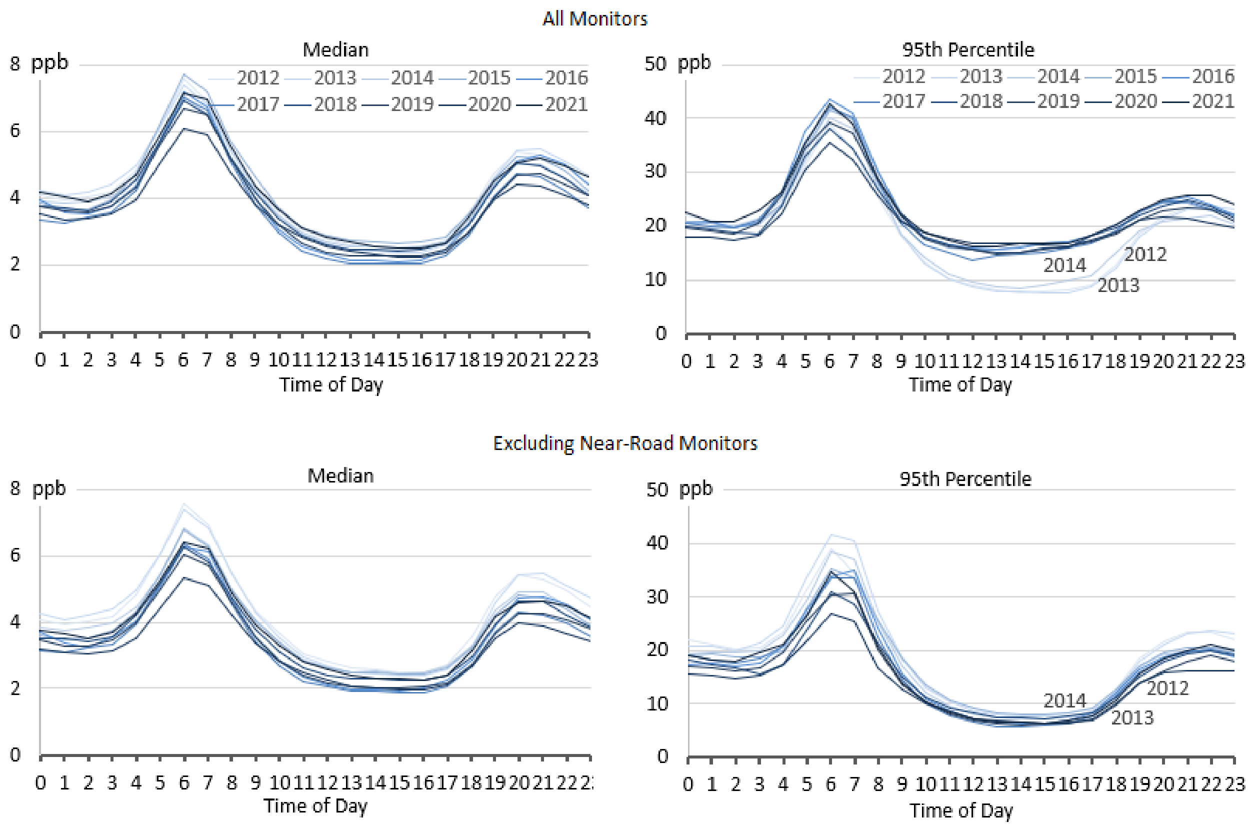


Figure 3-3: Ozone Season Hourly NO_x Trends in the DFW Area

This pattern with near-road monitors becomes clear when presented for individual monitors as shown in Figure 3-4: *Ozone Season NO_x Trends by Monitor in the DFW Area.* The top two panels of the figure include the two near-road monitors, while the bottom two panels exclude them. Because those two monitors record the highest annual medians and 95th percentiles over the decade, they obscure variation at other monitors when plotted on the same scale. While some monitors showed increases in medians and others showed decreases, what is apparent is that the two near-road monitors recorded medians that were much higher than any other DFW area monitor. These two monitors also reported among the highest 95th percentile NO_x concentrations, although they were not always the highest. Dallas Hinton typically recorded the highest 95th percentile NO_x concentrations, although NO_x monitoring at this monitor ceased after 2019.

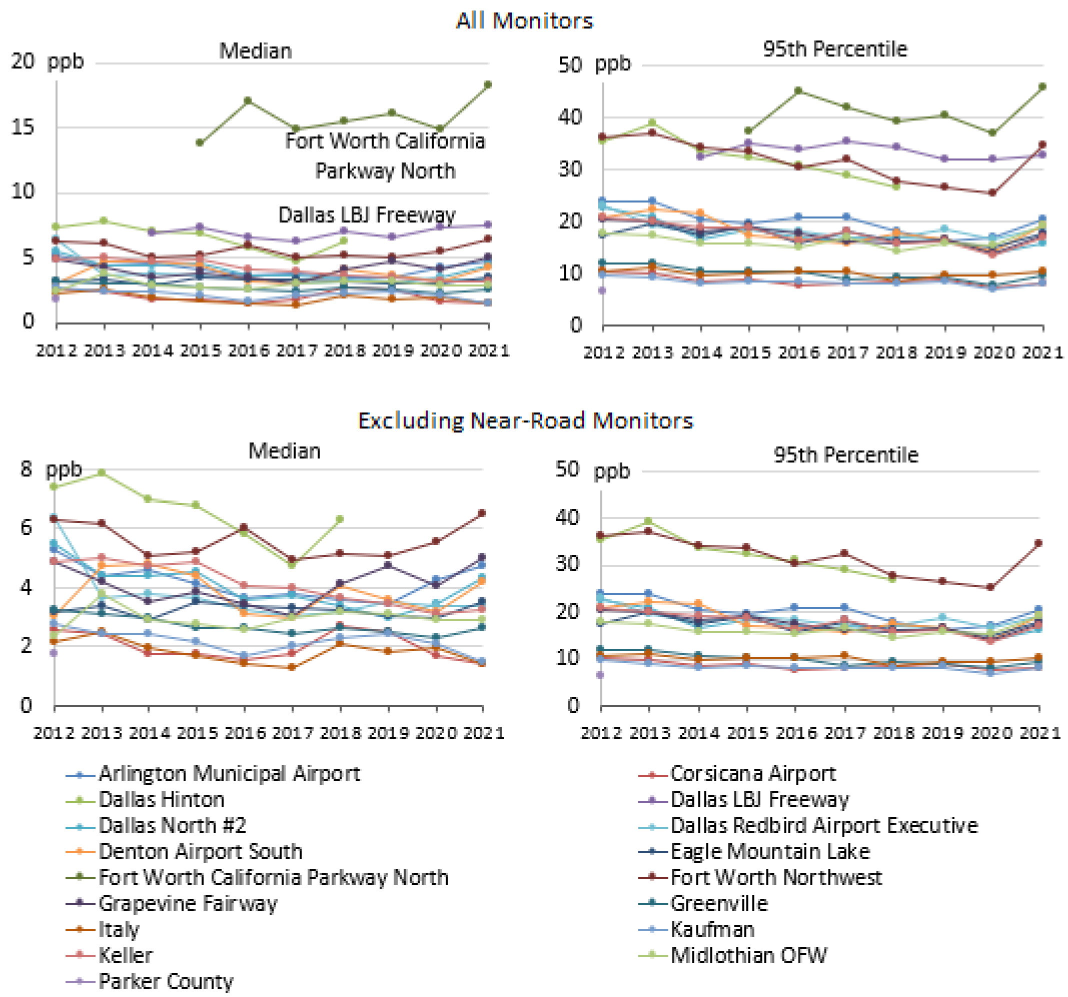


Figure 3-4: Ozone Season NO_x Trends by Monitor in the DFW Area

NO_x changes are more apparent when displayed on a map. To show 2021 NO_x concentrations along with how they have changed since 2012, a bivariate color scale was employed. Figure 3-5: *Median and 95th Percentile 2021 NO_x Concentrations and Change from 2012 in the DFW Area* shows that the highest NO_x concentrations are trending down over the decade over the entire DFW area and reductions are not isolated to a few locations. Medians are presented in the left panel and 95th percentiles are presented in the right panel. In the map color scale, monitors plotted in red are those that are above either the median (top) or 95th percentile (bottom) and also increased from 2012 to 2021, pink are above and decreasing, dark blue are below either the median or 95th percentile but decreased from 2012 to 2021, and light blue are below and decreasing. Both near-road monitors are excluded from this analysis because they were not installed until after 2012.

In the left panel of the figure, nine of seventeen monitors recorded decreases in median NO_x concentrations over the decade, while four recorded increases. Four other monitors lacked data for this analysis. Two monitors plotted in red, Denton Airport South and Grapevine Fairway, had medians that were above the average median in 2021 and higher than 2012. Two other monitors, Eagle Mountain Lake and Midlothian

OFW had increases but were below the average of the medians in 2021. Three of these four monitors are in the north or northwest of the DFW area, while one is in the south. Of the nine monitors with decreases, three shown in pink had medians that were above the average of the medians in 2021: Arlington Municipal Airport, Dallas North #2, and Fort Worth Northwest. The remaining six monitors in light blue recorded decreases and were also below the average of the medians in 2021. All of these nine monitors were either in the central portion of the metropolitan area, to the south, or to the east.

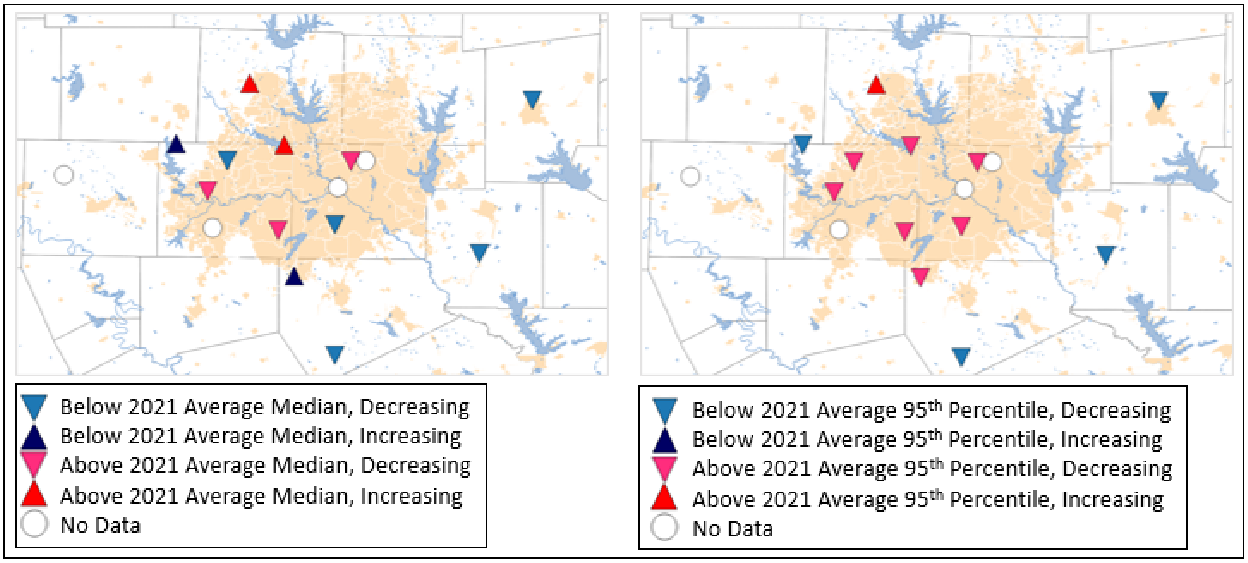


Figure 3-5: Median and 95th Percentile 2021 NO_x Concentrations and Change from 2012 in the DFW Area

In the right panel, only one monitor in red, Denton Airport South, recorded both an increase in the 95th percentile NO_x concentration and a 95th percentile NO_x concentration above the series average of 11.8 ppb in 2021. Seven other monitors plotted in pink recorded 95th percentile NO_x concentrations above the series average in 2021 but decreased over the decade. The other five monitors in light blue recorded decreases and were below the series average in 2021. There were no monitors that recorded an increase over the decade and a 2021 95th percentile NO_x concentration below the series average. In the case of 95th percentile NO_x concentrations, four monitors on the periphery of the area, Corsicana Airport, Greenville, Italy, and Kaufman, had remarkably low 2021 values (5.3 ppb, 7.2 ppb, 6.5 ppb, and 5.6 ppb, respectively), which made the 2021 average low, resulting in ten monitors exceeding the average, although by only small amounts.

3.2 AMBIENT VOC COMPOSITION AND TRENDS

VOC participate in ozone formation chemistry in combination with NO_x and sunlight. VOC are emitted or evaporated from numerous sources including large industrial process, automobiles, solvents and paints, dry-cleaning chemicals, certain fossil fuels, and even natural sources such as trees.

3.2.1 Ambient VOC Trends

Two types of instruments record VOC concentrations in the DFW area. Automated gas chromatographs, referred to as auto-GCs, record hourly concentrations. Canister samplers record 24-hour totals. The DFW area currently has 15 sites with auto-GC instruments, shown in Figure 3-7: *Map of Auto-GC Monitors in the DFW Area*. Due to the reactive nature of some VOCs, hourly auto-GC measurements are preferred when assessing trends.

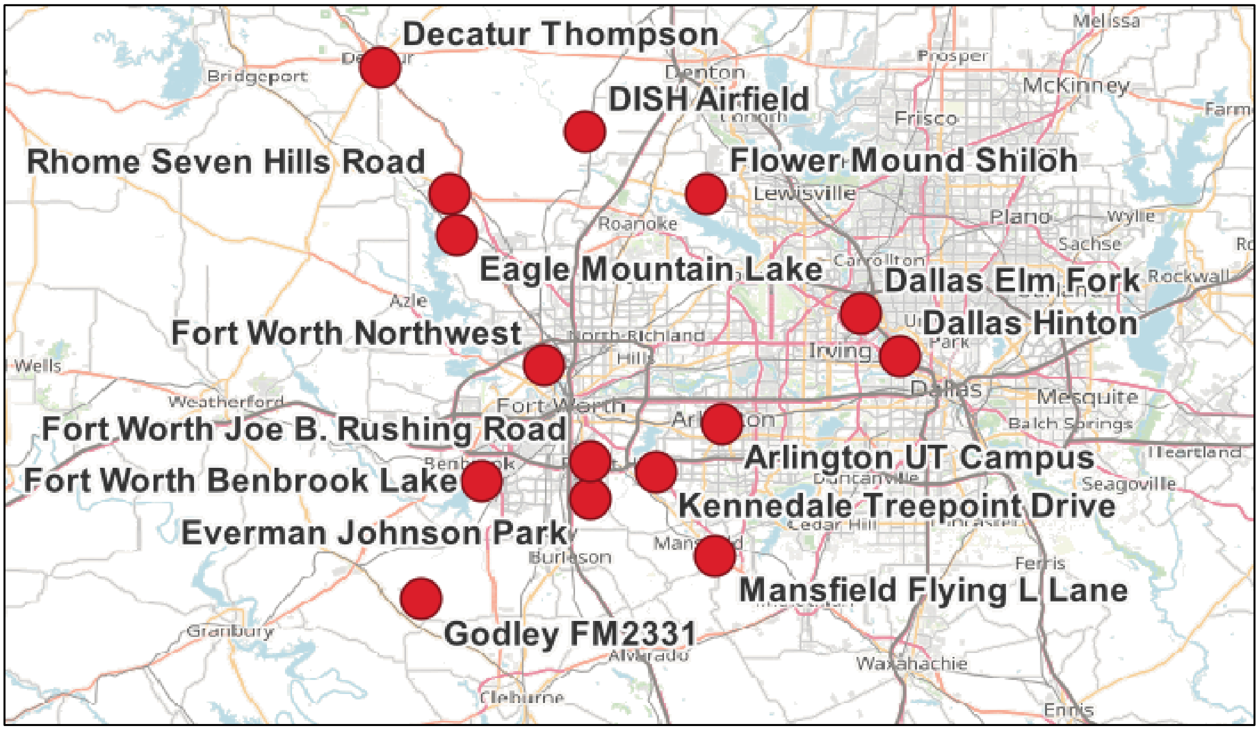


Figure 3-6: Map of Auto-GC Monitors in the DFW Area

Auto-GCs measure both total non-methane organic carbon (TNMOC), which can be used as a surrogate for total VOC, and speciated concentrations for roughly 50 VOC species, which include highly reactive VOC (HRVOC). While methane is an organic compound, TNMOC is commonly used to distinguish more reactive species of organic compounds from methane, which is naturally more abundant in the atmosphere, less reactive in the ozone formation process, and thus less relevant as a measure of precursor patterns. Trends in TNMOC concentrations provide insight into variation in overall VOC levels. Only about ten species are detected in sufficient concentrations in the DFW area to affect ozone formation. Only two of these species, ethylene and propylene, are HRVOC. The other less-reactive species found in elevated concentrations in the DFW area are isoprene, ethane, isopentane, propane, n-butane, m/p xylene, toluene, and isobutane. The following analysis will first describe trends in TNMOC, followed by trends in these other VOC species.

To focus on VOC concentrations that affect ozone formation, this analysis uses only ozone season data. To remove effects of incomplete data on VOC trends, data was first checked for validity. Only monitors that had eight or more valid years of data for the ozone season from 2012 through 2021 were used in this analysis. A year was considered valid if there were at least 75% valid days of data during the ozone season and a day was considered valid if there were at least 75% valid hours of data recorded for that day. All valid hours and years of data were used to calculate yearly median and 95th percentile TNMOC trends.

Figure 3-8: *Ozone Season Median and 95th Percentile TNMOC Trends in the DFW Area* shows TNMOC in parts per billion carbon (ppbC) rather than the standard parts per billion by volume used with other compounds, which is more commonly referred to as ppb. Overall, both median and 95th percentile TNMOC appear to be decreasing from 2012 through 2021, by 16.7% and 27.2% respectively, despite an anomalous drop in both measures in 2016 and 2017.

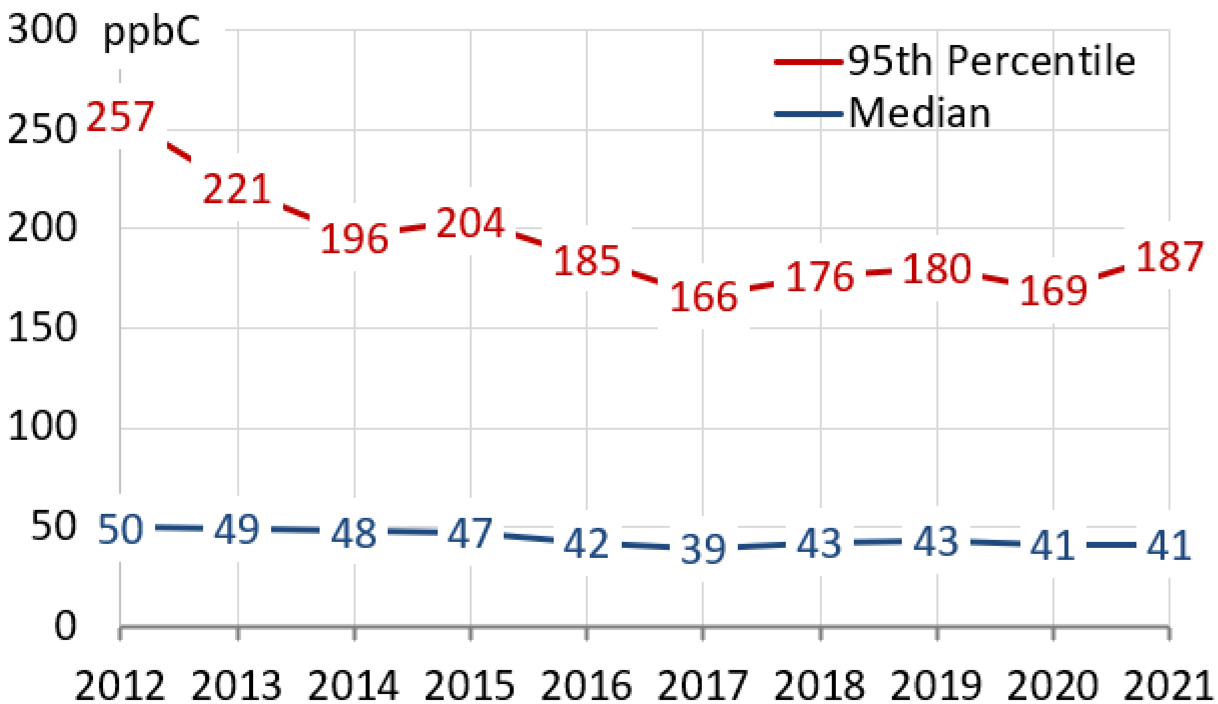


Figure 3-7: Ozone Season Median and 95th Percentile TNMOC Trends in the DFW Area

Median and 95th percentile TNMOC concentrations for the DFW area are shown in Figure 3-9: Monthly TNMOC Trends in the DFW Area. Ambient TNMOC concentrations follow a seasonal pattern, typically lower in summer and higher in winter for both medians and 95th percentiles. Only one month, July, exhibited an increase over the decade for one of the statistics, the median, and this increase was only 2% in 2021. The 2021 median was 16% below the highest median of the decade.

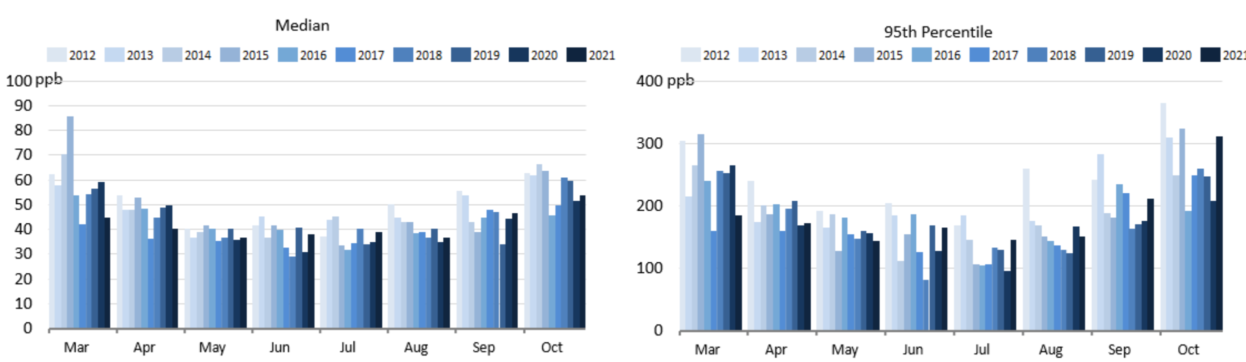


Figure 3-8: Monthly TNMOC Trends in the DFW Area

Individual VOC species concentrations were also investigated, as well as speciated concentrations weighted by maximum incremental reactivity (MIR). MIR indicates ozone formation potential of a given VOC species (Carter, 2010) and is generally defined as the maximum change in mass of ozone formed by adding a compound to an existing mixture of reactive gases, when conditions are most conducive. Because concentrations of VOC species are skewed right, that is, there are a few high values that are much higher than the rest, the mean is not a robust measure of the location of the center of the distribution. A better measure which is employed here is the geometric mean, the square root of the sum of squared values. Geometric mean VOC concentrations in rank order are shown in Figure 3-10: *VOC Species Ranked by Geometric Mean Concentration (left) and MIR Weighted Concentration (right) in the DFW Area*. All monitors and all years were included.

The VOC species with the largest geometric mean concentrations over the decade were ethane (16.11 ppb) and propane (5.53 ppb), two light alkanes with low ozone formation potentials. Both compounds are associated with oil and gas extraction. These are followed by other light alkanes with low ozone formation potentials. When VOC species are weighted by MIR, the most influential species is isoprene, a biogenic compound emitted by vegetation such as trees. Ethane remains the second highest contributing VOC species, even with its low reactivity, while ethylene, also called ethene, ranks third. Ethylene is associated with motor vehicle exhaust and is classified as an HRVOC. Other VOC contributors when weighted by MIR include toluene, propane, n-butane, and propylene. Propylene, also called propene, is another HRVOC associated with motor vehicle exhaust. Propane and n-butane have lower ozone formation potential and are associated with oil and gas extraction. Toluene is associated with numerous hydrocarbon combustion activities and has a high MIR.

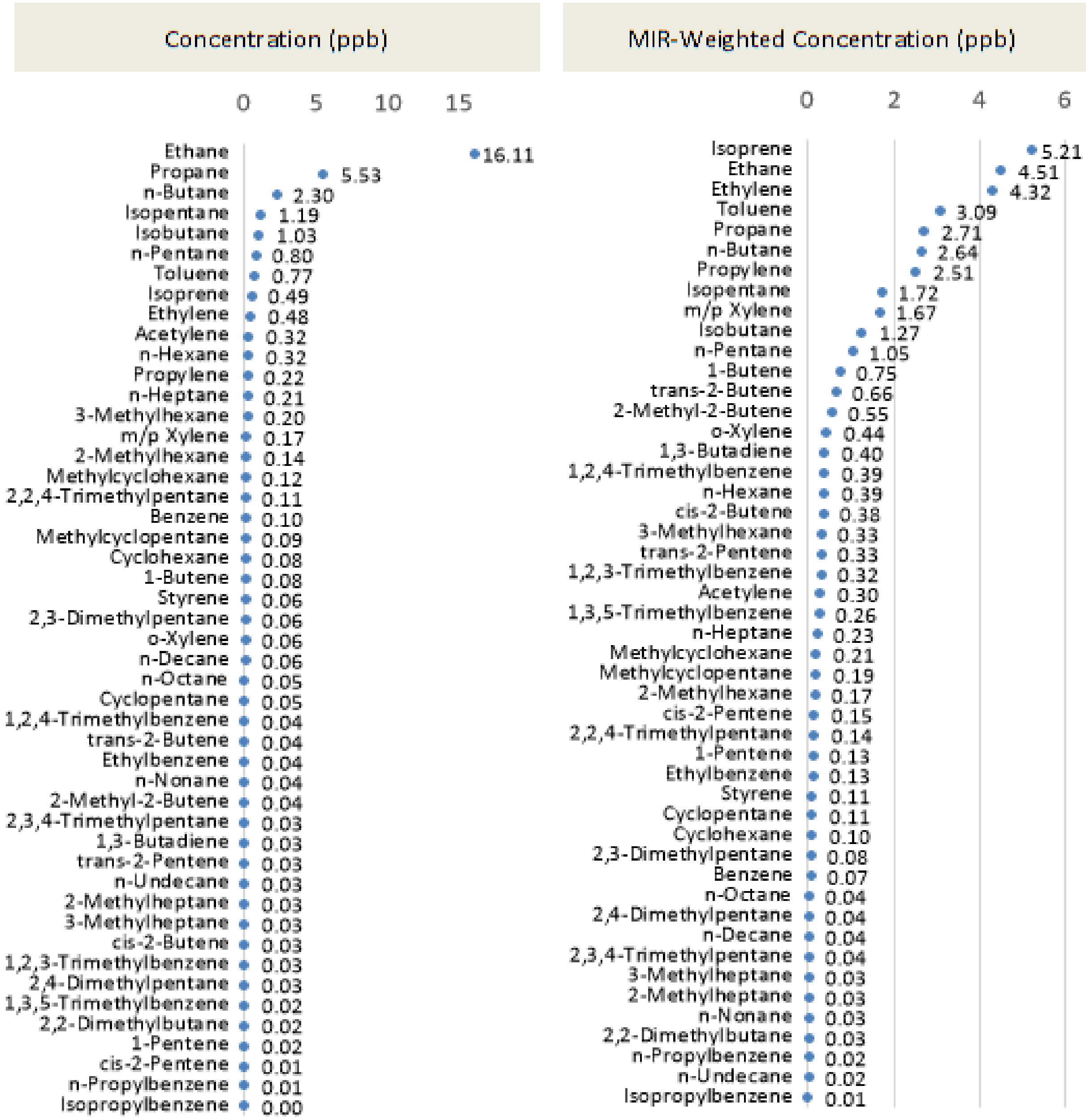


Figure 3-9: VOC Species Ranked by Geometric Mean Concentration (left) and MIR Weighted Concentration (right) in the DFW Area

A time series plot of the seven greatest MIR weighted contributors to ozone is presented in Figure 3-11: *Trends in Top Seven MIR-Weighted VOC Species in the DFW Area*. In general, ambient geometric mean concentrations of all these species have declined from 2012 through 2021 although the declines in most cases were small and there is variability in all species. Declines ranged from 3% for toluene to 31% for n-butane.

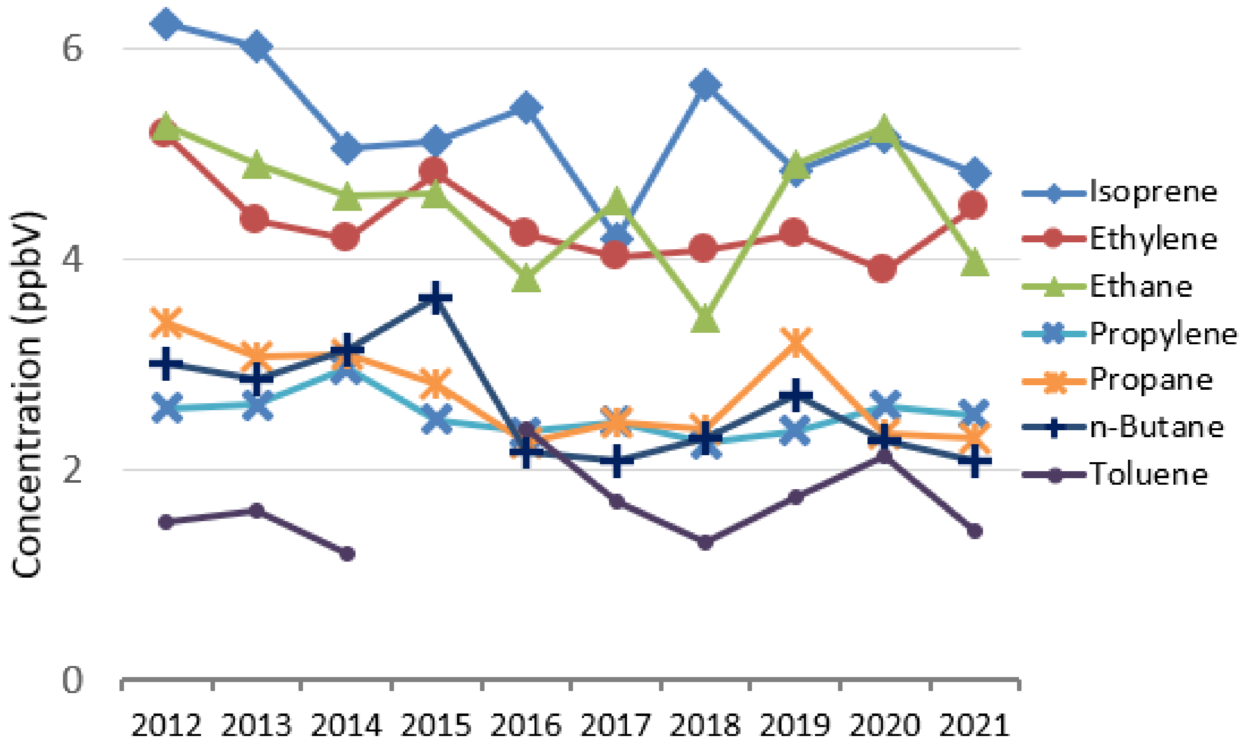


Figure 3-10: Trends in Top Seven MIR Weighted VOC Species in the DFW Area

3.2.2 Principal Components Analysis of Ambient VOC Trends

A more detailed understanding of ambient VOC in the DFW area is provided through the application of principal component analysis (PCA). PCA is a statistical technique that can identify underlying patterns in complex datasets by grouping variables that are correlated with each other. Grouping reduces dimensionality by eliminating noise and redundancy, representing the variance of the original dataset in the fewest possible number of non-correlated components. PCA can be used to reduce the number of original variables, in this case VOC species, into a smaller number of new variables, called principal components, which explain most of the variance in the original dataset. These principal components can be used to identify source types for the area. For example, a study of the Colorado Front Range area in 2015 (Abeleira 2017) found six principal components in ambient VOC measurements that could be traced to emissions sources including: short- and long-lived alkane species from oil and natural gas extraction, toluene and other olefins from motor vehicle traffic, background, secondary chemical production, and biogenic isoprene.

The first step in PCA is to identify the number of potential principal components by calculating and comparing eigenvalues for all possible principal components. Eigenvalues are the variances of the principal components. The larger the eigenvalue, the greater the influence of that factor on the variance of the original dataset. A scree plot presented in Figure 3-12: *Scree Plot of Principle Components of Ambient VOC Concentrations in the DFW Area* plots these eigenvalues ranked from highest, principal component number one, to lowest, principal component number 50. The slight discontinuity between the fourth and fifth principal components suggests that there are four primary principal components in this set of ambient VOC concentrations. The remainder of the computed eigenvalues are low enough that they provide no additional information compared to the original variables.

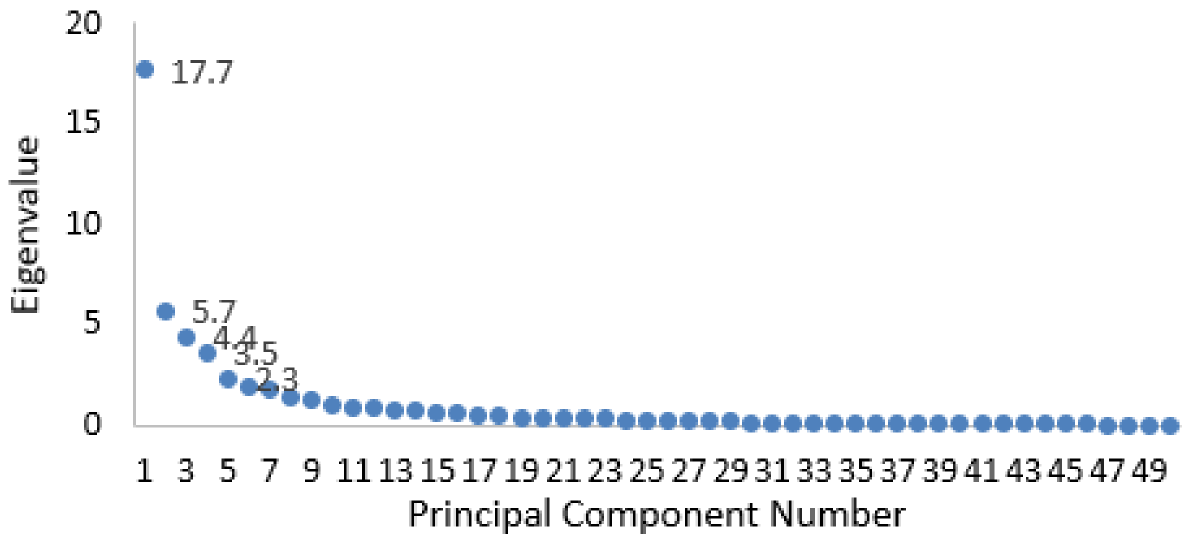


Figure 3-11: Scree Plot of Principal Components of Ambient VOC Concentrations in the DFW Area

Factor loadings, or contributions, of each original species to each principal component can be used to identify which species are acting in concert, revealing the likely emissions source type. It is important to remember that these relationships are very complex, such that the resulting associations are preliminary, not definitive, and are suggestive of further investigation. The first principal component is dominated by biogenic isoprene, typically emitted by trees and other vegetation. The second principal component is dominated by propane, ethane, and other lower reactivity light alkanes, signatures of oil and gas extraction. Abeleira (2017) further classifies these as long-lived species, to distinguish from short-lived species also emitted during oil and gas extraction. Many other species contribute to this principal component, but in smaller amounts. The third principal component is dominated by heavier alkanes, such as 2-methyl hexane, 3-methyl hexane, and n-heptane, which are also associated with oil and gas extraction, and which Abeleira classifies as short-lived species. This principal component also includes many other contributing species. The fourth principal component is dominated by toluene, 2,3-dimethyl pentane, 2-methyl hexane, and 3-methyl hexane, among others. These species are associated with both oil and gas extraction and motor vehicle exhaust. Studies have found that VOC from oil and gas extraction are typically smaller, photochemically-produced oxygenates and crude oil compounds of aromatics, cyclic alkanes, and alkanes (Koss 2017).

Table 3-1: Variable Loadings of the Top 15 Components of the Four Principal Components

rotation.PC1		rotation.PC2		rotation.PC3		rotation.PC4	
Isoprene	0.008	Propane	0.175	Toluene	0.261	2,3-Dimethylpentane	0.335
Methylcyclopentane	-0.21	Cyclohexane	0.169	3-Methylhexane	0.248	**3-Methylhexane**	0.319
Total NMOC	-0.21	n-Hexane	0.166	n-Heptane	0.244	**Toluene**	0.317
n-Pentane	-0.2	n-Pentane	0.154	2-Methylhexane	0.242	**2-Methylhexane**	0.294

rotation.PC1		rotation.PC2		rotation.PC3		rotation.PC4	
Sum of PAMS Target Comps	-0.2	Isobutane	0.138	2,3-Dimethylpentane	0.212	n-Heptane	0.227
Isopentane	-0.2	Methylcyclohexane	0.138	n-Decane	0.148	trans-2-Pentene	0.198
3-Methylheptane	-0.2	n-Heptane	0.133	1,3,5-Trimethylbenzene	0.143	2-Methyl-2-Butene	0.190
Cyclohexane	-0.19	Sum of PAMS Target Comps	0.128	m/p Xylene	0.14	cis-2-Pentene	0.187
n-Hexane	-0.19	**Ethane**	0.125	n-Undecane	0.136	2,4-Dimethylpentane	0.185
2-Methylheptane	-0.19	Total NMOC	0.118	n-Nonane	0.135	1-Pentene	0.167
Cyclopentane	-0.19	n-Butane	0.112	Methylcyclohexane	0.133	2,2,4-Trimethylpentane	0.135
n-Butane	-0.18	2-Methylheptane	0.106	o-Xylene	0.132	**cis-2-Butene**	**0.117**
n-Octane	-0.18	Methylcyclopentane	0.098	**Ethylbenzene**	0.126	**trans-2-Butene**	**0.109**
2,4-Dimethylpentane	-0.18	2-Methylhexane	0.092	2-Methylheptane	0.12	2,3,4-Trimethylpentane	0.102
Isobutane	-0.18	Cyclopentane	0.088	Isopropylbenzene	0.114	1-Butene	0.081

Table 3-1: *Variable Loadings of the Top 15 Components of the Four Principal Components* reports the variable loadings of the top fifteen VOC compounds in each of the four principal components identified. In very simplified terms, these are the distances (eigenvalues) along the four major axes (eigenvectors) of the original covariance matrix after transformation. Eigenvalues explain the variance of the original data along the new axes in the transformed feature space.

3.3 OZONE PRECURSOR EMISSIONS

In addition to trends in ambient concentrations of ozone and ozone precursors, trends in ozone precursor emissions inventories were also investigated. The categories of on-road, non-road, EGUs, and point sources have historically been primary sources of anthropogenic NO_x and VOC emissions in ozone nonattainment areas.

3.3.1 On-Road and Non-Road Emissions Trends

From the late 1990s to the present, federal, state, and local measures have resulted in significant NO_x and VOC reductions from on-road and non-road sources within the DFW area. The Texas Commission on Environmental Quality (TCEQ) funded a study by the Texas Transportation Institute (TTI) to estimate on-road emissions trends throughout Texas from 1999 through 2050 using the 2014a version of the Motor Vehicle Emission Simulator (MOVES2014a) model (TTI 2015). On-road emissions in the DFW area are estimated to have large decreases from 1999 through 2021 and beyond, even as daily VMT is estimated to increase. This reduction in on-road NO_x and VOC is 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 using the Texas NONROAD (TexN) model. Non-road emissions are estimated to decrease from 1999 through 2021 and beyond even as the number of non-road engines, based on equipment population, has increased. As with the on-road fleet turnover effect, reductions in non-road NO_x and VOC emissions are projected to continue as older, higher-emitting equipment is removed from the fleet and replaced with newer, lower-emitting equipment.

3.3.2 NO_x Emissions Trends

Figure 3-13: *Map of Stationary NO_x Emissions Sources in the DFW Area* shows that NO_x emissions sources are scattered throughout the metropolitan area, with the largest NO_x emitters located south and southeast. On high ozone days, typically winds travel from the southeast, where the largest NO_x sources are located, and carry these emissions over the city centers where they mix with other urban emissions and form ozone. Over the course of the morning and early afternoon, this ozone is then conveyed to the north and northwest, where it is measured by surface monitors in mid-afternoon.

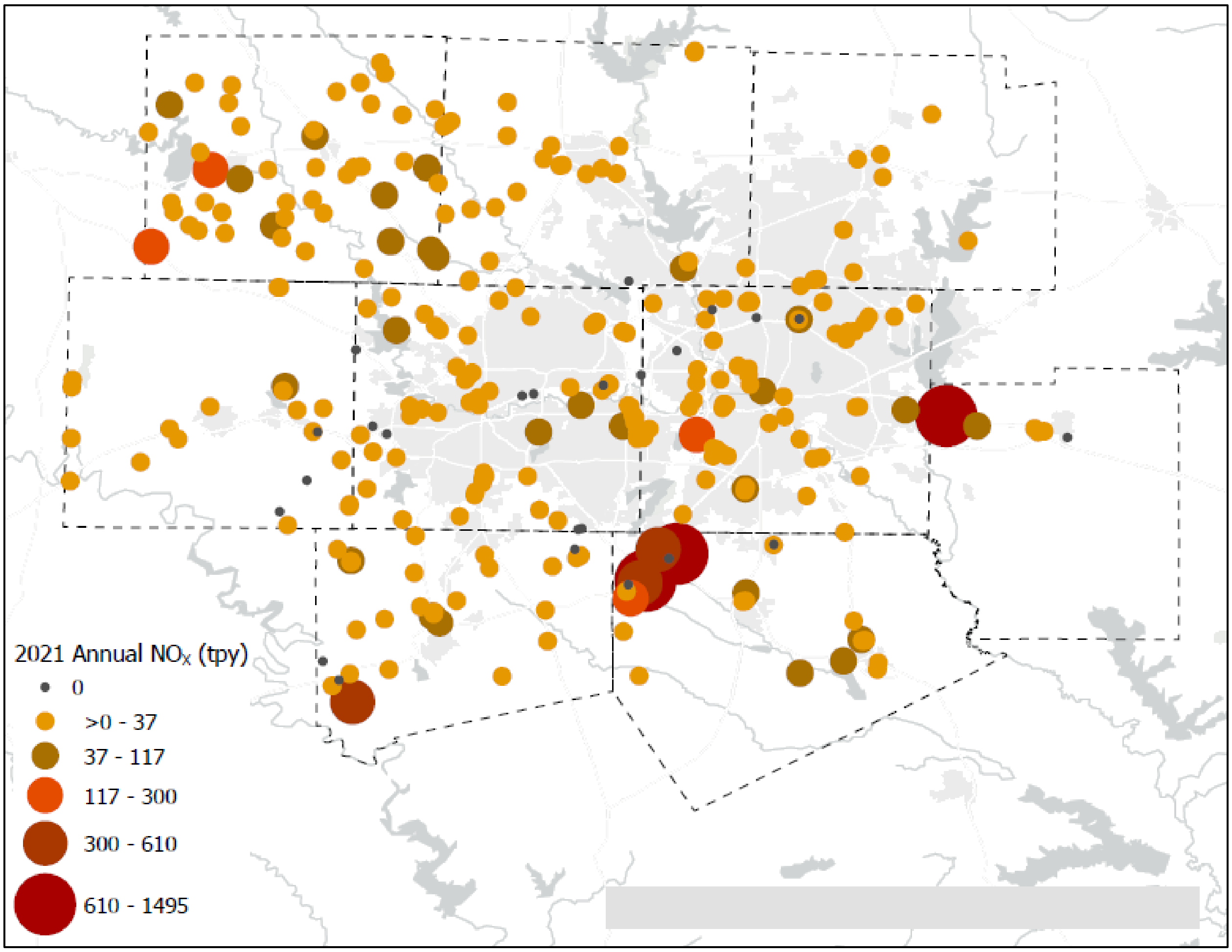


Figure 3-12: Map of Stationary NO_x Emissions Sources in the DFW Area

Point source NO_x emission trends from the State of Texas Air Reporting System (STARS) were also investigated. These emissions are from sources that meet the reporting requirements under the TCEQ emissions inventory rule (30 TAC §101.10). Emissions from 2021 were not available in time to be included in this analysis. The emissions trends analysis uses ten years of data from 2011 through 2020.

Emissions trends by site are displayed in Figure 3-14: *Point Source NO_x Emissions by Site in the DFW Area*. Because the DFW area has so many point sources, only the top emitters are displayed on each chart. All other point source emissions in the DFW area were added together and displayed as the Sum of All Others. Point source NO_x

emission trends show that the top nine reporting sites accounted for 60% of the total point source NO_x emissions in the DFW area in 2021. Each of these sites report total NO_x emissions exceeding 200 tons in 2020. The overall trend in NO_x emissions is a decline of 26% since 2012.

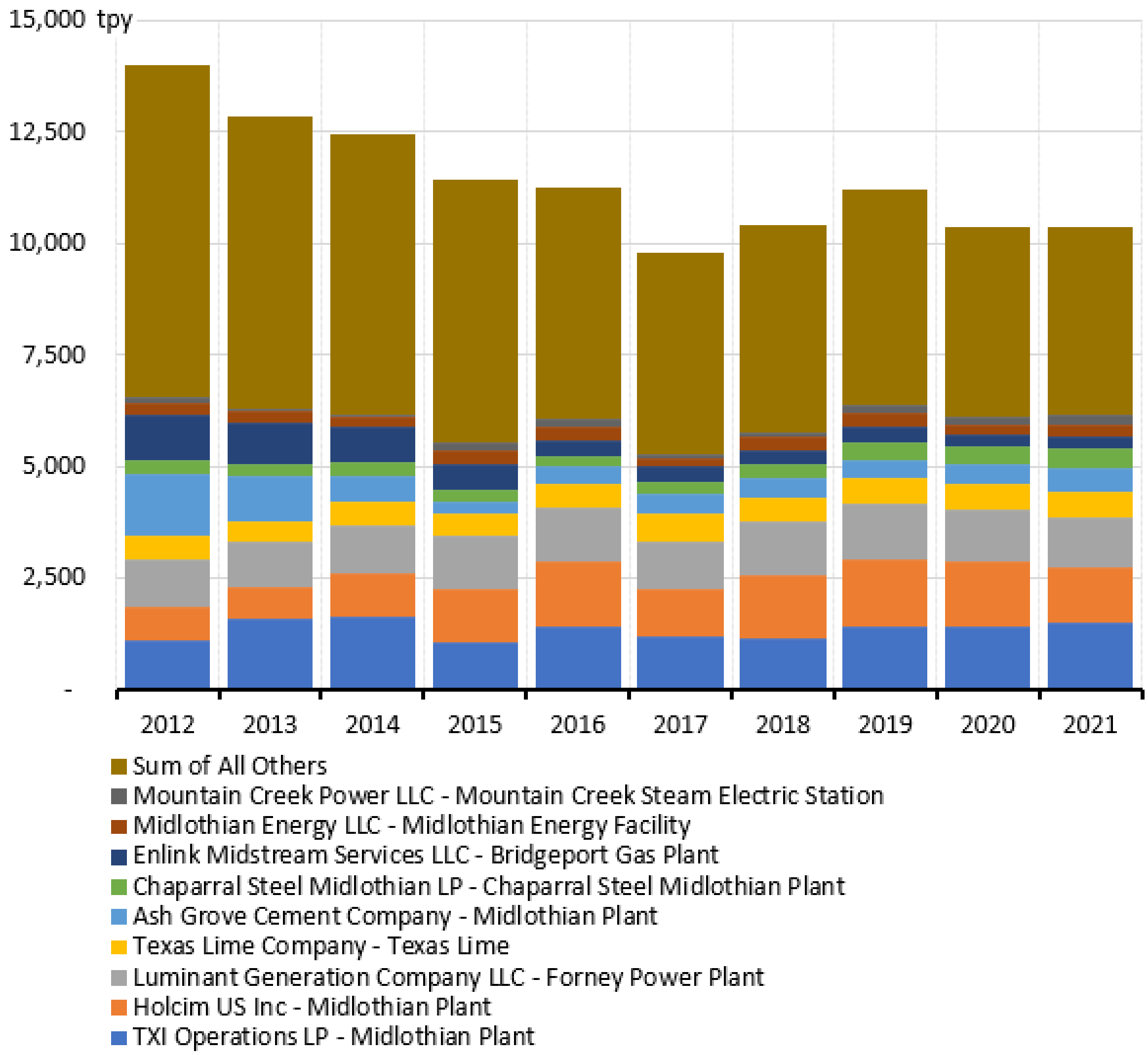


Figure 3-13: Point Source NO_x Emissions by Site in the DFW Area

3.3.3 VOC Emissions Trends

From the late 1990s to the present, federal, state, and local measures have resulted in VOC reductions from on-road and non-road sources within the DFW area. The TCEQ studies mentioned in Section 3.3.1 showed decreases in on-road and non-road VOC from 1999 through the present. These reductions are projected to continue as older, higher-emitting vehicles and equipment are removed from the fleet and replaced with newer, lower-emitting ones.

Locations of larger anthropogenic VOC emissions sources are shown in Figure 3-15: *Map of Large Anthropogenic VOC Emissions Sources in the DFW Area*. Most of these are clustered in the east-central portion of the DFW area, although there are several in the northeast, northwest, and southeast, some of which are oil and gas extraction facilities.

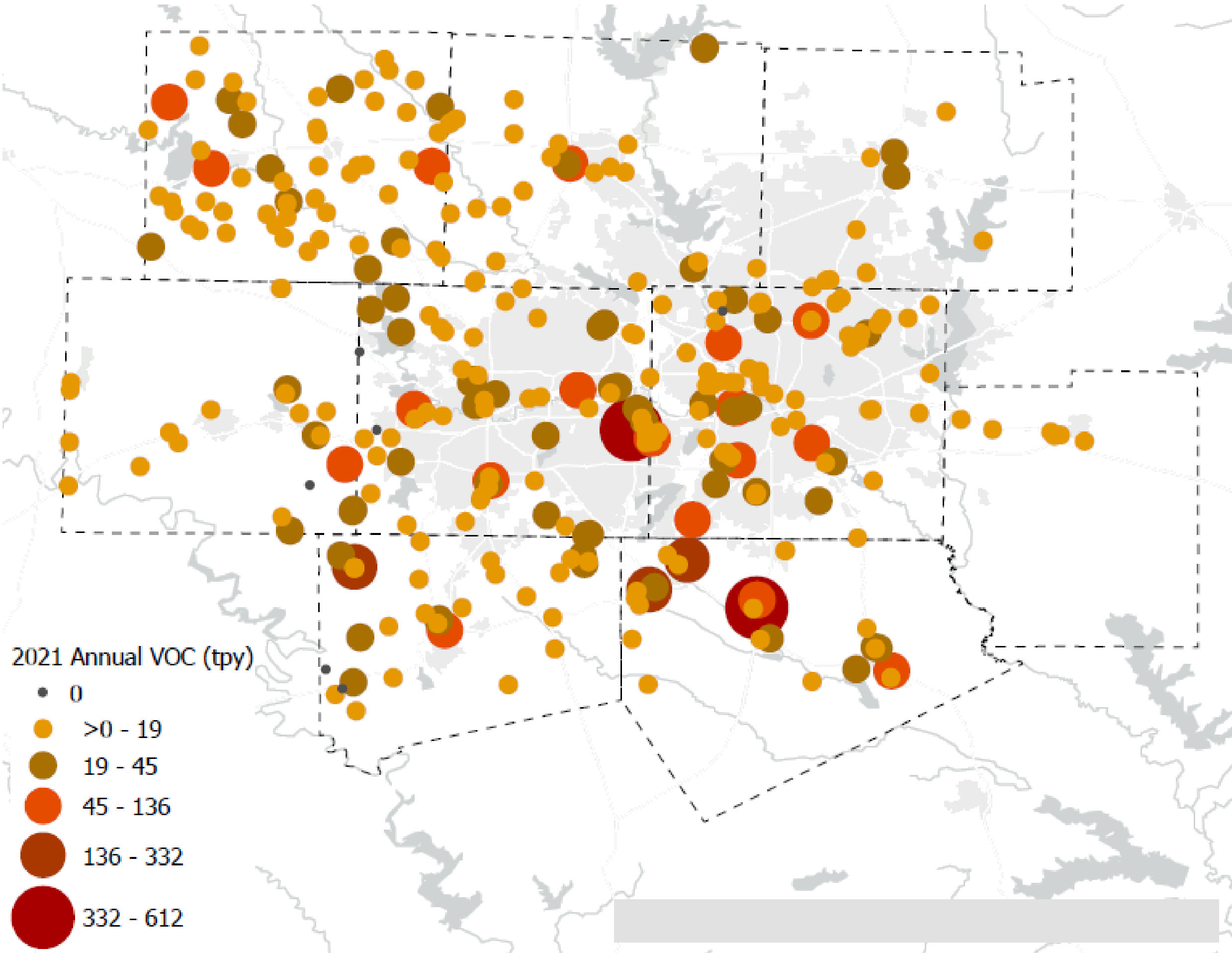


Figure 3-14: Map of Large Anthropogenic VOC Emissions Sources in the DFW Area

Point source VOC emission trends from STARS were also investigated. Figure 3-16: *Point Source VOC Emissions by Site in the DFW Area* shows that the top six reporting sites accounted for 27% of the total DFW area point source VOC emissions in 2021. Each of these sites reported total VOC emissions exceeding 250 tons in 2020, with the three largest emitters reporting 20% of the total. Overall, VOC emissions are decreasing, with a 32% decrease from 2012 through 2021, though the rate of decline slowed after 2016. This correlates with ambient VOC trends for the DFW area.

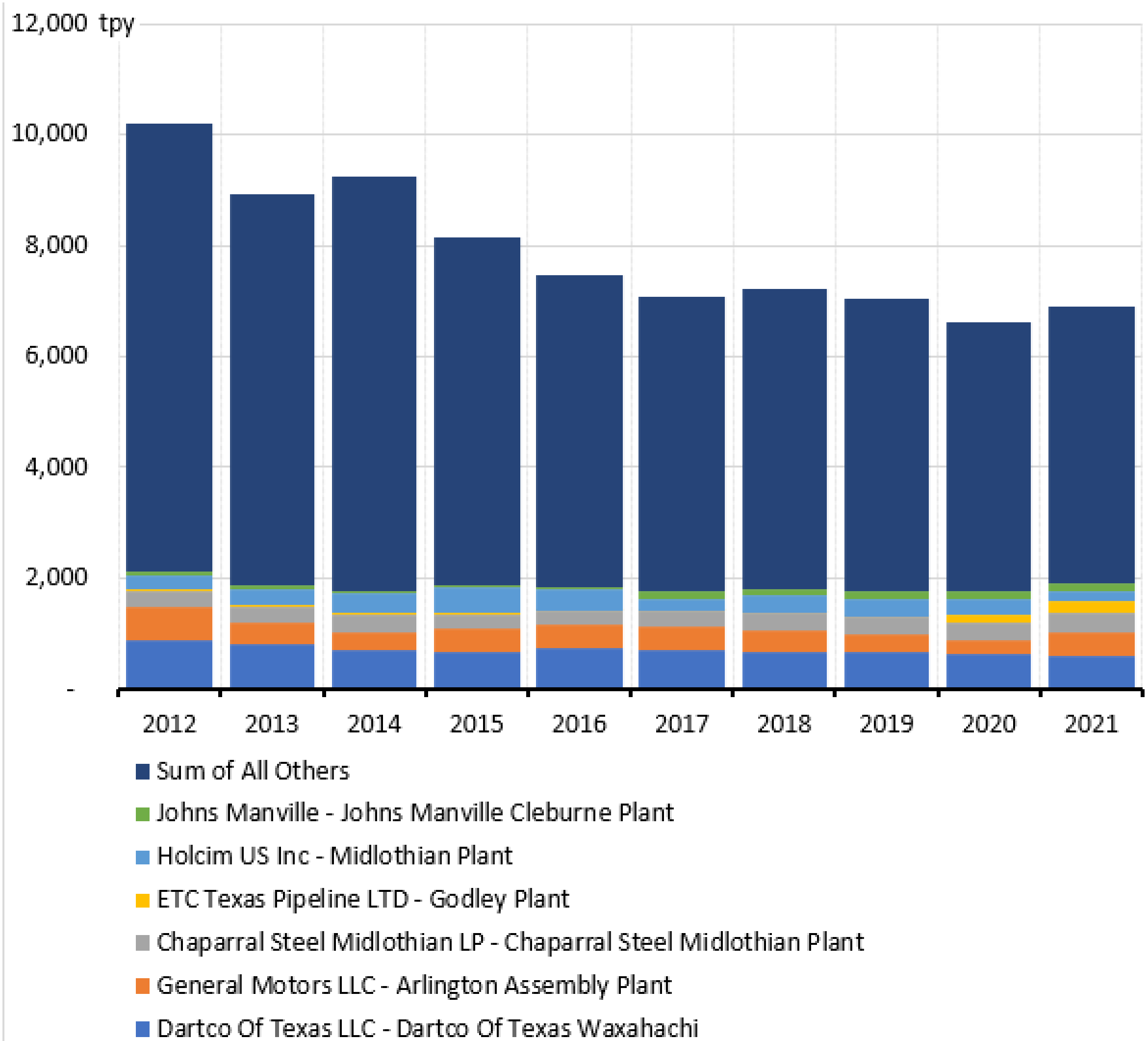


Figure 3-15: Point Source VOC Emissions by Site in the DFW Area

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 interactions between ozone and its precursors helps explain how precursors are contributing to ozone formation in the Dallas-Fort Worth (DFW) 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 DFW area.

4.1 VOC AND NO_X LIMITATION

Ozone is formed from precursors in proportions determined by their molecular properties, therefore, unless precursors are present in these exact proportions in an airshed, ozone formation will be governed by whichever precursor is scarcer or limited. If one is in excess in the atmosphere, that excess will be unused in reactions. In this situation, reducing that compound through emissions control strategies will be unlikely to affect the amount of ozone ultimately generated. The limiting factor in ozone production in that airshed would be the other compound that is not in surplus. An airshed with surplus VOC is termed NO_X-limited, while an airshed with surplus NO_X is termed VOC-limited.

The relative proportion of VOC and NO_X, in relation to each other in an airshed, the VOC-to-NO_X ratio, can be an important indicator of the likely efficacy of different control strategies because it suggests the chemical nature of the environment in which emissions reductions would be applied. The VOC or NO_X limitation of an air shed can suggest how immediate reductions in VOC and NO_X concentrations might affect the duration and magnitude of ozone formation. A NO_X-limited regime occurs when 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 might be expected to reduce ozone concentrations in these regions.

VOC-to-NO_X ratios are calculated by dividing hourly total non-methane hydrocarbons (TNMHC) concentrations in parts per billion-carbon (ppbC) by hourly NO_X concentrations in parts per billion-volume (ppbv). 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. Our understanding of VOC-to-NO_X ratios in an airshed is limited by the number of collocated VOC and NO_X monitors available in the area. In addition, VOC monitors are often source-oriented, and therefore they primarily provide information on the air mass located near the source and may not be generally reflective of the wider area.

The DFW area has twelve auto-GC instruments, three of which are collocated with NO_X monitors: Dallas Hinton, Eagle Mountain Lake, and Fort Worth Northwest. Data from March through October 2012 through 2021 were used in creating Figure 4-1: *Median Hourly VOC-to-NO_X Ratios at Three DFW Area Monitors by Hour of the Day*.

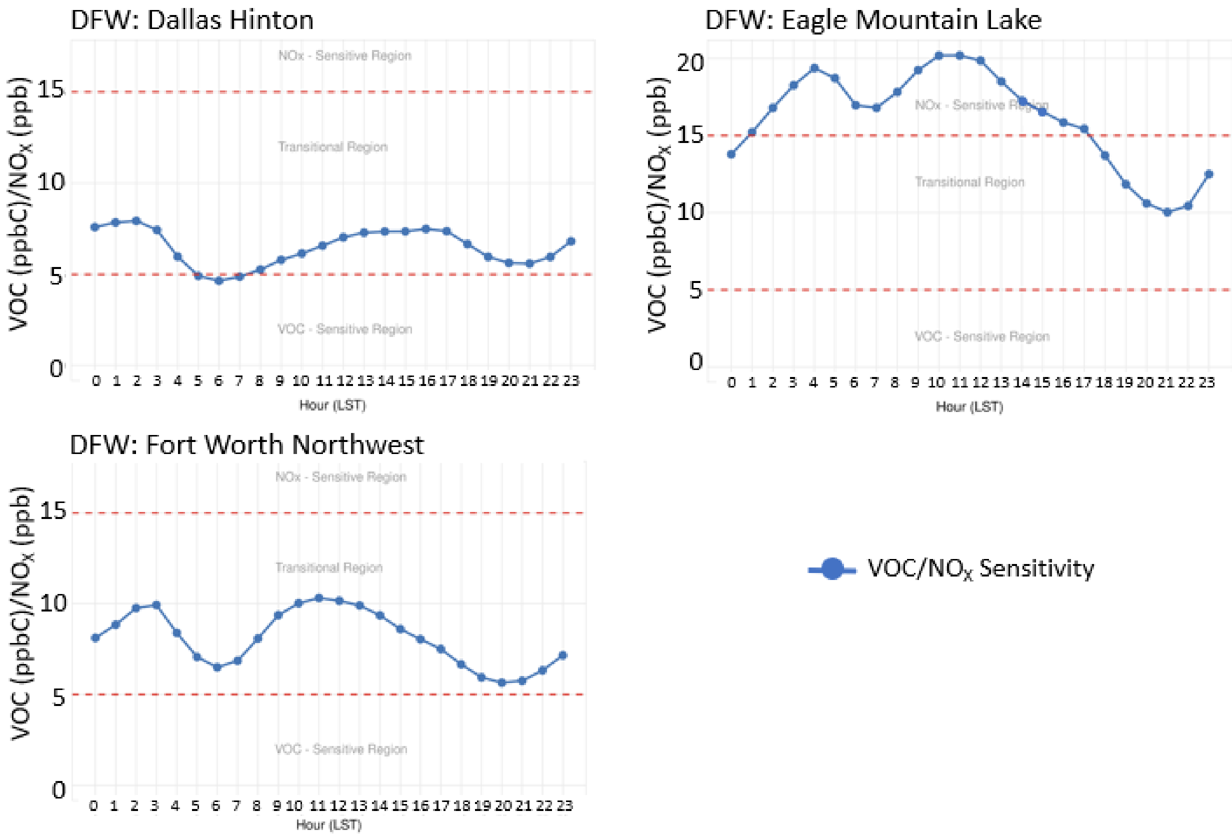


Figure 4-1: Median Hourly VOC-to-NO_x Ratios at Three DFW Area Monitors by Hour of the Day

Results show that the ratio fluctuates over the course of a day at all three sites, rising into a more NO_x limited regime overnight and into early morning, dropping to become more VOC limited during morning rush hour, when motor vehicles emit substantial quantities of NO_x. Mobile sources contribute roughly three-quarters of total anthropogenic NO_x emissions in DFW. Ratios rise in the afternoon, before dropping again in late evening.

While diurnal patterns are similar across sites, absolute values of the ratios differ substantially, suggesting there are distinct differences in the chemical characteristics of the atmosphere depending on where in the region a site is located. Ratios at Dallas Hinton, located in a heavily urbanized eastern portion of the metro area, are primarily at the lower end of the transitional range throughout the day, with a slight excursion into the VOC limited range from 5:00 a.m. to 7:00 a.m. This suggests an abundance of NO_x in the ambient air, likely related to enhanced emissions from motor vehicles during morning commute hours. Dallas Hinton Street is located near Interstate 35E, a large source of mobile source NO_x emissions. Limiting VOC emissions could contribute to less vigorous ozone production in this area.

Farther west, at Fort Worth Northwest, while ratios follow a similar diurnal pattern with only slightly higher values, they remain entirely within the transitional range, suggesting neither VOC nor NO_x is overly abundant. Control of either VOC or NO_x

could be effective in this region. Ratios at Eagle Mountain Lake, located in a more suburban portion of the metro area, are primarily in the NO_X limited range during the day, from 1:00 a.m. to 5:00 p.m., suggesting an abundance of VOC. Overnight, ratios decline into the transitional region, though never becoming VOC limited. This suggests an abundance of VOC in this area downwind of the more urbanized portions of the metro area and oil and gas exploration and production in the Barnett Shale play. These VOC could be travelling downwind from anthropogenic sources in the metro area, or from non-anthropogenic sources, such as isoprene from vegetation. Control of NO_X could be effective in this region.

This evolution from more VOC limited to more NO_X limited as a site is more westerly and northerly in the DFW area has important implications for ozone formation. Sites in the DFW area with the highest measured ozone concentrations, ones that determine the regulatory design value for the area, such as Pilot Point, Frisco, and Grapevine Fairway, tend to be to the north and west. It is likely that controlling NO_X would be more effective at influencing the DFW area design value than controlling VOC, although ozone formation may respond to VOC reductions in some parts of the metro area and at certain times of day.

Figure 4-2: *Frequency of VOC Limited, NO_X Limited, and Transitional Regimes During Ozone Season Mornings in the DFW Area* shows the crucial 5 a.m. to 8 a.m. period when motor vehicles begin emitting during morning commutes, residual precursors from the previous day are mostly unreacted, and the sun is beginning to provide the necessary solar radiation to form ozone. At Eagle Mountain Lake, the highest frequency of occurrence are NO_X-limited regimes, followed by transitional regimes. VOC-limited regimes are almost never observed at this location. Conversely, at Dallas Hinton, the chemical regime is almost entirely VOC-limited or transitional, as expected at a location near urban emissions activity. Although it appears this monitor was beginning to record more transitional regimes in recent years, this monitor discontinued NO_X monitoring in 2019, so the most recent years are not available. Fort Worth Northwest records mostly transitional chemical regimes, with higher frequencies of VOC-limited regimes in recent years. Since a VOC-limited regime occurs when NO_X is in surplus, this monitor could be recording changing emissions due to changing land use patterns, such as increased suburban development.

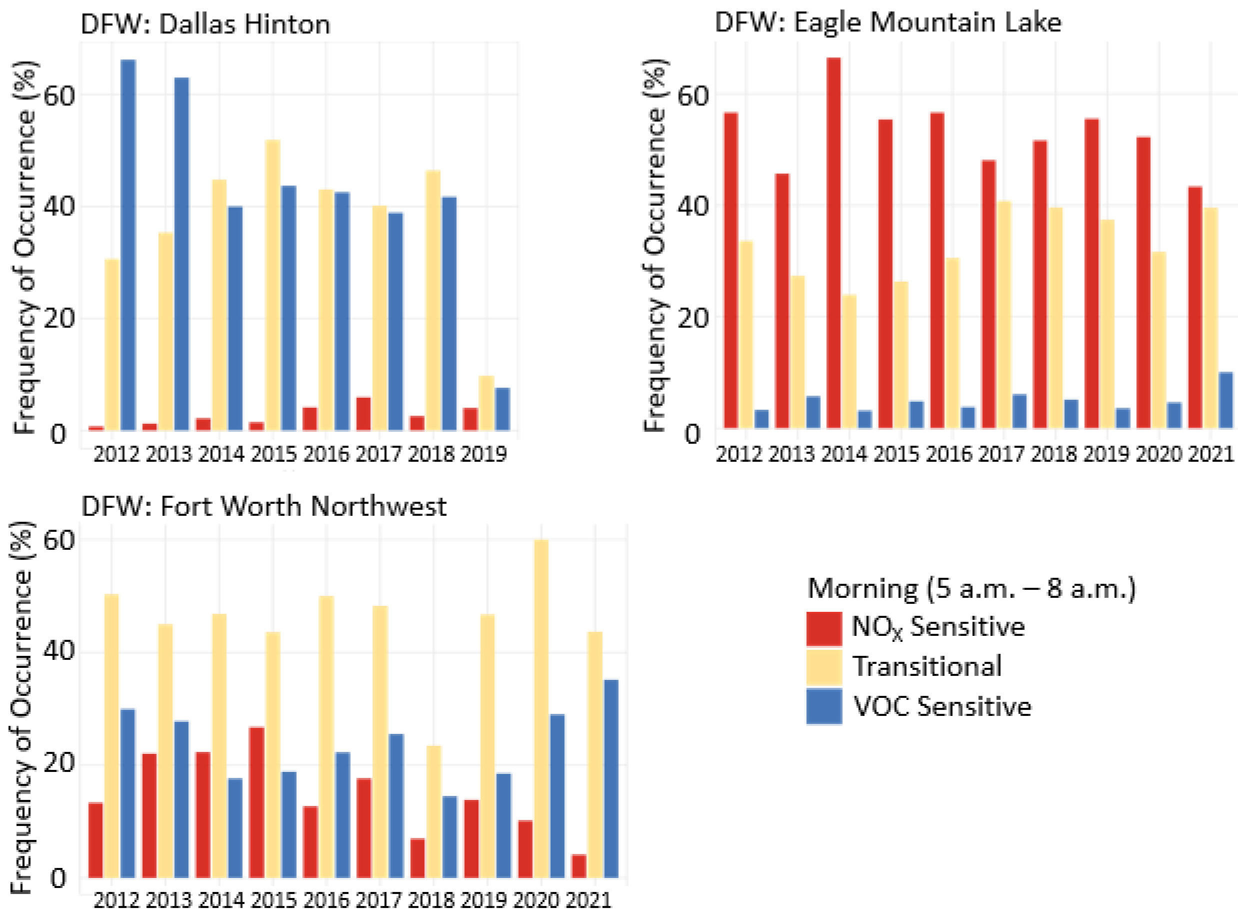


Figure 4-2: Frequency of VOC Limited, NO_X Limited, and Transitional Regimes During Ozone Season Mornings in the DFW Area

Figure 4-3: *Median VOC-to-NO_X Ratios at Three DFW Area Monitors* shows the evolving nature of the relationship between these two ozone precursors. At Dallas Hinton, the ratio began the decade near the VOC-sensitive region, rising further into the transitional region later in the decade. Eagle Mountain Lake began the decade in the NO_X-sensitive region, then declined to the edge with the transitional. Eagle Mountain Lake is in an area likely to have ample biogenic VOC. Fort Worth Northwest was more like Dallas Hinton, with annual fluctuations but consistent residence in the transitional range.

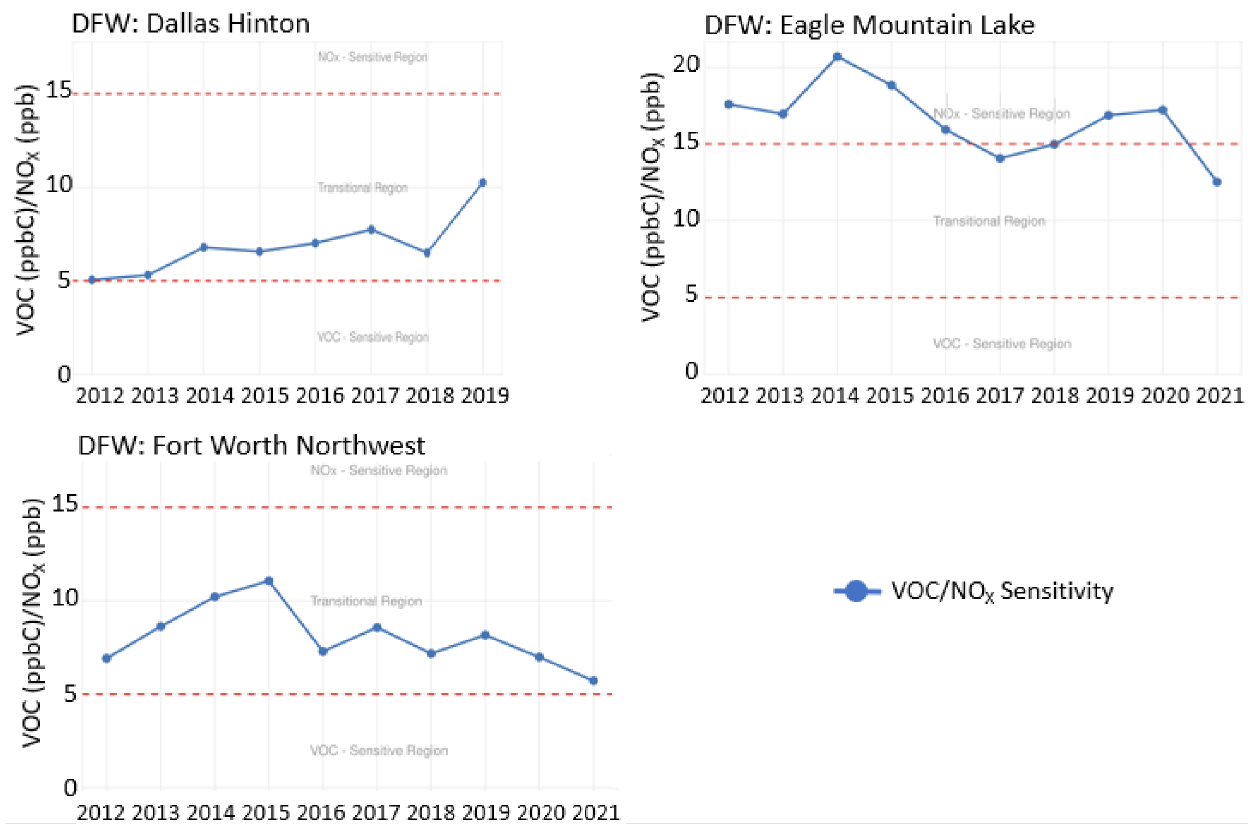


Figure 4-3: Median VOC-to-NO_X Ratios at Three DFW Area Monitors

4.2 WEEKDAY VERSUS WEEKEND ANALYSIS

Studies (Croes et al., 2003; Fujita et al., 2003a; Fujita et al., 2003b; Heuss et al., 2003) have shown that ozone concentrations can exhibit weekly patterns. These studies have found that some cities exhibit substantially greater ozone concentrations on weekends, while others do not. Identifying a weekend effect can be valuable for guiding ozone photochemical modeling and control strategy development. Because a weekend effect is hypothesized to result from emissions from specific types of emitters, for example, mobile rather than point sources, its presence, if confirmed, could be used to tailor policies to target specific sources. A weekend effect can provide inferences as to whether an area is VOC-limited or NO_X-limited, providing clues to the efficacy of candidate control strategies. A decrease in monitored ozone on weekends compared to weekday indicates NO_X-limitation, since weekend NO_X concentrations are generally lower compared to their weekday counterparts. Conversely, a weekend increase in ozone concentrations can indicate VOC-limitation. Finally, a weekend effect provides a natural laboratory for evaluating photochemical model response. If the model can reproduce observed weekend effects, then there is greater confidence in its ability to correctly predict the effects of future emissions changes.

VOC and NO_X limitations in the DFW area may impact temporal and spatial patterns of the frequency of ozone exceedance days. A study found that the average ozone concentration significantly increased on weekends compared to weekdays in the DFW area (Blanchard and Tanenbaum, 2006). This weekend increase is likely due to the VOC and NO_X limitations found in the DFW area. To determine the effects these limitations might have on the frequency of ozone events in the area, eight-hour ozone exceedance day counts and peak NO_x by day of the week were examined from 2012 through 2021. Only the ozone season months were used when looking at the peak NO_x data.

The number of days with an ozone exceedance was found for each day of the week at all available ozone monitors in the DFW area from 2012 through 2021. Figure 4-4: *Eight-Hour Ozone Exceedance Days by Day of the Week in the DFW Area* shows how these 324 days over the ten-year period are distributed by day of the week. The day with the most exceedances was Fridays, with 58 days, followed by Thursdays with 56. Sundays recorded the fewest exceedance days at 24 days. It appears that lower ozone occurs on the weekends, with the likelihood of experiencing an exceedance increasing over the week. This apparent weekly pattern could be a random artifact of the series, which will be explored statistically below.

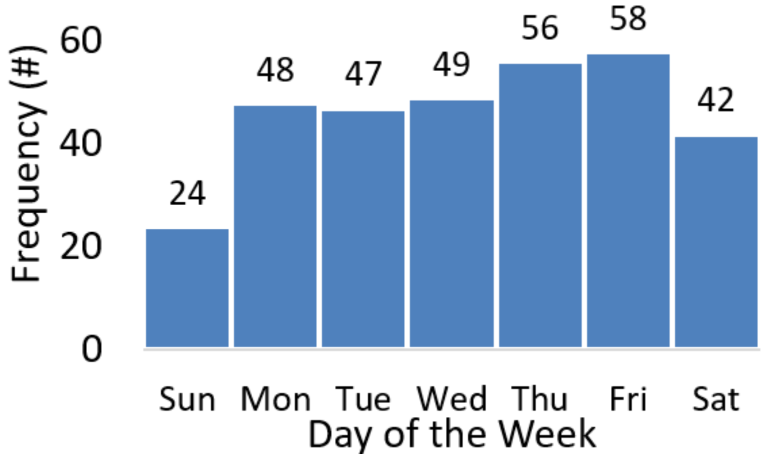


Figure 4-4: Eight-Hour Ozone Exceedance Days by Day of the Week in the DFW Area

As discussed earlier, the number of exceedance days in the DFW area has declined over the decade, dropping from a total of 60 days in 2012 to 30 in 2021. Figure 4-5: *Percentage of Ozone Exceedance Days by Day of the Week in the DFW Area for Two Periods, 2012 through 2016 and 2017 through 2021* compares exceedance days by day of the week for two five-year periods to examine whether the weekly pattern observed above remains roughly the same from the first half of the decade to the second. Percentages were used, instead of number of days, to simplify analysis since the number of days is substantially different over the period. Of the 1,225 ozone season days per five-year period, 192, or 16%, recorded exceedances from 2012 through 2016, while 132, or 11%, recorded exceedances from 2017 through 2021. This is a roughly 31% drop from the earlier period to the later. Weekly patterns for the two periods appear to be quite similar, with weekends recording the smallest percentage of exceedance days, 21% in both periods. No day is more than three percentage points different from one period to the other.

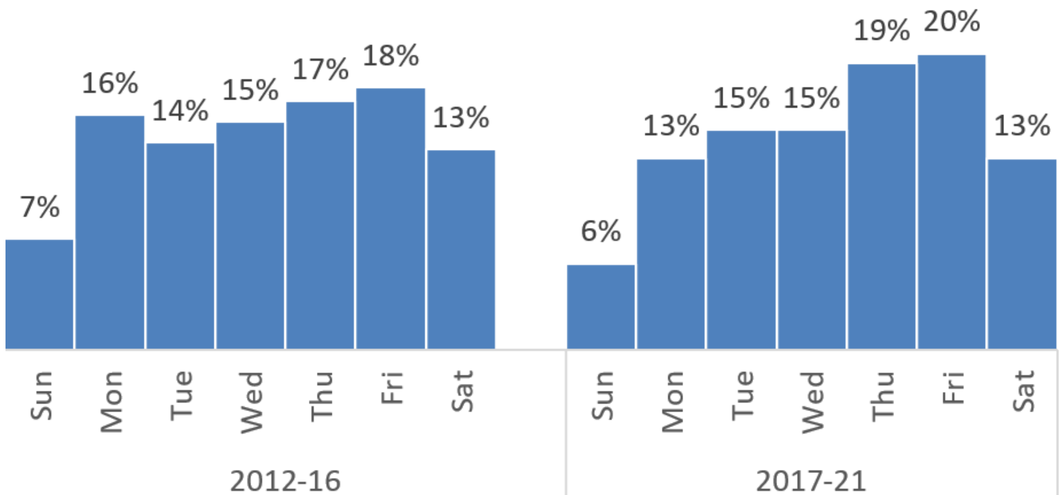


Figure 4-5: Percentage of Ozone Exceedance Days by Day of the Week in the DFW Area for Two Periods, 2012 through 2016 and 2017 through 2021

In the absence of a weekend effect, each day would be expected to have an equal likelihood of observing an eight-hour ozone exceedance at any monitor in the metro area, roughly 14.3% each day. Sundays recorded fewer exceedance days than would be expected, if there were no weekend effect, and Thursdays and Fridays recorded many more than would be expected. This is evidence that there is a weekend effect affecting ozone in the DFW airshed.

A chi-squared goodness of fit test was performed to test whether exceedance days were independent of day of the week. The test compares the observed distribution to a hypothetical pattern of equal likelihood of exceedance on any day. The test does not determine whether a particular day is out of the ordinary but it does assess whether the overall distribution is what would be expected based on random assignment of observations to days. The chi squared test ($\chi^2 = 16.9$, $p = 0.05$) determined that the observed distribution was statistically different from what would be expected if eight-hour ozone exceedance days were observed randomly, suggesting there is a day of the week effect. The contribution to the total chi-squared value of exceedance on each day is also presented in Table 4-1. The chi-square value for high ozone days on Sundays and Fridays was much larger than any of the other days. Chi-squared values for non-exceedance days are not presented. This analysis is limited by the assumption of the chi squared test that all instances must be independent. It is possible that two or more days in a multiday episode are not independent, so these results should be interpreted with caution.

Table 4-1: High Eight-Hour Ozone Days and Chi Squared by Day of the Week

Year	Observed Number of Exceedance Days	Observed Number of Days that did not Exceed	Expected Number of Exceedance Days	Computed χ^2	Critical Value of χ^2 Distribution* (χ^2crit)
2012	60	185	33	22	
2013	45	200	33	4	
2014	26	219	33	1	
2015	44	201	33	4	
2016	18	227	33	7	
2017	24	221	33	2	
2018	31	214	33	0	
2019	29	216	33	0	
2020	21	224	33	4	
2021	31	214	33	0	
sum:	**329**	**2121**	**329**	**46**	**16.92**

*0.05 level of significance (95%) with degrees of freedom = 9

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CHAPTER 5: METEOROLOGY AND ITS EFFECT ON OZONE

Meteorological factors play an important role in ozone formation. Ozone-conducive meteorological conditions, such as low wind speeds, low humidity, and clear, sunny skies, can affect how ozone precursors react, where ozone is formed, and how much ozone accumulates in an area. This section will look at these various meteorological factors at both the local-scale and the large-, or synoptic-, scale, to determine their effects on ozone formation in the Dallas-Fort Worth (DFW) area. These meteorological correlations and associations are rough approximations of underlying relationships because they use coarse temporally aggregated measures intended to simplify complex underlying meteorological phenomena.

5.1 TEMPERATURE

While ambient temperature is not a direct factor in ozone formation photochemistry, it has repeatedly been shown to be positively correlated with ozone, suggesting it can be useful as a proxy for ozone-conducive atmospheric conditions. Warmer temperatures often indicate sunny, cloudless days, which are ideal for ozone formation. To investigate the role of temperature on ozone formation in the DFW area, area-wide daily-maximum temperature was compared to area-wide daily-maximum eight-hour averaged (MDA8) ozone concentrations at monitors that measure both ozone and temperature. All hours were included to identify the daily maximum temperature, although data completeness at each monitor was not assessed. Results are displayed in Figure 5-1: *Ozone Season Daily-Maximum Temperature Versus MDA8 Ozone in the DFW Area*.

Results show the expected positive relationship between temperature and ozone; however, at higher temperatures there is more variability, with both high and low ozone levels recorded during days with high temperatures. In the figure, ozone exceedance days are highlighted in red. There were no days with eight-hour ozone values above 70 parts per billion (ppb) and temperatures less than 74 degrees Fahrenheit (˚F). Also, note that some ozone exceedance days occurred when temperatures were below 80˚ F, indicating that higher temperature are not necessary for high ozone in the DFW area, but are suggestive of ozone-conducive conditions or other contributing factors.

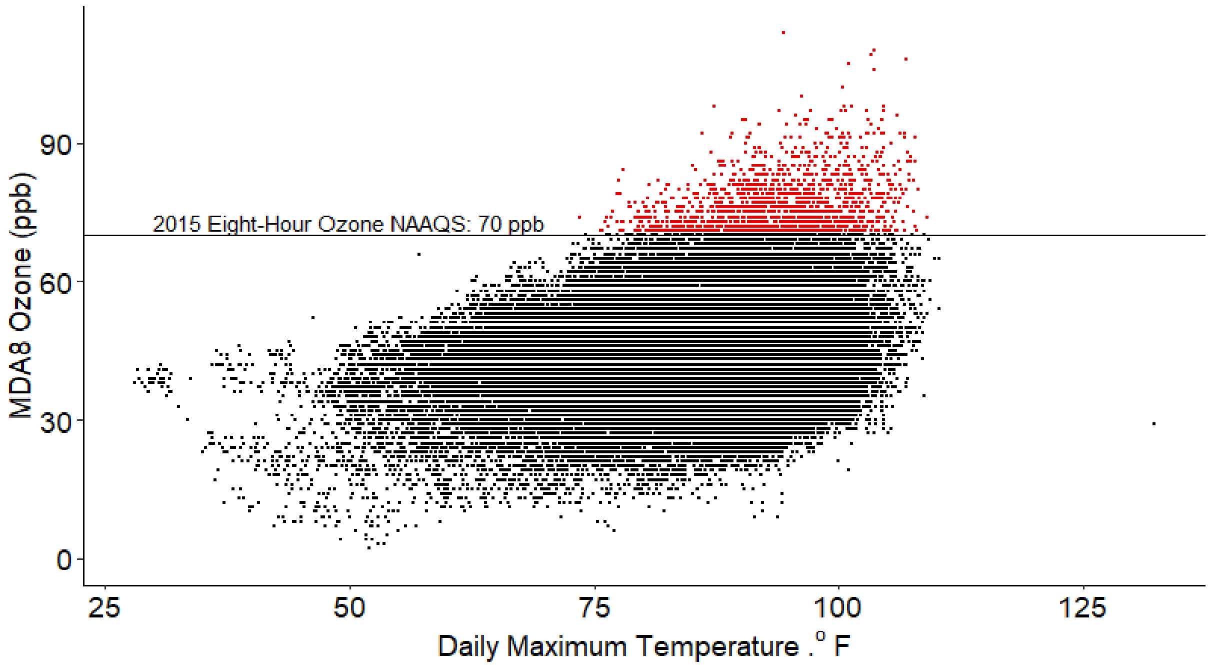


Figure 5-1: Ozone Season Daily-Maximum Temperature Versus MDA8 Ozone in the DFW Area

5.2 RELATIVE HUMIDITY

Relative humidity is another meteorological factor that is not a direct factor in ozone formation photochemistry but has been shown repeatedly to negatively correlate with ozone concentrations. Four regulatory sites in the DFW area measure both relative humidity and ozone (Denton Airport South, Italy, Kaufman, and Grapevine Fairway). Daily average relative humidity measurements from these sites were compared to daily-maximum eight-hour ozone for the DFW area. For this comparison, only daytime hours, defined as 07:00 local standard time (LST) through 19:00 LST, were used to calculate daily average relative humidity. The analysis used only days with at least 75% complete relative humidity data for the 13 hours investigated and used only ozone season data from 2012 through 2021. Results are displayed in Figure 5-2: *Ozone Season Average Daytime Relative Humidity versus MDA8 Ozone in the DFW Area.*

This plot shows the negative correlation between average daytime relative humidity and daily maximum eight-hour ozone. Low relative humidity indicates less moisture in the air. The negative correlation suggests that as the air is more saturated with moisture, less ozone is formed. Ozone exceedance days are highlighted in red. During the decade under consideration, no high ozone days in the DFW area occurred when average daytime relative humidity was greater than 63 percent, and only two exceedance days saw relative humidity over 60 percent. Typically, drier air follows cold fronts as they move through the DFW area. Several studies have shown that post frontal conditions can be conducive to ozone formation in the HGB area, and the negative correlation of ozone and relative humidity for the DFW area indicates that these conditions may lead to ozone formation in the DFW area as well (Lefer 2010; Rappenglueck 2008).

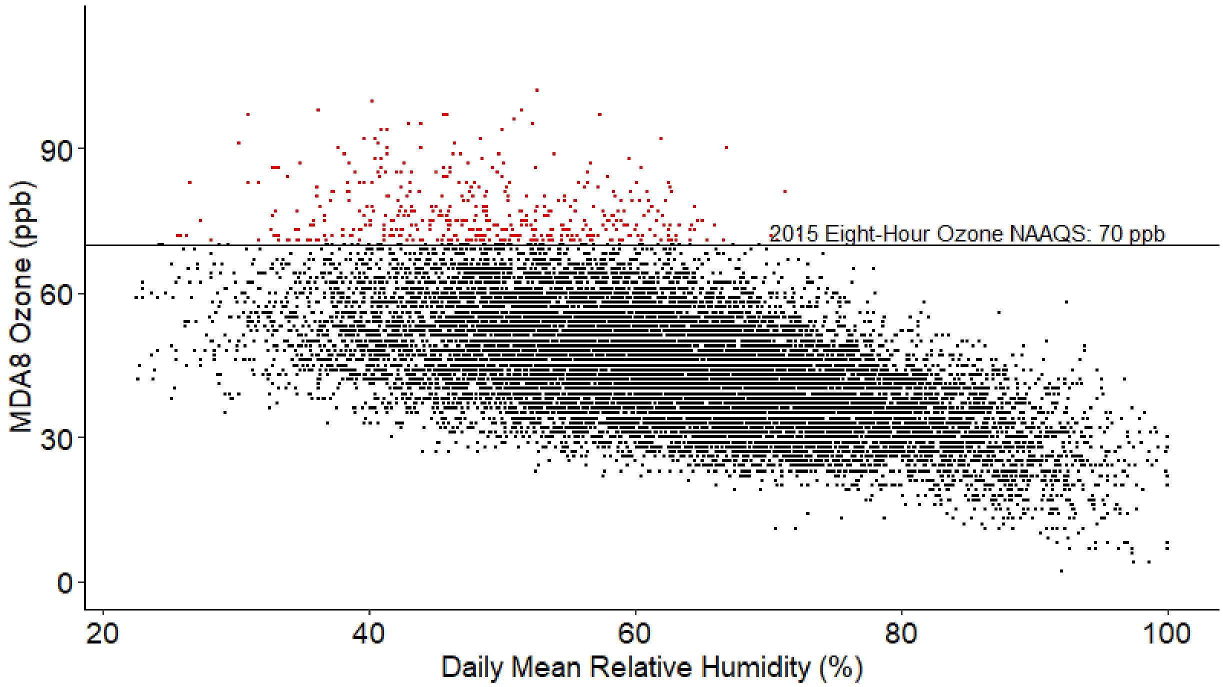


Figure 5-2: Ozone Season Average Daytime Relative Humidity Versus MDA8 Ozone in the DFW Area

5.3 WIND

Winds are a crucial factor in ozone formation as they can contribute to ozone-conducive conditions in an airshed. Winds are typically characterized by speed, direction, and altitude. Low surface wind speeds can allow accumulation of ozone and its precursors in the mixing layer, while high wind speeds can lead to dispersion and dilution of ozone and its precursors. Changing wind directions, such as flow reversals, can recirculate precursors over sources multiple times. Winds transport ozone and precursors from other areas or bring them from sources upwind to areas downwind.

Figure 5-3: *Ozone Season Average Daytime Resultant Wind Speed Versus MDA8 Ozone in the DFW Area* shows the relationship between wind speed and ozone. Wind speed is the daily mean, so it is a rough proxy of how fast winds were throughout the duration of a day. Ozone is the maximum daily eight-hour averaged (MDA8) concentration, so it is a measure of the severity of ozone on a particular day. Days when MDA8 ozone exceeded 70 ppb are highlighted in red. These days are clustered at very low wind speeds, most well below ten miles per hour. Ventilation due to higher wind speeds prevents ozone from forming and accumulating in higher concentrations, those above about twelve miles per hour, except in a few rare cases.

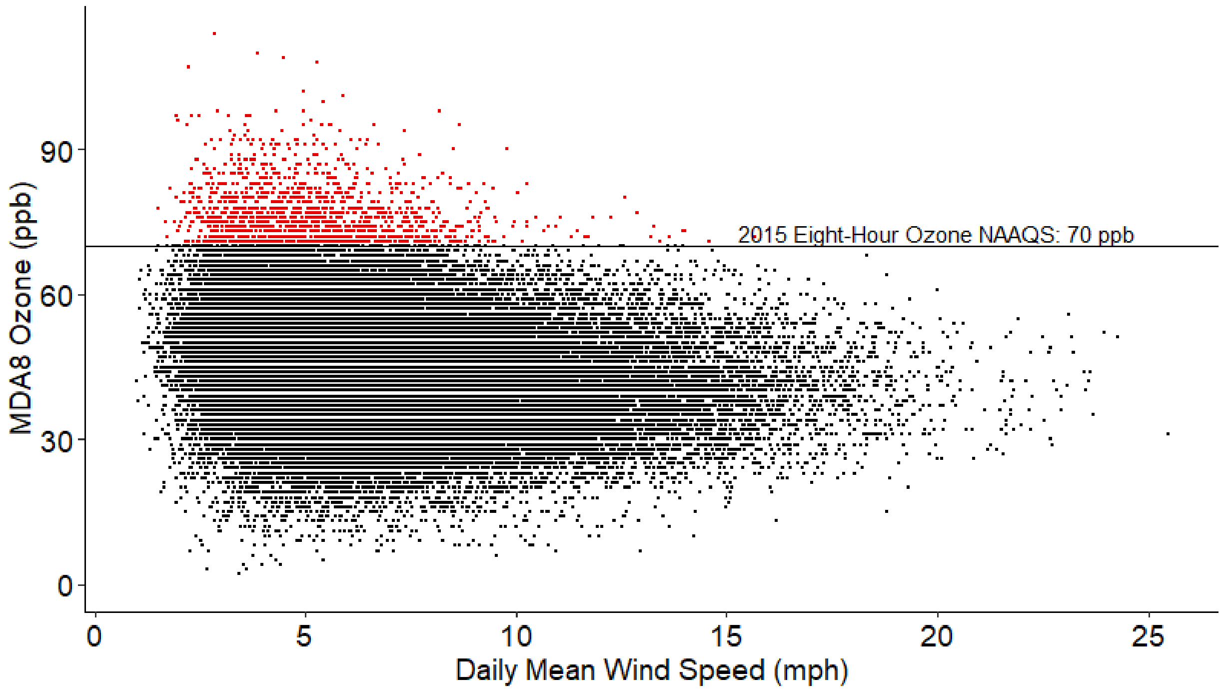


Figure 5-3: Ozone Season Average Daytime Resultant Wind Speed Versus MDA8 Ozone in the DFW Area

5.3.1 Prevailing Wind Patterns

Identifying unique patterns of prevailing winds on high or low ozone days can inform our understanding of ozone formation dynamics. One tool for summarizing and displaying wind patterns is a wind rose. In a wind rose, the length of each petal signifies the incidence, or frequency, with which winds arrive at a measuring device from a particular direction, with the petals further divided according to wind speed. One weakness of wind roses is that, while petal lengths accurately represent the frequencies, the areas of the petals distort these frequencies visually. Petal segments that are farther from the center appear visually larger than they should, due to the expanding circumference of the circle. For this analysis, daytime, defined as 7:00 LST. to 18:00 LST, ozone season wind speeds and directions for 43 surface monitors in the DFW area from 2012 through 2021 were examined.

Figure 5-4: *Wind Roses on High and Low Ozone Days in the DFW Area* shows that low ozone days record a high frequency of winds from the south (15%), south-southeast (14%), southeast (10%), and south-southwest (8%), with other directions reported at much lower frequencies. Typically, these winds are greater than 5 miles per hour (mph) (89%), represented by yellow, orange, and red. Note the almost complete lack of winds less than 2.5 mph (2%), represented by blue on low ozone days.

On high ozone days, winds are more varied directionally, and predominantly arrive with about equal frequencies from the east-southeast (12%), southeast (12%), south (12%), and south-southeast (11%). Winds on high ozone days also arrive with slightly lower frequencies from the east (10%) and south-southwest (8%), though all directions are represented. Winds on high ozone days are typically much slower than on low ozone days, averaging 5.3 mph, and often do not exceed 5 mph (19%), represented by blue and aqua, which are considered stagnant wind conditions. Note the lower frequency of winds over 10 mph (29%), represented by red, on high ozone days.

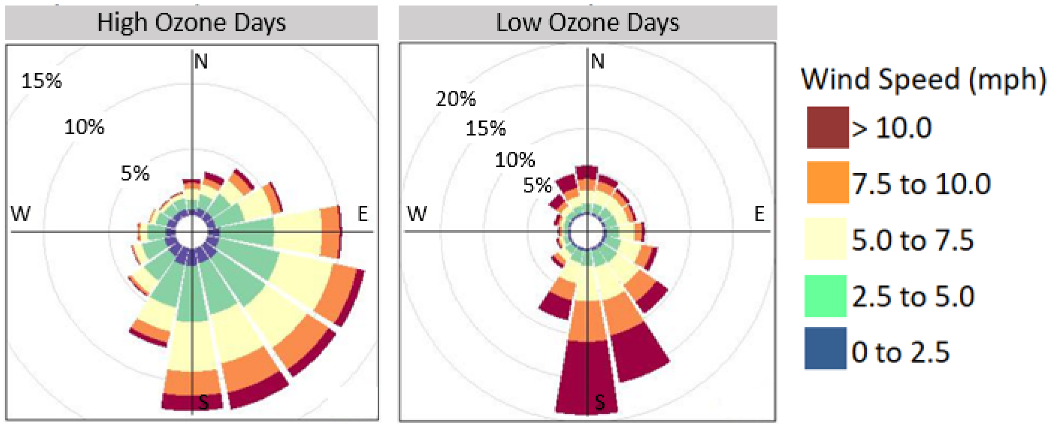


Figure 5-4: Wind Roses on High and Low Ozone Days in the DFW Area

Meteorology affecting ozone differs by season, as shown in Figure 5-5: *Wind Roses on High and Low Ozone Days During Spring and Summer in the DFW Area.* These plots present wind roses for the spring (April-June; left two panels) and summer (July-September; right two panels), for high and low ozone days. Notice that wind speeds were typically much faster on low ozone days during both spring and summer than on high ozone days in spring or summer. Low wind speeds, those less than 5 mph, are substantially longer on high ozone days than on low ozone days, indicating slow winds occur often on high ozone days. This difference is especially pronounced during summer months, as wind speeds were less frequently above 7.5 mph (29%; red) on summer high ozone days. Winds arrived predominantly from the south and south-southeast on spring low ozone days (31%), and were only slightly more varied in the summer, also arriving in notable frequencies from the south-southwest and southeast.

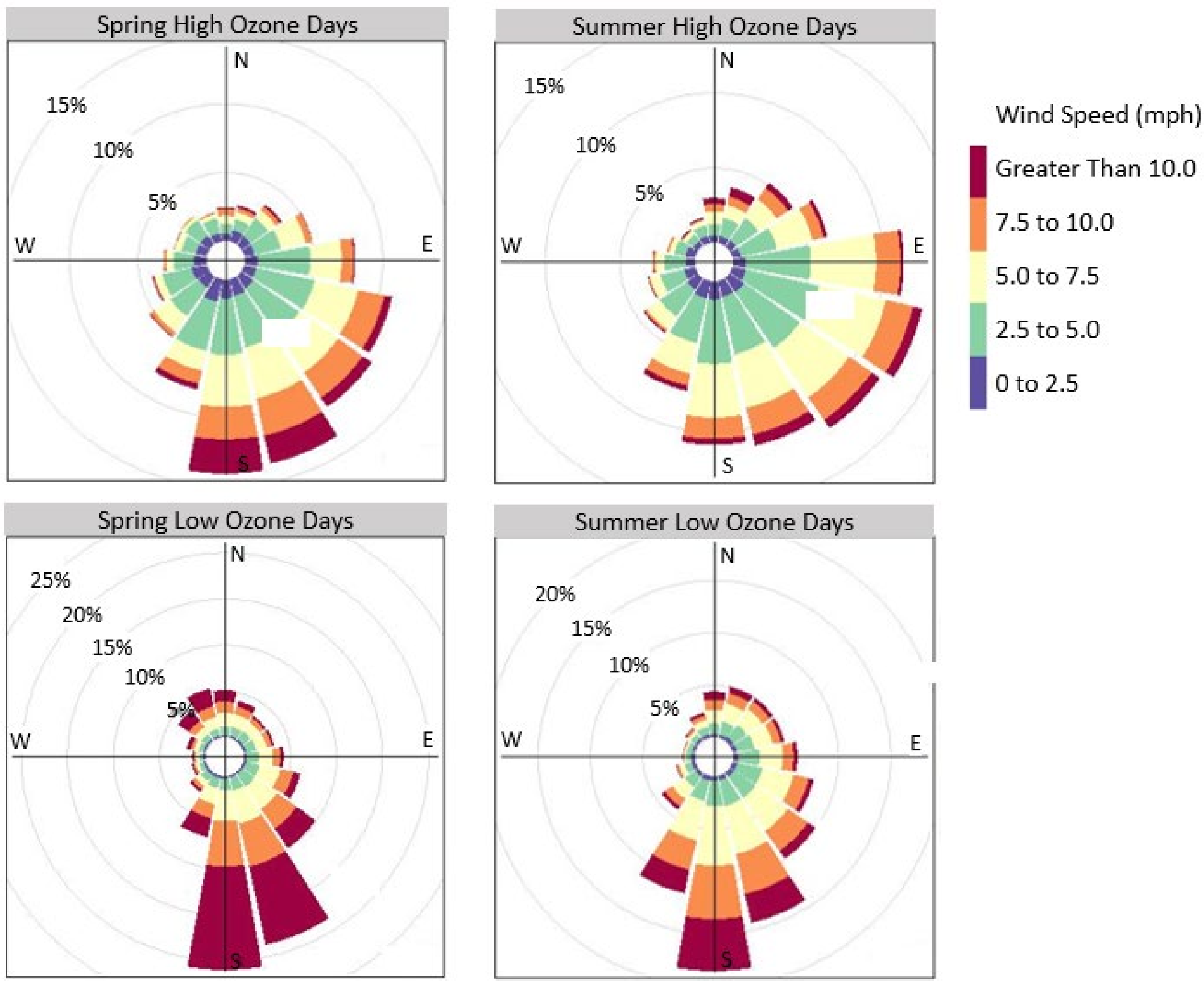


Figure 5-5: Wind Roses on High and Low Ozone Days During Spring and Summer in the DFW Area

Figure 5-6: *Wind Roses on Ozone Exceedance Days in the DFW Area* shows wind speeds and directions at the twenty ozone monitors in the DFW area but only on those days that each monitor recorded an exceedance. That is, a day when three monitors exceeded the 2015 ozone NAAQS would only be included in wind roses for those three monitors. Monitors located closer to the center of the urbanized area tend to record higher frequencies of slower wind speeds (blue and aqua) on days when they record exceedances.

Most monitors located on the periphery of the DFW area record wind originating from the center of the metropolitan area on days when those monitors record exceedances. Those winds arrive more frequently at those monitors at higher speeds (orange and red). This supports the contention that slower wind speeds are more conducive to ozone formation, but only in areas where there is a surfeit of precursor emissions, such as an urban downtown. Once ozone is formed, it can be transported to downwind monitors at higher speeds. Since most winds in the DFW area arrive from south and east directions, monitors to the north and west will typically be downwind. Two monitors that do not follow this pattern are Corsicana Airport and Kaufman, though there were only 11 and 12 exceedance days, respectively, over the ten-year period at these two monitors. These two monitors are located east and southeast of the center of the DFW region, so are typically upwind, and are likely influenced by sources other than DFW urban emissions.

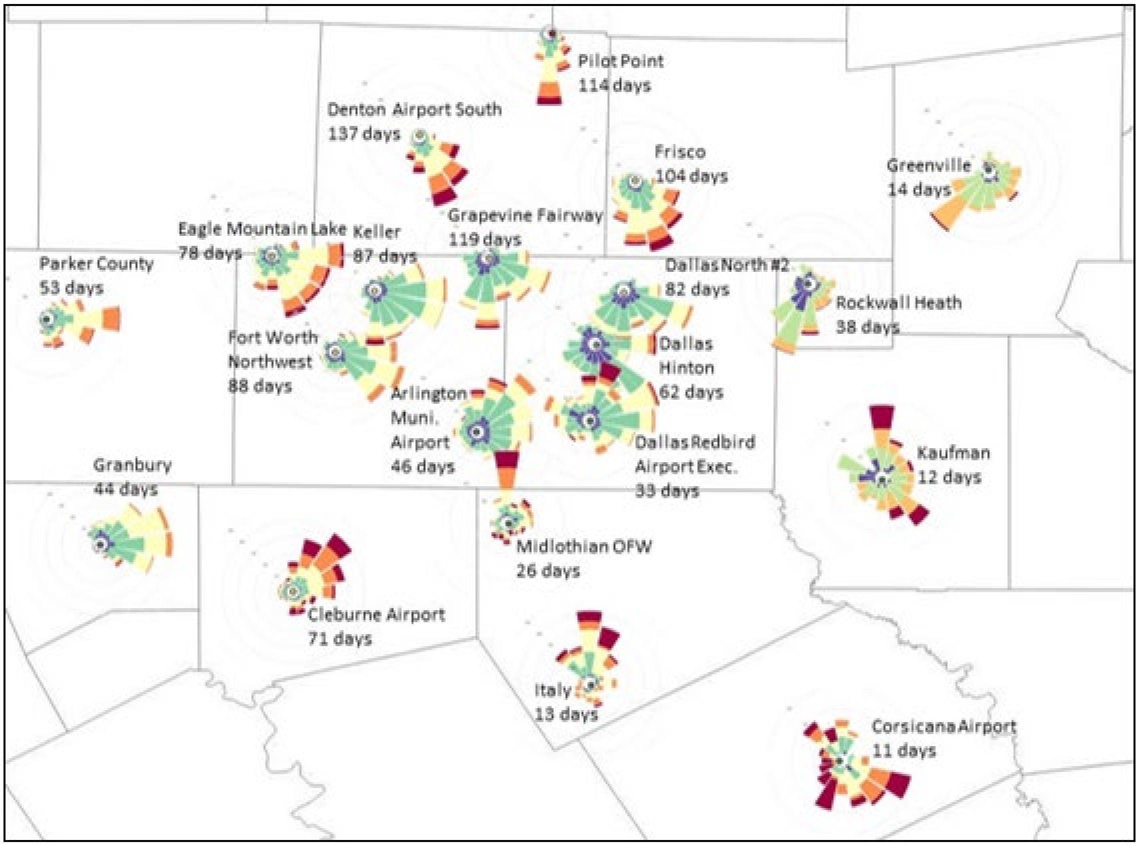


Figure 5-6: Wind Roses on Ozone Exceedance Days in the DFW Area

Figure 5-7: *Daily Average Wind Speed and MDA8 Ozone at Periphery and Non-Periphery Monitors in the DFW Area* reveals this difference between monitors located closer to more populated parts of the DFW area and those located on the periphery. Thirteen of twenty DFW monitors were classified as periphery monitors (Cleburne Airport, Corsicana Airport, Denton Airport South, Eagle Mountain Lake, Frisco, Granbury, Greenville, Italy, Kaufman, Midlothian OFW, Parker County, Pilot Point, and Rockwall Heath), while seven were not. Ozone exceedance days are colored red, and all other days are blue. Both plots trace the expected negative relationship of slower wind speeds associated with higher ozone concentrations. The left panel shows this relationship for monitors on the periphery of the DFW area, where higher wind speeds are more frequent. Maximum daily average wind speed on high ozone days at non-periphery monitors was 13.8 mph. Maximum daily average wind speed on high ozone days at periphery monitors was 17.5 mph.

Of 37 exceedances (over 22 high ozone days) that occurred at monitors when average daily wind speeds were 10 mph or greater, only two occurred at non-periphery monitors (Grapevine Fairway and Keller), while 35 occurred at periphery monitors. Both exceedances occurred on May 18, 2012, a day when three other monitors also exceeded. Even these two monitors are in suburban areas located several miles downwind of the most populated areas of DFW.

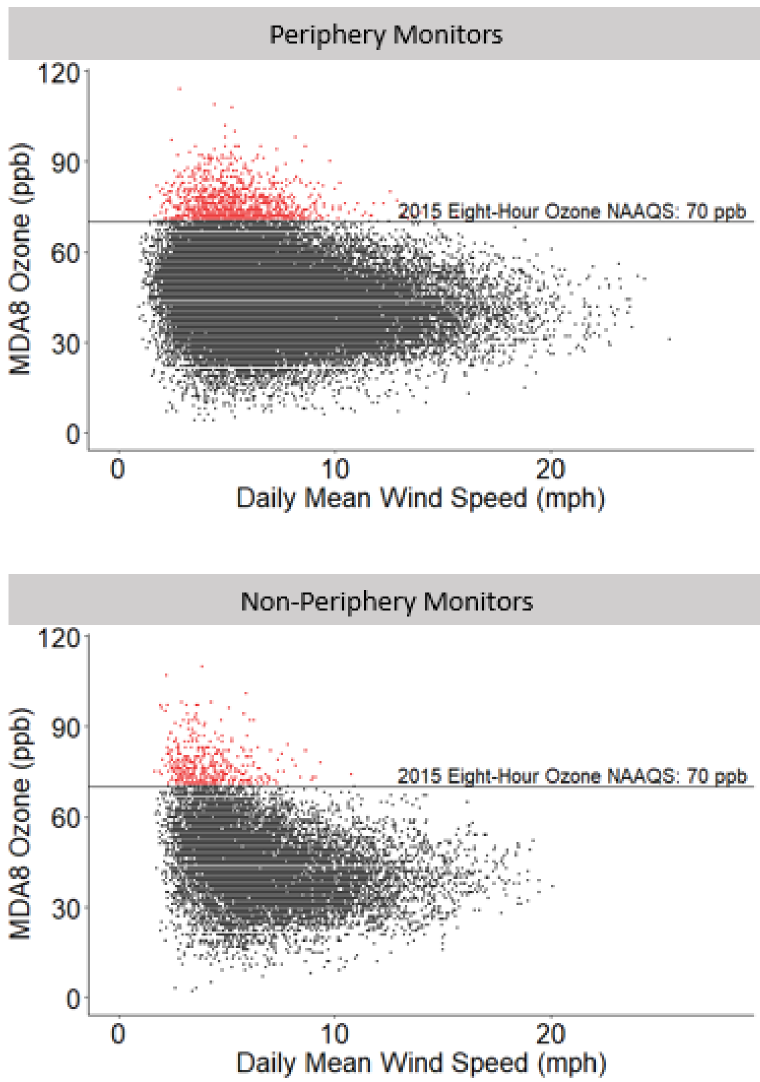


Figure 5-7: Daily Average Wind Speed and MDA8 Ozone at Periphery and Non-Periphery Monitors in the DFW Area

5.3.2 Upper-Level Winds

While surface winds can show how ozone is transported and mixed locally, upper-level wind characterization can identify potential sources of emissions and ozone that can be transported into the area from other regions. Upper-level winds were examined using the HYSPLIT model developed by the National Oceanic and Atmospheric Administration's (NOAA) Air Resources Laboratory (ARL) (Stein et al. 2015; Rolph et al. 2017). Data from the North American Mesoscale (NAM) 12-kilometer meteorological model were used.

Figure 5-8: *Map of HYSPLIT Back Trajectories from Pilot Point on High Ozone Days* plots hourly coordinates of HYSPLIT 72-hour back trajectories from the Pilot Point monitor, initiated at the time of peak one-hour ozone at 800 meters (m) altitude on 46 ozone exceedance days over the 2018 through 2021 period. These trajectories predominantly arrived from the south, south-southwest, south-southeast, southeast, and east. This means that these trajectories traversed the more urbanized parts of the DFW area, including numerous emissions sources in Fort Worth, Dallas, and other cities in Tarrant County, before arriving at the Pilot Point monitor, which is downwind to the north. Points that are closer together indicate slower wind speeds, which allow accumulation of precursors which could form ozone. No single emissions source can be identified as the primary contributor.

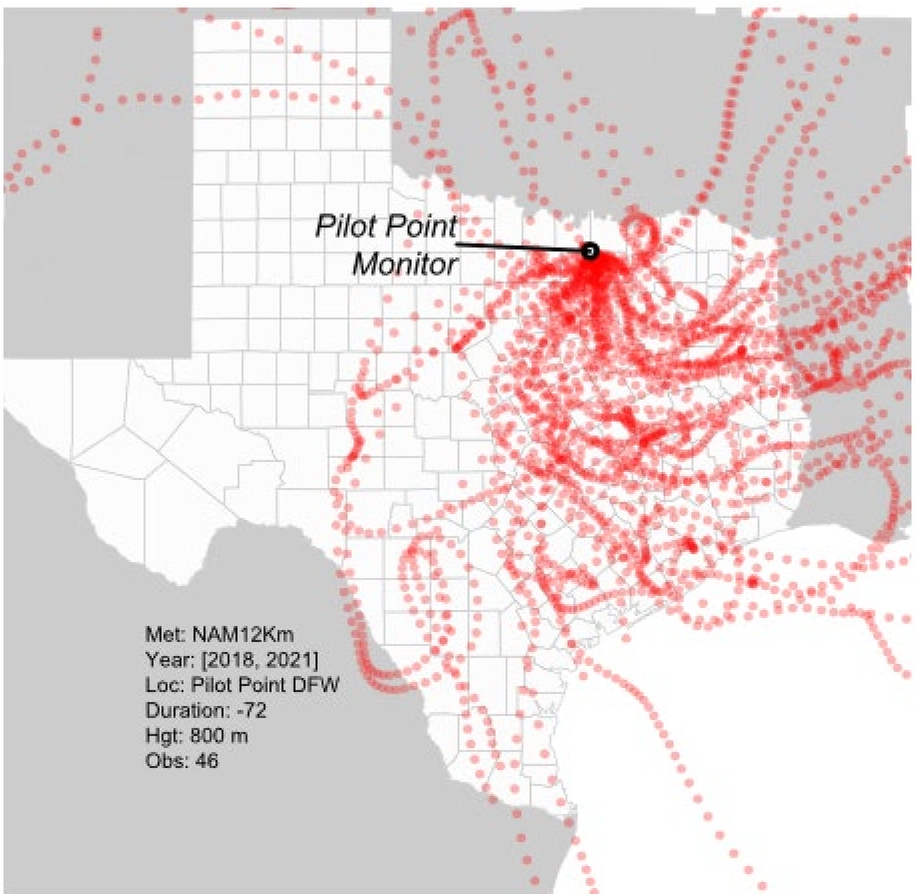


Figure 5-8: Map of HYSPLIT Back Trajectories from Pilot Point on High Ozone Days

Ozone exceedance days could exhibit different meteorology than other days. To examine this, HYSPLIT 72-hour back trajectories were computed for all days during ozone season and then the frequencies with which endpoints of the hourly segments of these trajectories fell within defined grid cells were computed. These are displayed graphically in Figure 5-9: *Map of Frequencies of One-Hour Trajectory Endpoints of HYSPLIT 72-Hour Back Trajectories from Pilot Point during Ozone Season*. This map shows that trajectories traverse regions to the south, southeast and east at a much higher frequency than other directions on all days, not just high ozone days. Trajectories also arrive from the north and northeast but at lower frequencies. Beyond Texas, the lowest frequencies are seen with trajectories from the far northwest, west, southwest, east, and northeast.

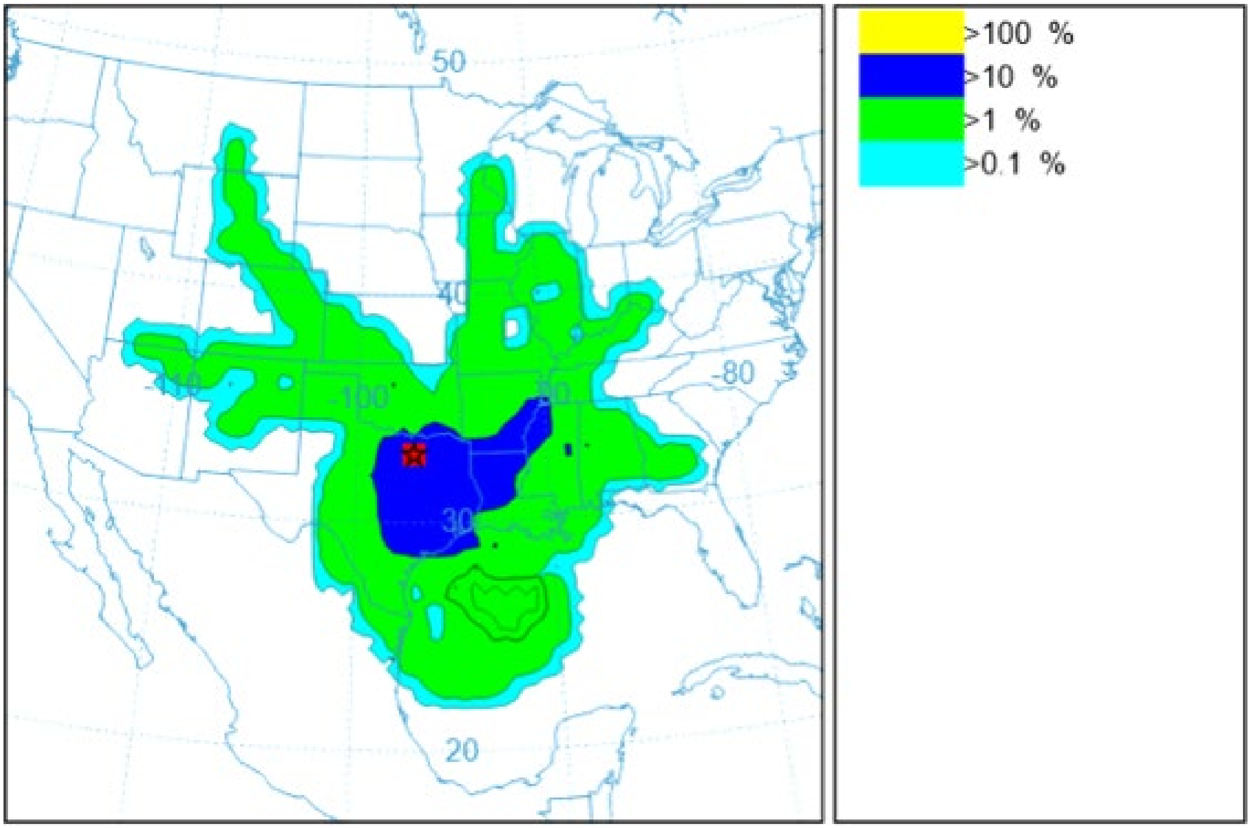


Figure 5-8: Map of Frequencies of One-Hour Trajectory Endpoints of HYSPLIT 72-Hour Back Trajectories from Pilot Point during Ozone Season

Trajectories with similar patterns can be combined, or clustered, to distinguish between paths that lead to higher or lower than average ozone concentrations. This analysis used a HYSPLIT clustering algorithm to group and average 1,291 ozone season back trajectories based on trajectory length and shape. The clustering algorithm groups similar trajectories to facilitate an objective assessment of directional influences. A scree plot was used to identify an appropriate number of clusters by comparing eigenvalues of clusters. Thirteen was identified as the optimal number of trajectory clusters, meaning variation among clusters was lowest with that number of clusters. Results of the cluster analysis are displayed in Figure 5-10: *Mean of 72-Hour Back Trajectory Clusters for Ozone Season (top) and Boxplots of One-Hour Ozone Concentrations for Each Cluster (bottom) at Grapevine Fairway*. The clustering algorithm reports the frequency of trajectories in each cluster, which are annotated on the trajectory plots, along with cluster number.

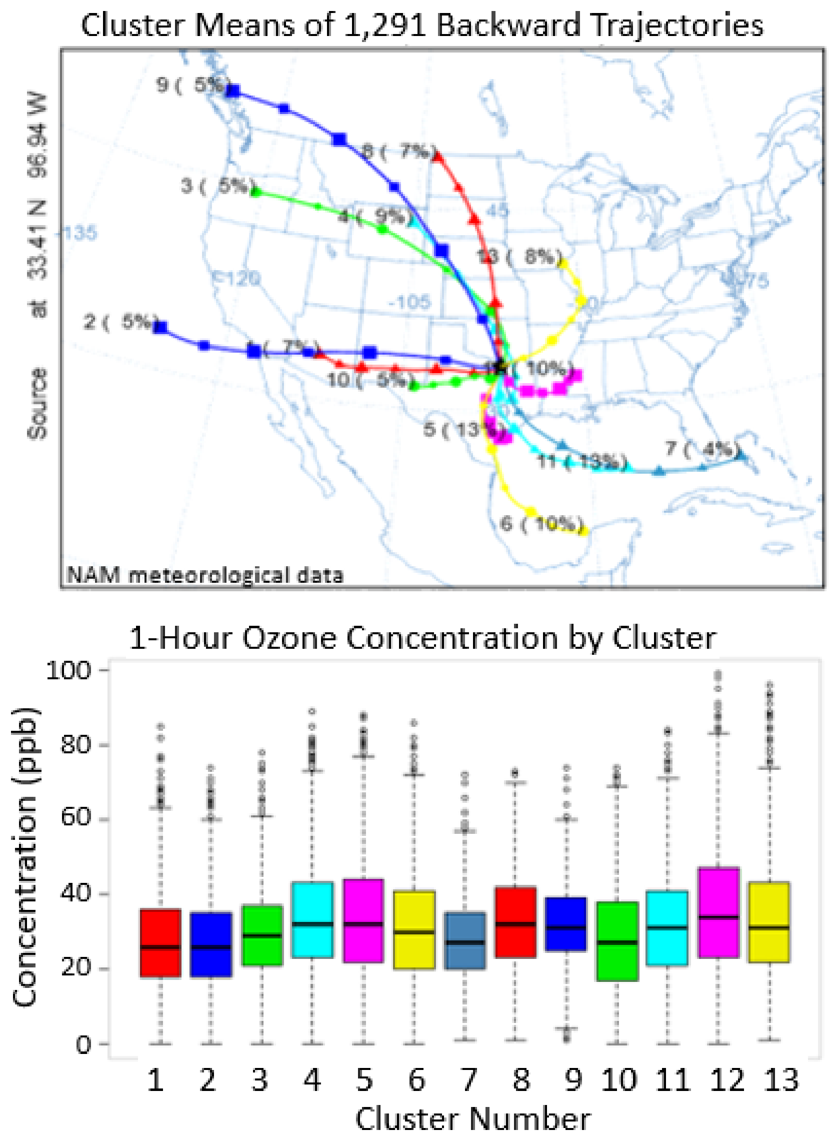


Figure 5-9: Mean of 72-Hour Back Trajectory Clusters for Ozone Season (top) and Boxplots of One-Hour Ozone Concentrations for Each Cluster (bottom) at Grapevine Fairway

Results in Figure 5-10 and Table 5-1: *DFW Area Ozone Statistics from Cluster Analysis* show that cluster 12 has the highest cluster maximum concentration, 83 ppb. This cluster arrives from the east and is very short, indicating very slow wind speeds. A grouping of clusters, clusters 5, 6, and 11, all arrive from the south with cluster maximum concentrations of 77 ppb, 72 ppb, and 71 ppb, respectively. These correspond to trajectories traversing the large blue region to the south of the DFW area shown in the previous figure. Cluster 7, with a maximum ozone concentration of only 57 ppb, arrives from the southeast, as well, but the trajectories in this cluster travel over the Gulf of Mexico before reaching Texas and are likely bringing cleaner marine parcels. The cluster with the next highest cluster maximum concentration, cluster 13 (74 ppb) arrives from the northeast, corresponding to the blue “finger” pointing northeast from the DFW area in the previous figure. Only one other cluster, cluster 4, has a cluster maximum ozone concentration over 70 ppb (71 ppb). This cluster arrives from the northwest and is very similar to clusters 3 and 9, except cluster 4 is shorter, indicating slower winds, and contains trajectories that rotate around the DFW area, collecting precursors before arriving at the monitor. Cluster 0 includes trajectories that did not fit any cluster well and is not shown in the cluster-mean path plot because that mean path would be meaningless. Caution should be taken attributing higher ozone via this analysis. Since the trajectory is 72 hours in duration, many sources along the way can influence the ozone at the monitor, especially closer sources.

Statistics of the cluster analysis are presented in Table 5-1: *DFW Area Ozone Statistics from Cluster Analysis*. Overall, trajectory cluster analysis shows that continental air likely brings large amounts of transported ozone and ozone precursors into the DFW area. Further, it is shorter trajectories, representing slower wind speeds, that correlate with the highest ozone in the DFW area. High ozone in the DFW area appears to occur under two scenarios. The first is that continental air with low wind speeds brings high levels of ozone and ozone precursors into the DFW area, which combine with local emissions to produce high ozone. The second is winds from the direction of the Gulf of Mexico bring slightly cleaner air to the DFW area, but low wind speeds lead to large amounts of local ozone production and high ozone concentrations.

Table 5-1: DFW Area Ozone Statistics from Cluster Analysis

Percentile	1†	2†	3†	4†	5†	6†	7†	8†	9†	10†	11†	12†	13†
Min††	0	0	0	0	0	0	1	1	4	0	0	0	1
25th	18	18	21	23	22	20	20	23	25	17	21	23	22
50th	26	26	29	32	32	30	27	32	31	27	31	34	31
75th	36	35	37	43	44	41	35	42	39	38	41	47	43
Max††	63	60	61	73	77	72	57	70	60	69	71	83	74

†Cluster Number
††Values of data points that lie beyond the extremes of the whiskers.

5.3.3 Ozone and Nitrogen Oxides (NO_x) Concentrations Versus Winds

Wind speed and direction can be used to identify potential sources for any measured compound using bivariate polar plots at receptor locations (Uria-Tellaetxe and Carslaw, 2014). Bivariate polar plots are bivariate because they combine two covariates by conditioning one upon the other. They are polar because they apply trigonometry and a Cartesian coordinate system to wind information to determine the approximate location from which an air mass traveled before it reached a receptor monitor. From the distribution of the measure of interest, for example ozone or NO_x, it is possible to identify the frequency with which measured values of the compound exceed selected values, for example the 95th percentile. Conditioning filters the compound to those occasions when the receptor measured specific values of the compound and the bivariate polar plot identifies the direction and, potentially, the general locations of sources of those compounds when they were at or above the level of interest.

This analysis used NO_x, ozone, resultant wind speed, and resultant wind direction for the ozone season from 2012 through 2021 at ten monitors in the DFW area that record all four of these parameters: Arlington Municipal Airport, Corsicana Airport, Dallas North #2, Dallas Redbird Airport Executive, Denton Airport South, Eagle Mountain

Lake, Grapevine Fairway, Greenville, Italy, Kaufman, Midlothian OFW, and Parker County. Because several of these sites are located on the periphery of the DFW metropolitan area, it could be possible to identify ozone or NO_x sources when these sites are downwind of major emissions sources. Other sites are surrounded by sources in multiple directions, which could also be identifiable.

Figure 5-11: *Bivariate Polar Plots of the Frequency of Ozone Exceeding 70 ppb at Monitors in the DFW Area* shows probabilities of ozone exceeding 70 ppb when winds arrive at these twelve monitors from the directions and distances indicated by blue cells. Monitor locations are indicated in red. Inset titles include a designation of where within the metro area the monitor is located (NW, N, etc.). Darker blue shades indicate higher probabilities of high ozone from that direction. The distance nearer or farther from the monitor indicates the wind speed so that faster wind speeds are identified by locations farther from the monitor. Blank areas indicate there was no ozone over 70 ppb arriving from that distance and direction.

Monitors in the north and northwest of the region, such as Eagle Mountain Lake and Denton Airport South show higher likelihoods of ozone concentrations over 70 ppb when winds are from the east and southeast, which is the direction of the more urbanized part of the metropolitan area. It is noteworthy that there are few winds with high ozone arriving at these monitors from the north or west. If and when winds arrive from those directions, they do not contain high ozone concentrations. Similarly, Parker County, which is west of Fort Worth, shows higher probabilities of high ozone when winds arrive from the east. Monitors to the south of the metro area, Midlothian OFW, Italy, and Corsicana Airport report high probabilities when winds arrive from the north, again suggesting influence from more urbanized areas. Greenville is to the east of the metro area and has higher probabilities when winds are from the west. Monitors such as Dallas North No. 2, Dallas Executive Airport, and Arlington Municipal Airport are located more centrally and record high ozone influences from every direction. These results illustrate the influence of meteorological conditions on ozone measurements and are useful for determining patterns of ozone transport within the region.

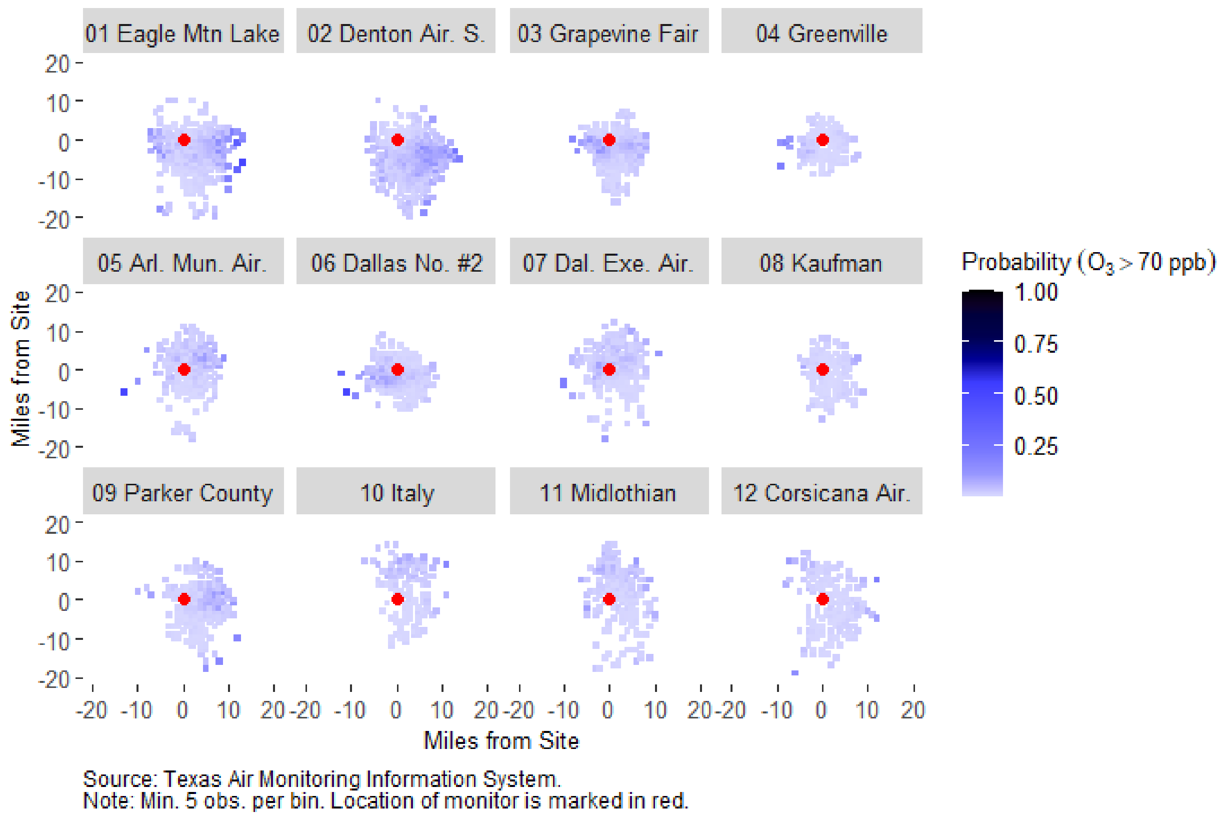
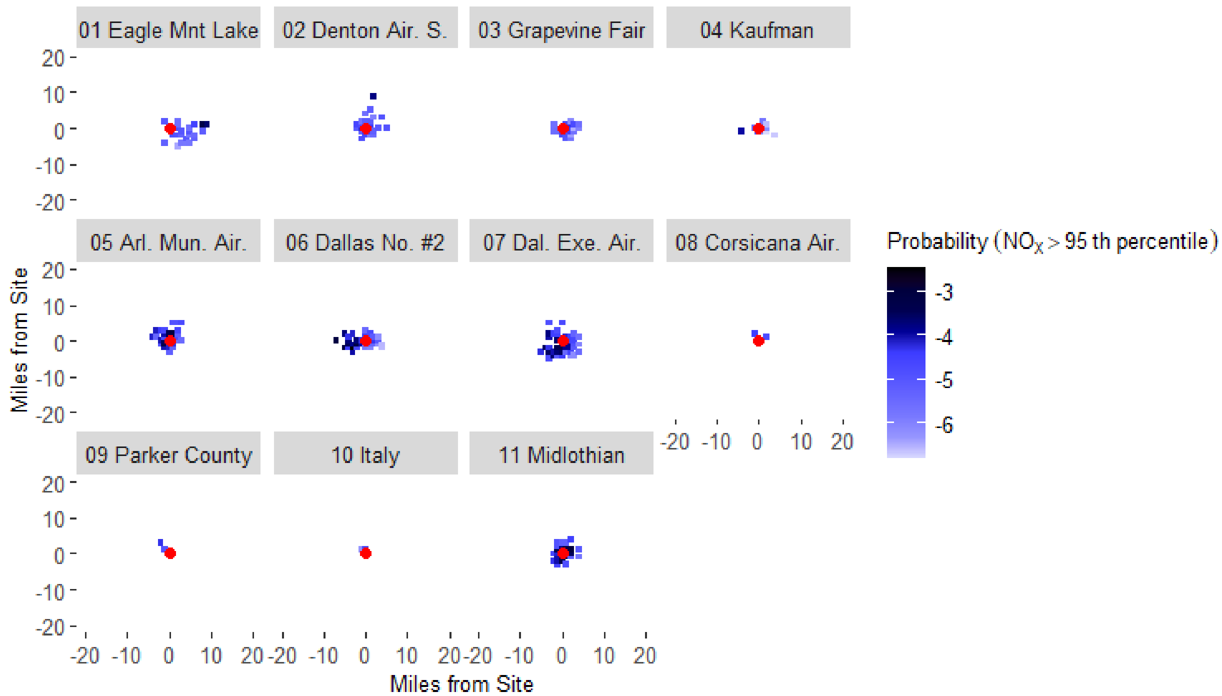


Figure 5-11: Bivariate Polar Plots of the Frequency of Ozone Exceeding 70 ppb at Monitors in the DFW Area

Figure 5-12: *Bivariate Polar Plots of the Frequency of NO_x Exceeding the 95th Percentile at Monitors in the DFW Area* illustrates a similar situation for NO_x. The 95th percentile was chosen to account for instances when NO_x is likely to have the greatest impact on ozone; however, it results in fewer data points to evaluate. Points typically cluster near the monitor location, indicating very slow wind speeds. Eagle Mountain Lake and Denton Airport South appear to point back towards the urban area, as seen with ozone. The west-to-east cluster of points at Dallas North No. 2 could indicate sensitivity to NO_x emissions from motor vehicle NO_x on nearby I-635.



Source: Texas Air Monitoring Informatin System.
Note: Minimum 5 observations per bin. Location of monitor is marked in red.

Figure 5-10: Bivariate Polar Plots of the Frequency of NO_x Exceeding the 95th Percentile at Monitors in the DFW Area

5.3.4 NO_x Versus Ozone

Because NO_x is a critical precursor of ozone, it is informative to investigate the correlation between the two. Typically, ozone concentrations are low over night, due to lack of solar radiation that drives the ozone reaction. NO_x generated from emissions activity in the morning or NO_x left over from the previous day will decrease as solar radiation increases and NO_x is converted into ozone. High NO_x is often observed with low ozone. Then, as NO_x is converted into ozone, ozone rises. Once available NO_x has been converted to ozone, it will be low while ozone will be high.

This negative relationship is apparent in Figure 5-13: *One-Hour NO_x versus One-Hour Ozone (top) and Daily Maximum NO_x versus MDA8 Ozone (bottom) in the DFW Area* which shows the relationship between the two at co-located monitors. The top panel shows the highest one-hour values of NO_x are recorded at the same time as the lowest values of ozone, and vice versa. This illustrates the inverse relationship between NO_x and ozone. The bottom panel of the figure shows the daily maximum NO_x concentration plotted with the maximum daily eight-hour average ozone concentration. This figure captures the complex relationship between these two compounds at the daily scale by filtering out very low values of both. On days with very low or very high MDA8 ozone, the maximum NO_x is often very low, while the highest values of NO_x are observed when ozone is moderate. In the left panel, NO_x never exceeds 30 ppb when ozone exceeds 70 ppb, while ozone never exceeds 40 ppb when NO_x exceeds 50 ppb. Between these two cases, typically under non-ozone-conducive conditions, moderate values of ozone are observed with low values of NO_x and low values of ozone are observed with both low and moderate values of NO_x.

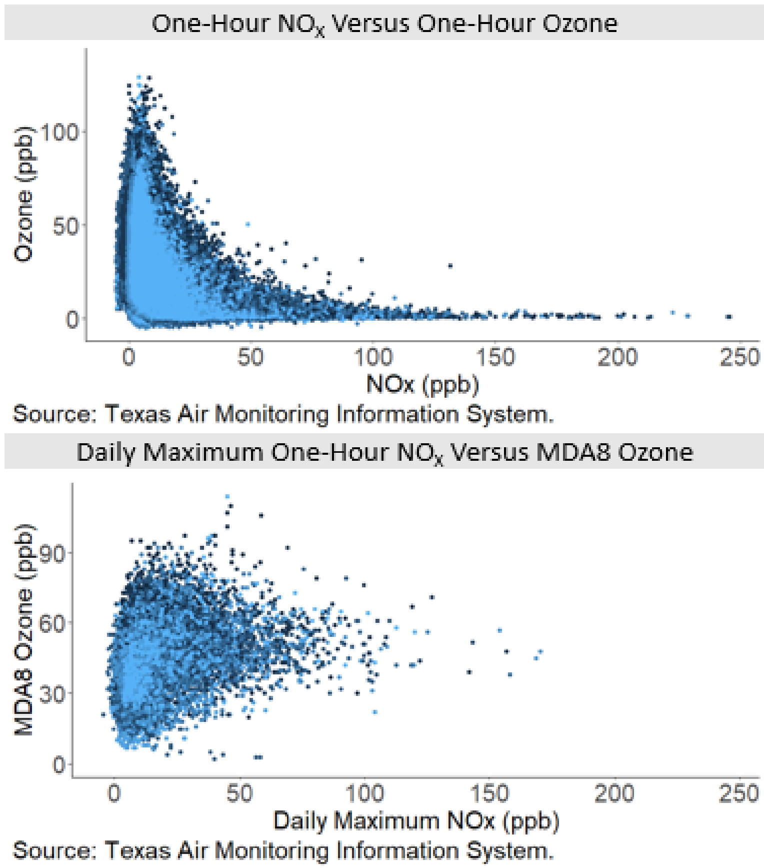
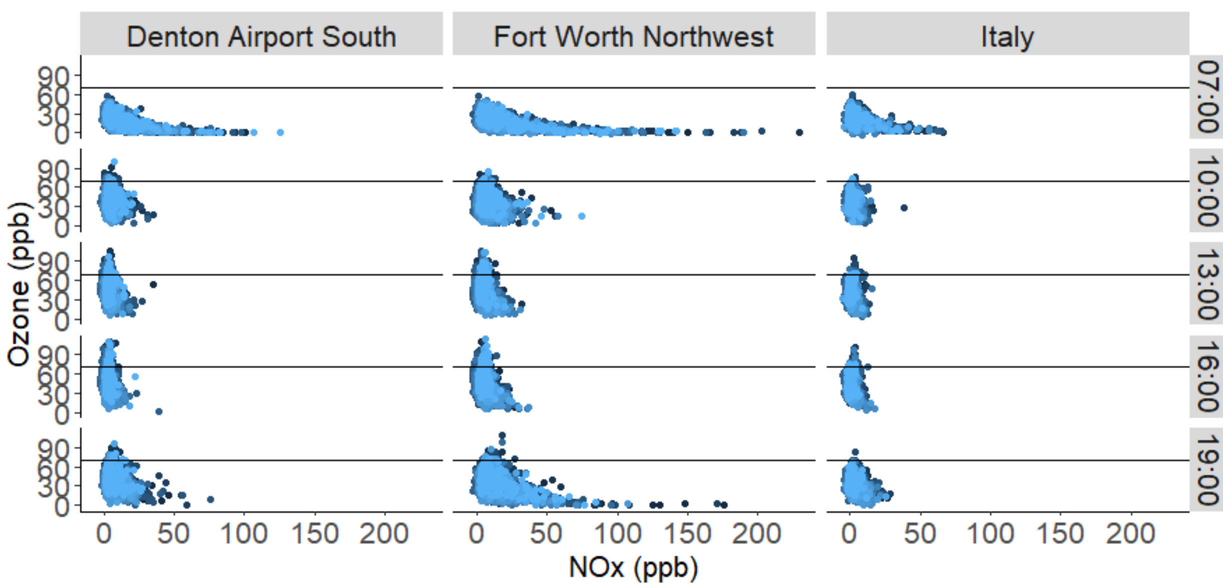


Figure 5-11: One-Hour NO_x versus One-Hour Ozone (top) and Daily Maximum NO_x versus MDA8 Ozone (bottom) in the DFW Area

Since NO_x can be converted into ozone in a photochemical process that depends on both meteorological and chemical conditions, it matters where and when high NO_x concentrations prevail. Where atmospheric conditions are favorable for ozone production, such as low wind speeds and high solar radiation, the negative relationship between ozone and NO_x is more easily detected. Under favorable conditions, NO_x tends to be higher in early morning hours before solar radiation converts it into ozone. As ozone concentrations increase during the day, NO_x concentrations fall. Later, as ozone production slows and reverses, NO_x concentrations climb again. This pattern varies greatly depending on where a site is located within the airshed. In upwind areas, where little NO_x is generated, both ozone and NO_x will be low. In an area near sources of NO_x, one may be high while the other is low, or vice versa. In areas downwind of NO_x sources, where NO_x has had sufficient time to be converted to ozone, NO_x will typically be low and ozone high.

These patterns can be seen in Figure 5-14: *One-Hour NO_x and One-Hour Ozone on High Ozone Days at Three Sites in the DFW Area* which traces the evolution of the ozone-NO_x correlation over the course of the day. Sites were selected to represent conditions upwind of the metro area (Italy), downwind (Denton Airport South), and roughly midway (Fort Worth Northwest). The first row of the figure shows the situation at 7:00 LST, the next row is three hours later, and so on through 19:00 LST. This figure illustrates that in the early morning (7:00 LST), all three sites occasionally record high concentrations of NO_x with ozone always well below the 2015 NAAQS of 70 ppb. Peak one-hour ozone at 7:00 LST on ozone exceedance days was 52.8 ppb, while maximum one-hour NO_x was 117.4 ppb. Reading down the chart for each site, it is evident that high NO_x concentrations early in the morning disappear, as ozone concentrations increase. By midday, the third and fourth rows, very few high NO_x concentrations remain, while the highest ozone concentrations are observed. By 10:00 LST in the morning, most of the high NO_x concentrations have disappeared from all three sites, with a maximum of 30.8 ppb and only a few other slightly elevated values. One-hour ozone, though, has begun to exceed 70 ppb in several instances, but only by small amounts. Maximum one-hour ozone at 10:00 LST on ozone exceedance days was 81.9 ppb. By the end of the day, ozone has begun to fall, and NO_x concentrations rise. By afternoon, 13:00 LST and 16:00 LST, no site recorded NO_x over 15 ppb, while maximum ozone was 105.4 ppb at 13:00 LST and 113.2 ppb at 16:00 LST.

This pattern is less pronounced at the upwind site, Italy, where NO_x sources are less dominant. At the urban site, Fort Worth Northwest, the highest NO_x concentrations are recorded, as well as some of the higher ozone concentrations, indicating that ozone production is proceeding. The downwind site, Denton Airport South, has high NO_x concentrations in the early morning, but not the highest, while ozone concentrations there in the afternoon are among the highest observed in the metro area. This suggests that NO_x from upwind has been converted into ozone by the time it reaches the downwind site. As solar radiation begins to fall in the late afternoon and the ozone reaction reverses, NO_x begins to accumulate once again, with a one-hour maximum of 59.0 ppb and a one-hour ozone maximum of 107.7 ppb.



Source: Texas Air Monitoring Information System.

Figure 5-12: One-Hour NO_x and One-Hour Ozone on High Ozone Days at Three Sites in the DFW Area

5.4 METEOROLOGICALLY-ADJUSTED OZONE CONCENTRATIONS

Variation in ozone concentrations is impacted by variations in emissions and transport of ozone precursors, both local and non-local, and the meteorological environment in which those precursors interact to form ozone. Comparisons of ozone concentrations across years can be confounded by natural variation in meteorology from year to year but accounting for this variation is complex.

To facilitate meteorologically-unbiased comparisons, the EPA uses a complex statistical approach (Wells, 2021) to estimate annual mean, 90th and 98th percentile values of meteorologically-adjusted maximum daily eight-hour average (MDA8) ozone concentrations at individual surface monitors. Discussion of the approach and selected model results are on the EPA web site (www.epa.gov/air-trends/trends-ozone-adjusted-weather-conditions). Trends for each ozone monitor are fit independently using local ozone and meteorological measurements.

98th percentile values were selected for analysis because that statistic is most similar to an annual fourth highest value, which is the value used to compute the three-year design value. The minimum and maximum ranges of the annual distributions of these values for the twenty ozone monitors in the DFW area are plotted in Figure 5-15: *Meteorologically Adjusted Ozone Trends for May through September in the DFW Area*. Thick lines were overlaid on the plot to highlight and connect annual medians of these distributions. Both meteorologically-adjusted and unadjusted 98th percentile ozone concentrations appear to have declined over the decade, although there is a great deal of variation even in the adjusted distributions. It is noteworthy that annual 98th percentile MDA8 ozone concentrations declined even when adjusted for meteorology, suggesting that other factors besides meteorology, particularly local emissions, are contributing less to ozone formation. However, excluding the first two years, the trend has been mostly flat. Note that the median annual adjusted 98th percentile MDA8 ozone concentration in 2021 was 72.7 ppb at Grapevine Fairway, compared to the actual unadjusted 2021 value of 75.7.

Ordinary least squares regression on annual median adjusted and unadjusted values estimated an annual rate of decline of roughly 0.81 ppb per year for the unadjusted median, while the model estimate of the rate of decline of adjusted medians is lower, 0.54 ppb per year. Even though the slope of the adjusted model is flatter than the unadjusted slope, the adjusted model has a larger coefficient of determination (R^2): 0.43 compared to 0.29, suggesting that there is less variability after adjustment. This is intuitive because adjusting for meteorology removes one very large and influential factor resulting in less variability in ozone, a sort of "regression to the mean." Unadjusted values above the mean adjust down and unadjusted values below the mean adjust up.

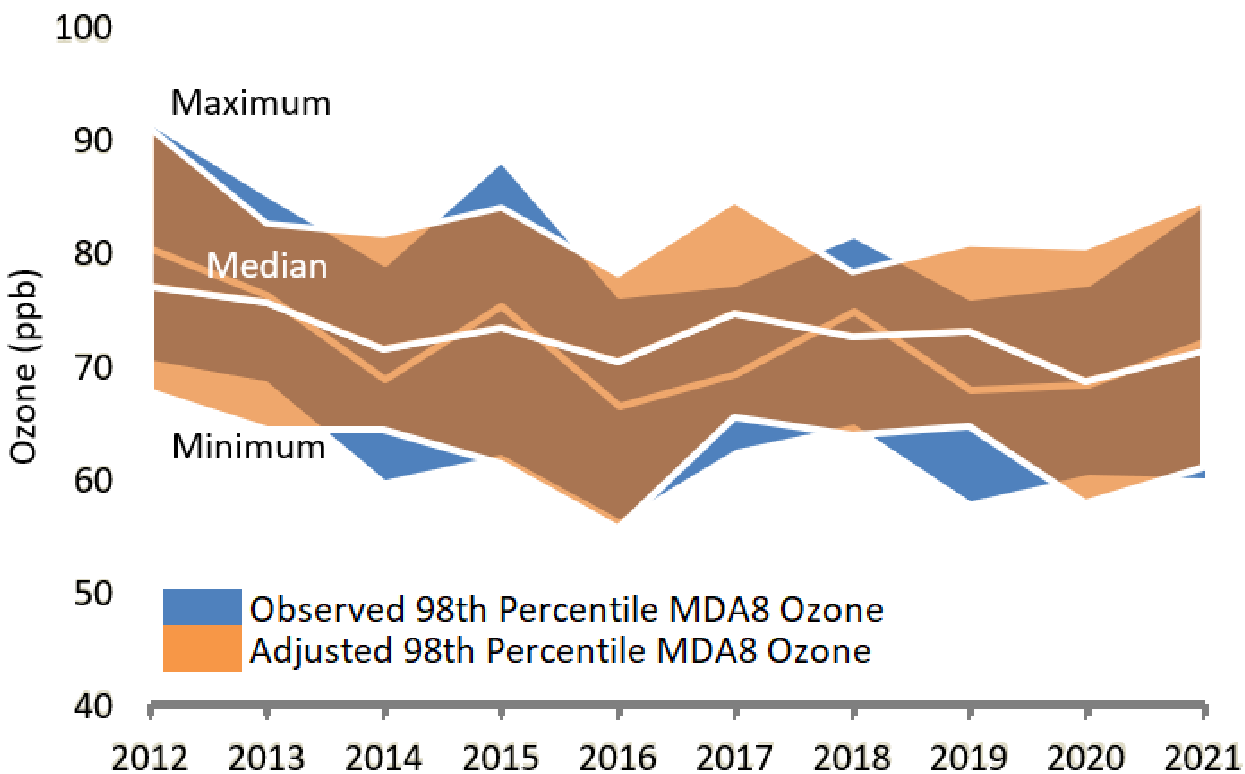


Figure 5-13: Meteorologically Adjusted Ozone Trends for May through September in the DFW Area

CHAPTER 6: CONCLUSIONS

This conceptual model provides a detailed examination of ozone formation in the Dallas-Fort Worth (DFW) area with a focus on ozone levels above 70 parts per billion (ppb). Most of the analyses in this conceptual model focus on ten years of ozone season data, 2012 through 2021. This focus allowed the analyses to incorporate newer data and to investigate recent changes in how, when, and where ozone forms in the DFW area.

From 2012 through 2021, eight-hour ozone design values in the DFW area have decreased 12.6%. The area monitors attainment of the 1997 eight-hour ozone standard of 84 ppb but was designated as nonattainment of the 70 ppb 2015 eight-hour ozone standard. Maximum eight-hour ozone design values typically occur in the north and northwest portion of the DFW area, while the lowest eight-hour ozone design values occur to the southeast. Fourth-highest eight-hour ozone values, which are used to calculate design values, have remained flat.

At a threshold of 70 ppb, the ozone season in the DFW area peaks in May and again in August, with a low occurring in July. Although peak ozone occurs in May and August, high ozone concentrations can occur anytime from March through October. Much of the analysis in this conceptual model focused on the months of March through October to capture the ozone formation process during this important period.

During the ozone season, the highest one-hour ozone occurs between 15:00 Local Standard Time (LST) through 17:00 LST. 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 the metropolitan area 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 north and northwest, where the highest ozone concentrations typically occur.

Regional background ozone coming into the DFW area is well correlated with daily-maximum eight-hour ozone concentrations. Trends in ozone in the DFW area appear to change primarily with changes in background ozone concentrations. Although it varies year-to-year, overall, estimates of local ozone production in the DFW area has not changed much over the past ten years. On high ozone days, both background ozone and ozone produced locally increase proportionally, indicating that meteorological conditions that cause high ozone in the DFW area also cause high regional background ozone. The spring season observed the highest background ozone while the late summer season observed the highest local ozone production. This indicates that the spring ozone season is characterized by high background ozone coming into the DFW area while the late-summer ozone season is characterized by more local ozone production.

Ozone is not directly emitted into the atmosphere, but rather formed through a photochemical reaction with nitrogen oxides (NO_X) and volatile organic compounds (VOC). Examination of ambient NO_X concentrations showed that, over the past ten years, peak NO_X has decreased across the DFW area. Comparing only monitors that were in operation for the full ten years, median NO_X concentrations dropped 10.4%

from 4.0 ppb to 3.5 ppb, while 95th percentile NO_x concentrations fell 13.0% from 20.0 ppb to 17.4 ppb. Two near-road monitors deployed in 2014 and 2015 now record among the highest NO_x values, underscoring the importance of motor vehicle emissions in the DFW airshed.

Median ambient total nonmethane organic compounds (TNMOC) concentrations dropped by 16.7% over the ten-year period, 2012 through 2021, while 95th percentile ambient concentrations fell 27.2%. Isoprene, ethylene, toluene, and propylene, all VOC with high ozone formation potential, and ethane, propane, and n-butane, VOC with low ozone formation potential, contribute the most to total VOC concentrations observed in the DFW area. When weighted by reactivity, isoprene, ethane, ethylene, and toluene contribute the most to total VOC. The VOC with lower reactivities have such large concentrations in the DFW area that they still contribute a large portion to total VOC composition even when weighted by reactivity. Principal Components Analysis was used to group individual VOC species that have similar characteristics into four factors. The first factor was dominated by isoprene from vegetation. Two factors included compounds associated with emissions from oil and gas extraction, one made up of short-lived compounds and the other longer-lived compounds. The fourth factor included compounds associated with many industrial activities, as well as motor vehicle exhaust.

From 2012 through 2021, NO_x emissions decreased 26% and VOC emissions decreased 32% in the DFW area.

The VOC or NO_x limitation of an air mass can determine if decreases in either NO_x (NO_x limited) or VOC (VOC limited) would have a larger effect on ozone concentrations. VOC-NO_x ratios vary across the day at all sites studied, starting in the NO_x limited regime in the early morning hours, transitioning to more VOC limited or transitional as motor vehicle traffic increases. The ratio differs according to location in the urban area, with urban cites maintaining a transitional or more VOC limited regime, and rural sites being more NO_x limited, likely due to an abundance of VOC such as isoprene and fewer NO_x sources.

Analysis of ozone and precursors on weekdays versus weekends shows that there is lower NO_x and lower ozone on weekends, particularly Sundays. VOCs from mobile sources are also lower on weekends. The change is mostly due to changes in rush hour traffic patterns that occur on the weekends. The decreasing ozone concentrations that occur with the decreasing NO_x on the weekend are an indicator that the air mass in DFW is NO_x limited.

Meteorological conditions linked to high ozone in the DFW area include high temperatures, low relative humidity, and slow wind speeds. Ozone season winds are generally from the southeast. On high ozone days, surface winds indicate reversals in wind direction. 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 occurs when upper-level winds bring continental air into the area or when winds are slow and there is recirculation.

Investigation of NO_x and ozone by wind speed and direction shows high NO_x from downtown. At the Eagle Mountain Lake and Denton Airport South monitors, located to the north and northwest of the urban core, the highest ozone concentrations originate from the southeast. Other monitors located on the periphery of the urban area also indicate influence from the urban area, suggesting that ozone is first produced from emissions from the urban area and then transported downwind.

Overall, it appears that high ozone in the DFW area mostly occurs from April through June and from August through October. High ozone typically occurs on hot sunny days with dry conditions and slow wind speeds out of the southeast. Emissions located south and southeast of the area combine with urban area mobile-source emissions to create ozone and transport it to the monitors located in the north and northwest. Ozone accumulation is further exacerbated by shifting wind directions that occur throughout the day. In addition, these conditions also create high levels of regional background ozone, which combines with the local ozone and emissions to produce eight-hour ozone levels more than 70 ppb. Ozone chemistry on these days appears to be NO_x limited to transitional. Because the dominant VOCs in the area are either naturally occurring or have low ozone formation potential, NO_x controls would be expected to be more effective in decreasing ozone in the area compared to VOC controls.

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