#### **APPENDIX B**

#### CONCEPTUAL MODEL FOR THE DALLAS-FORT WORTH NONATTAINMENT AREA FOR THE 2008 EIGHT-HOUR OZONE NATIONAL AMBIENT AIR QUALITY STANDARD

Dallas-Fort Worth Severe Area Attainment Demonstration State Implementation Plan Revision for the 2008 Eight-Hour Ozone National Ambient Air Quality Standard

> Project Number 2023-107-SIP-NR SFR-122/2023-107-SIP-NR

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#### **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 75 parts per billion (ppb). Ozone formed through a photochemical reaction with nitrogen oxides ( $NO_x$ ) and volatile organic compounds (VOC) is investigated in this conceptual model. Most of the analyses in this conceptual model focus on March through October from 2012 through 2022. These analyses 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 11.5% from 2012 through 2022. Median annual ambient  $NO_x$  concentrations at monitors operating during the eleven-year period decreased 15.7%, while 95th percentile values at those monitors decreased 4.5%. Median annual ambient VOC concentrations, represented by total non-methane hydrocarbons (TNMHC), decreased 24.5%, while 95th percentile values decreased 27.2%.

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

- Ozone formation peaks with the highest frequency of high-ozone days occurring from April through June and then again from August through October, with a mid-summer minimum occurring in July. This minimum results from 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 75 ppb.
- Ozone chemistry in the DFW area appears to be NO<sub>x</sub> limited to transitional. The dominant VOC in the area are either naturally occurring isoprene from vegetation, or have low ozone formation potential; therefore, control of VOC would have less effect on ozone concentrations in the DFW area compared to NO<sub>x</sub> controls.

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## **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 tencounty Dallas-Fort Worth (DFW) non-attainment area for the 2008 eight-hour National Ambient Air Quality Standard (NAAQS) of 0.075 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, TCEQ 2023).

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 2022.

## 1.1 GENERAL DESCRIPTION OF OZONE FORMATION

Ozone is formed through a complex series of chemical reactions of oxides of nitrogen (NO<sub>x</sub>) 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: Collin, Dallas, Denton, Ellis, Johnson, Kaufman, Parker, Rockwall, 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.

Previous conceptual models for the DFW area were prepared as part of the serious (2020) and moderate (2016, 2023) 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.

## 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 in Texas, and among the most thoroughly monitored regions in the U.S. This conceptual model will focus on monitors in operation in 2022 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 NAAOS. Figure 1-1: Monitors in the DFW Nonattainment Area shows the locations of these sites. These twenty monitors include four located in counties that are not designated as nonattainment counties (Hood, Hunt, and Navarro) for ozone but are included because they were deployed for the specific purpose of monitoring atmospheric conditions on the extreme periphery of the DFW area. Details of each monitor, including the parameters measured, are in Table 1-1: Monitors in the DFW Nonattainment Area. More details on monitors can be found on the Texas Commission on Environmental Quality (TCEQ) Air Monitoring Sites webpage (https://www.tceg.texas.gov/airguality/monops/sites/air-mon-sites).

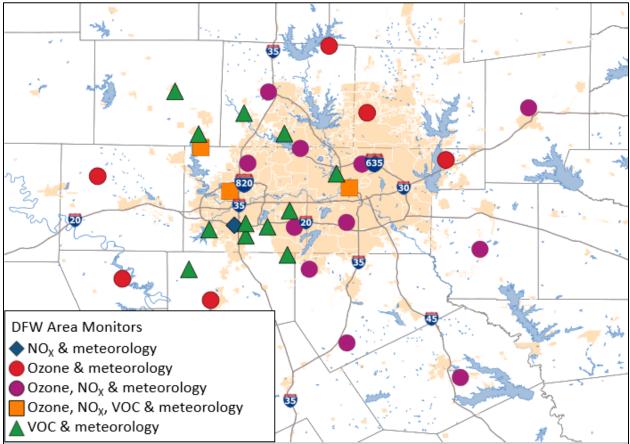


Figure 1-1: Monitors in the DFW Nonattainment Area

| Monitor Name                        | AQS No.1  | CAMS No.2                 | Compound or Parameter<br>Measured   |
|-------------------------------------|-----------|---------------------------|---|
| Frisco                              | 480850005 | 0031, 0680                | Ozone, meteorology  |
| Dallas Hinton                       | 481130069 | 0060, 0161,<br>0401, 3002 | Ozone, meteorology, VOC, PM <sub>2.5</sub> <sup>3</sup> , NO <sub>2</sub> |
| Dallas North #2                     | 481130075 | 0063, 0679                | Ozone, NO <sub>x</sub> , meteorology                                      |
| Dallas Redbird Airport<br>Executive | 481130087 | 0402                      | Ozone, NO <sub>x</sub> , meteorology                                      |
| Dallas LBJ Freeway                  | 481131067 | 1067                      | NO <sub>x</sub> , meteorology   |
| Dallas Elm Fork                     | 481131505 | 1505                      | VOC, meteorology  |
| Denton Airport South                | 481210034 | 0056, 0157,<br>0163       | Ozone, NO <sub>x</sub> , PM <sub>2.5</sub> ,<br>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 <sub>x</sub> , PM <sub>2.5</sub> ,<br>meteorology               |
| Italy                               | 481391044 | 1044                      | Ozone, NO <sub>x</sub> , meteorology                                      |
| Granbury                            | 482210001 | 0073, 0681                | Ozone, meteorology  |
| Greenville                          | 482311006 | 0198, 1006                | Ozone, NO <sub>x</sub> , meteorology                                      |

| Monitor Name                           | AQS No.1  | CAMS No.2  | Compound or Parameter<br>Measured                                |
|--|-----------|------------|--|
| Cleburne Airport                       | 482510003 | 0077, 0682 | Ozone, meteorology   |
| Mansfield Flying L Lane                | 482511063 | 1063       | VOC, meteorology   |
| Godley FM2331                          | 482511501 | 1501       | VOC, meteorology   |
| Kaufman                                | 482570005 | 0071       | Ozone, NO <sub>x</sub> , PM <sub>2.5</sub> ,<br>meteorology      |
| Corsicana Airport                      | 483491051 | 1051       | Ozone, NO <sub>x</sub> , PM <sub>2.5</sub> ,<br>meteorology      |
| Parker County                          | 483670081 | 0076       | Ozone, meteorology   |
| Rockwall Heath                         | 483970001 | 0069       | Ozone, meteorology   |
| Eagle Mountain Lake                    | 484390075 | 0075       | Ozone, NO <sub>x</sub> , VOC, meteorology                        |
| Fort Worth Northwest                   | 484391002 | 0013       | Ozone, NO <sub>x</sub> , VOC, PM <sub>2.5</sub> ,<br>meteorology |
| Everman Johnson Park                   | 484391009 | 1009       | VOC, meteorology   |
| Arlington UT Campus                    | 484391018 | 1018       | VOC, meteorology   |
| Fort Worth California<br>Parkway North | 484391053 | 1053       | PM <sub>2.5</sub> , NO <sub>x</sub> , meteorology                |
| Kennedale Treepoint<br>Drive           | 484391062 | 1062       | VOC, meteorology   |
| Fort Worth Joe B.<br>Rushing Road      | 484391065 | 1065       | VOC, meteorology   |
| Fort Worth Benbrook<br>Lake            | 484391503 | 1503       | VOC, meteorology   |
| Keller                                 | 484392003 | 0017       | Ozone, NO <sub>x</sub> , meteorology                             |
| Grapevine Fairway                      | 484393009 | 0070, 0182 | Ozone, NO <sub>x</sub> , meteorology                             |
| Arlington Municipal<br>Airport         | 484393011 | 0061       | Ozone, NO <sub>x</sub> , meteorology                             |
| Decatur Thompson                       | 484970088 | 0088       | VOC, meteorology   |
| Rhome Seven Hills<br>Road              | 484971064 | 1064       | VOC, meteorology   |

<sup>1</sup> AQS: EPA's Air Quality System.
 <sup>2</sup> CAMS: Continuous Air Monitoring System.
 <sup>3</sup> 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 2022. 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 2008 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 2008 eight-hour ozone NAAQS when its design value exceeds 0.075 parts per million (ppm), or 75 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 nonattainment.

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 Nonattainment Area*. The 2022 eight-hour ozone design value for the DFW nonattainment area is 77 ppb. This design value represents an 11.5% 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 four ppb from 2014 through 2022.

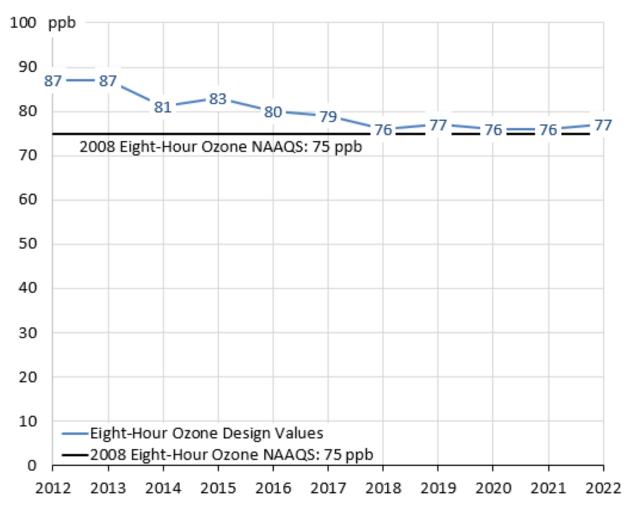


Figure 2-1: Eight-Hour Ozone Design Values in the DFW Nonattainment Area

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 Nonattainment Area* shows that the range of design values has been decreasing across the entire DFW area. While in 2012, 16 monitors failed to attain the 2008 ozone NAAQS of 75 ppb, by 2022, only five monitors did not attain the 2008 ozone NAAQS.

Five different monitors recorded the area-wide maximum design value over the tenyear 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 #2 recorded the maximum design value. Finally, in 2021 and 2022, Pilot Point recorded maximum area-wide design values of 76 and 77 ppb, respectively.

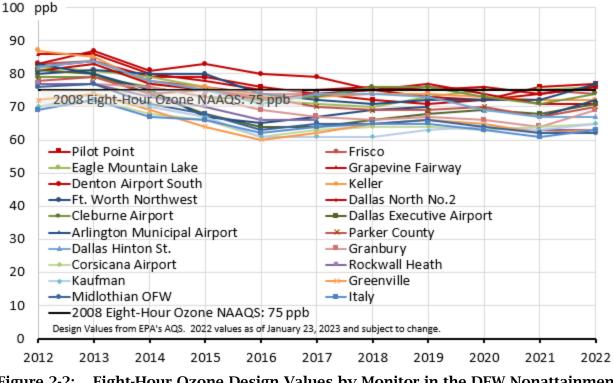


Figure 2-2: Eight-Hour Ozone Design Values by Monitor in the DFW Nonattainment Area

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, 2017, and 2022 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 Nonattainment 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.

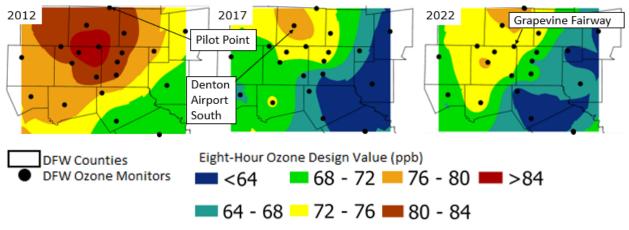


Figure 2-3: Eight-Hour Ozone Design Value Maps for the DFW Nonattainment Area

# 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 MDA8 Ozone Concentrations by Monitor in the DFW Nonattainment Area* spans 2010 through 2022 to encompass all years used in computations of design values over the eleven-year period.

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. 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.

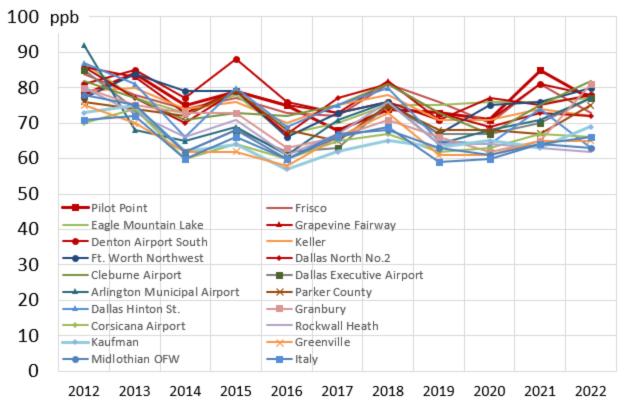


Figure 2-4: Fourth-Highest MDA8 Ozone Concentrations by Monitor in the DFW Nonattainment Area

This variability at individual monitors suggests that controlling fourth-highest values is a difficult task. For example, the Pilot Point monitor currently sets the eight-hour ozone design value for the DFW area, 77 ppb in 2022. This value is the truncated average of fourth-highest values of 71 ppb in 2020, 85 ppb in 2021, and 77 ppb in 2022.

# 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 2008 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 75 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 2008 NAAQS each year is presented in Figure 2-5: *Eight-Hour Ozone Exceedance Days in the DFW Nonattainment Area.* The number of ozone exceedance days declined over the eleven-year period from 60 days to 48 days, a 20% decrease.

There is substantial variability in the number of exceedance days per year over the eleven-year period.

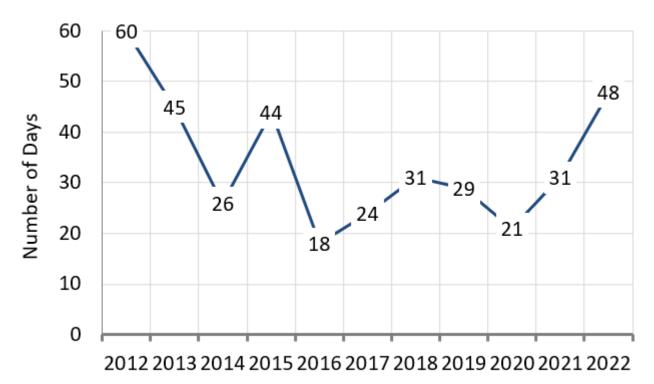


Figure 2-5: Eight-Hour Ozone Exceedance Days in the DFW Nonattainment Area

# 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 U.S., 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 standard of 75 ppb. Figure 2-6: *Ozone Exceedance Days by Year in the DFW Nonattainment Area* shows data from the twenty DFW area ozone monitors from 2012 through 2022. The number of 75 ppb exceedances dropped 72% from 2012 to 2017. In 2022, however, the number of days exceeding the 2008 standard increased to 43, 330%

higher than 2017 and even 19% higher than 2012. Since local emissions tend to not fluctuate within such a short periods of time, this is evidence that there was a non-local factor, such as meteorology, that affected the ozone concentrations in those years.

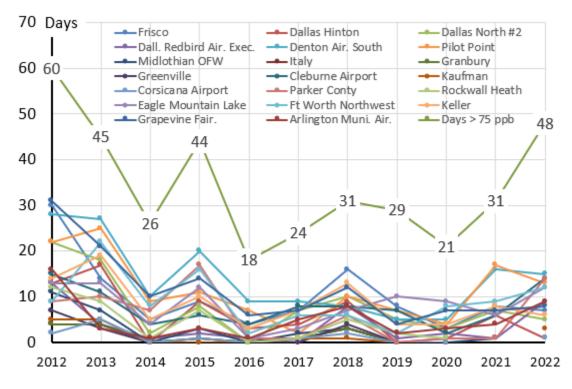


Figure 2-6: Ozone Exceedance Days by Year in the DFW Nonattainment Area

# 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 were 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 were also investigated. All days that do not meet the definition of high ozone days are classified as low ozone days.

Figure 2-7: *Time of Day of Peak Ozone in the DFW Nonattainment 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 31% of all daily maxima, with 70% of all daily maxima occurring within one hour of 16:00, either before or after. All sampling times are reported in LST even though the DFW area uses local daylight time (LDT) during most of ozone season.

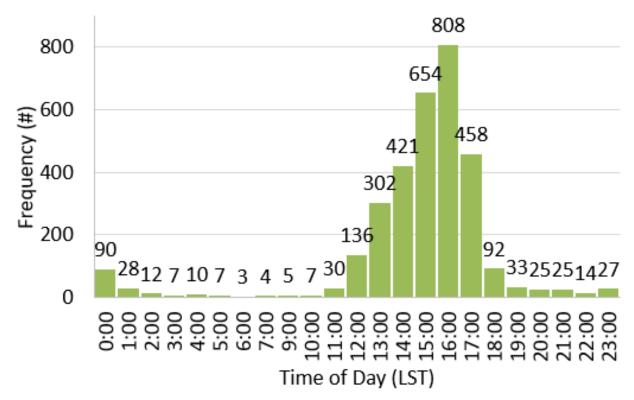


Figure 2-7: Time of Day of Peak Ozone in the DFW Nonattainment Area

The average time of peak one-hour ozone during the ozone season was calculated from 2012 through 2022 for both high and low eight-hour ozone days. The analysis used time values in local standard time (LST). Results are listed in Table 2-1: *Average Time of Maximum One-Hour Ozone in the DFW Area.* Although peak ozone times vary each year, there has not been an overall change in the time of peak ozone over the past eleven years. More notable is that ozone peaks later in the day on high ozone days compared to low ozone days. On average, ozone peaks around 14:26 LST on low ozone days but on high ozone days it peaks at around 15:34 LST. This is an indication of slower winds that are typical on high ozone days, which would allow for longer accumulation times for ozone.

| Nonattainment Area |                      |                       |                  |
|--------------------|----------------------|-----------------------|------------------|
| Year               | Low Ozone Days (LST) | High Ozone Days (LST) | Difference (LST) |
| 2012               | 14:28                | 15:13                 | 0:45             |
| 2013               | 14:18                | 15:22                 | 1:04             |
| 2014               | 14:50                | 15:25                 | 0:35             |
| 2015               | 14:12                | 15:38                 | 1:26             |
| 2016               | 14:19                | 15:38                 | 1:19             |
| 2017               | 14:43                | 16:00                 | 1:17             |
| 2018               | 14:10                | 15:40                 | 1:30             |
| 2019               | 14:22                | 16:09                 | 1:47             |
| 2020               | 14:11                | 15:45                 | 1:34             |

Table 2-1:Average Time of Maximum One-Hour Ozone in the DFWNonattainment Area

| Year    | Low Ozone Days (LST) | High Ozone Days (LST) | Difference (LST) |
|---------|----------------------|-----------------------|------------------|
| 2021    | 14:23                | 15:30                 | 1:07             |
| 2022    | 14:53                | 15:47                 | 0:54             |
| Average | 14:26                | 15:34                 | 1:08             |

## 2.6 BACKGROUND OZONE

Regional background ozone is defined as ozone present in the air entering an area from outside the area, or as ozone in the local air mass that has not been influenced by emissions from the area of interest. There are several ways 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, examination of background ozone provides insight into whether observed ozone changes are from locally produced ozone or from transported ozone.

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 was then estimated as the lowest MDA8 ozone value observed at the selected background sites for each ozone season day from 2012 through 2022.

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. These perimeter monitors were selected to avoid low biased ozone concentrations found in the urban core as a result of high NO<sub>x</sub> emissions, which scavenge ozone through NO<sub>x</sub> titration. NO<sub>x</sub>-influenced low urban ozone concentrations can underestimate background ozone concentrations.

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.

Over the entire decade, median background ozone was 35 ppb on low ozone days, increasing to 50 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 73%. Locally produced ozone accounted for approximately 27% 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 2-8: *Trends in MDA8 Ozone, Background Ozone, and Locally Produced Ozone for High versus Low Ozone Days,* simple linear ordinary least squares regressions were run. Annual average background ozone appeared to be declining by -0.72 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 0.69 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.

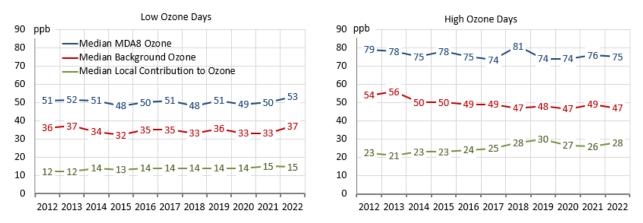


Figure 2-8: Trends in MDA8 Ozone, Background Ozone, and Locally Produced Ozone for High versus Low Ozone Days

Trends in background ozone for both high and low ozone days show little correlation with MDA8 ozone. This is seen in Figure 2-9: *Background Ozone versus MDA8 Ozone for the Ozone Season in the DFW Area from 2012 through 2022*. Ozone data from 2012 through 2022 show that background ozone and MDA8 ozone have little correlation on low ozone days, with a correlation coefficient of 0.56 for low ozone. High ozone days are even less correlated with background ozone, with a correlation coefficient of only 0.08. This indicates that ozone formation in the DFW area is driven by transported, or regional background ozone, as well as local ozone formation in the area.

Past conceptual models for the DFW area have also found a seasonality in background ozone concentrations, which was also corroborated by other studies (Mountain 2022). To investigate how background ozone may change throughout the ozone season, the median background ozone, median MDA8 ozone, and median locally produced eighthour ozone in the DFW area was calculated for each ozone season month from 2012 through 2021. Results were then further divided into high and low ozone days to explore possibly differences on ozone exceedance days.

Results are displayed in Figure 2-9: *Background Ozone, MDA8 Ozone, and Locally Produced Ozone by Month from 2012 through 2022 in the DFW Nonattainment Area.* 

There appear to be similar seasonal patterns for both high and low ozone days. The background ozone appears highest in the spring and early fall, with the lowest background levels observed in July and August. For low ozone days, locally produced ozone is larger than the background during the summer (June through August). This same pattern is observed on high ozone days as well, but the local ozone production on high ozone days in the summer is slightly lower than the background. These trends indicate that high ozone levels in the early part of the ozone season are driven by transported ozone rather than locally produced ozone. High ozone levels in the later part of the ozone season, most notably in August, appear to be driven more by local ozone production.

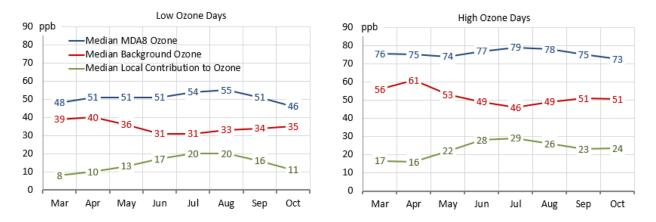


Figure 2-9: Background Ozone, MDA8 Ozone, and Locally Produced Ozone by Month from 2012 through 2022 in the DFW Nonattainment Area

### CHAPTER 3: OZONE PRECURSOR CONCENTRATIONS AND TRENDS

As a secondary pollutant, ozone is formed through photochemical reactions with nitrogen oxides (NO<sub>x</sub>) 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<sub>x</sub> and VOC concentration and emissions trends in the Dallas-Fort Worth (DFW) area.

#### 3.1 AMBIENT NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> concentrations, it is helpful to distinguish between days when NO<sub>x</sub> 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<sub>x</sub> concentrations during ozone season were used to calculate yearly median and 95th percentile NO<sub>x</sub> trends. The 95th percentile was examined to show the upper end of the NO<sub>x</sub> distribution while the median was examined to show the central tendency of NO<sub>x</sub> concentrations in the DFW area. Figure 3-1: *Ozone Season NO<sub>x</sub> Trends in the DFW Nonattainment Area* shows the 95th percentile ozone season NO<sub>x</sub> concentration rose 24.5% from 20.0 parts per billion (ppb) to 24.9 ppb, while the median dropped 5.6% to roughly 3.7 ppb. However, these trends are biased by inclusion of near-road monitors in 2022 values but not in 2012 values. Excluding near-road monitors, 95th percentile and median NO<sub>x</sub> concentrations fell 4.5% and 15.7%, respectively. Beginning in 2016, the first full year of measurements from

both near-road monitors, 95th percentile concentrations changed only modestly, increasing 6.0%, while median  $NO_x$  concentrations rose 2.8%.

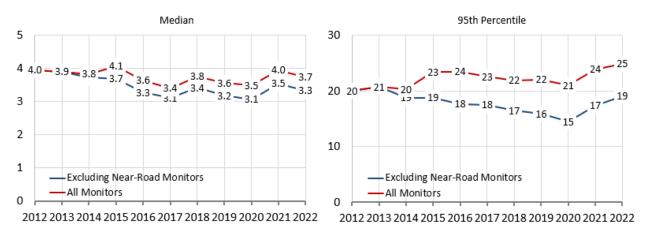


Figure 3-1: Ozone Season NO<sub>x</sub> Trends in the DFW Nonattainment Area

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 Nonattainment 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 nearroad  $NO_x$  monitors in April 2014 (Dallas LBJ Freeway) and March 2015 (Fort Worth California Parkway North).

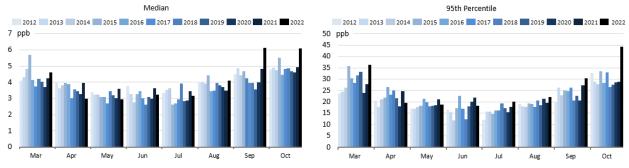


Figure 3-2: Monthly NO<sub>x</sub> Trends in the DFW Nonattainment Area

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 Nonattainment 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.

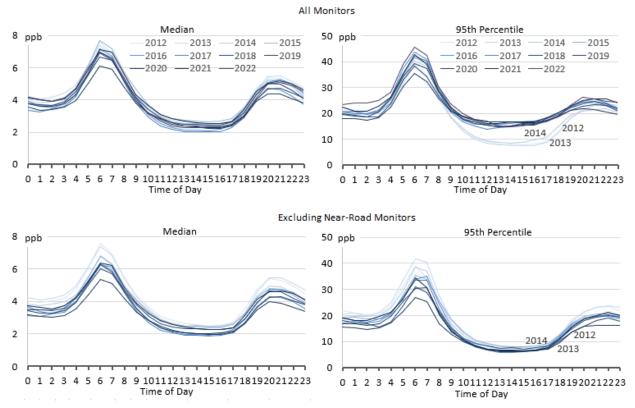


Figure 3-3: Ozone Season Hourly NO<sub>x</sub> Trends in the DFW Nonattainment Area

This pattern with near-road monitors becomes clear when presented for individual monitors as shown in Figure 3-4: *Ozone Season NO<sub>x</sub> Trends by Monitor in the DFW Nonattainment 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<sub>x</sub> concentrations, although they were not always the highest. Dallas Hinton typically recorded the highest 95th percentile NO<sub>x</sub> concentrations, although NO<sub>x</sub> monitoring at this monitor ceased after 2019.

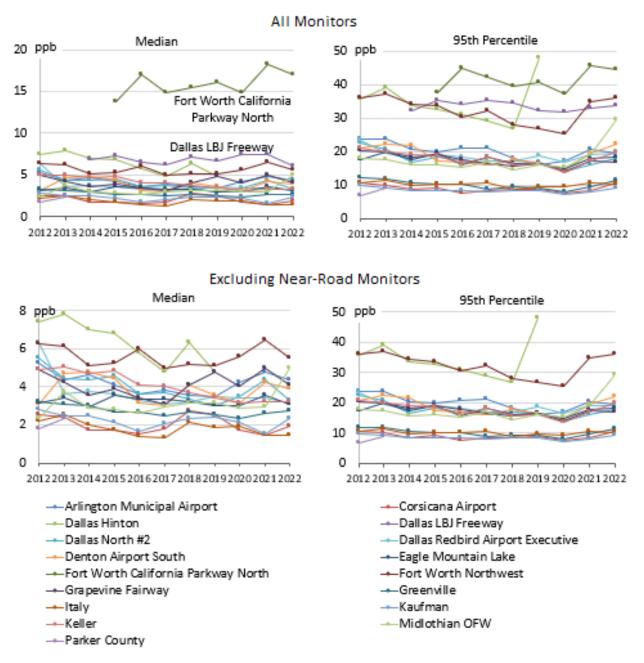


Figure 3-4: Ozone Season NO<sub>x</sub> Trends by Monitor in the DFW Nonattainment Area

### 3.2 AMBIENT VOC COMPOSITION AND TRENDS

VOC participate in ozone formation chemistry in combination with NO<sub>x</sub> 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. Due to the reactive nature of some VOC, hourly auto-GC measurements are preferred when assessing trends.

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 were first checked for validity. Only monitors that had eight or more valid years of data for the ozone season from 2012 through 2022 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. The 95th percentile was examined to show trends at the highest levels while the median was examined to show the central tendency of TNMOC concentrations in the DFW area. Ozone season trends for ambient TNMOC concentrations are presented in Figure 3-5: *Ozone Season Median and 95th Percentile TNMOC Trends in the DFW Nonattainment Area.* TNMOC is plotted 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 2022, by 24.5% and 27.2% respectively.

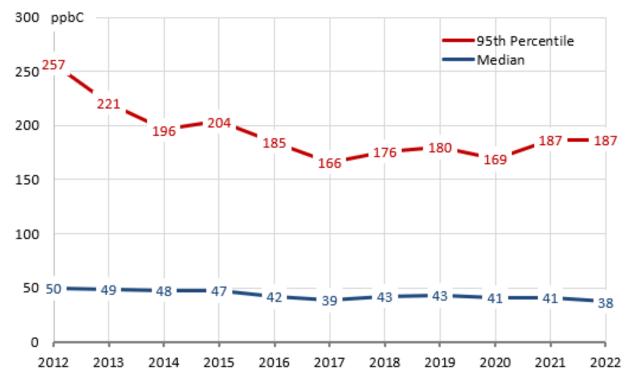


Figure 3-5: Ozone Season Median and 95th Percentile TNMOC Trends in the DFW Nonattainment Area

Monthly trends in median and 95th percentile TNMOC concentrations for the DFW area are shown in Figure 3-6: *Monthly TNMOC Trends in the DFW Nonattainment Area*. Ambient TNMOC concentrations follow a seasonal pattern, typically lower in summer and higher in winter for both medians and 95th percentiles. Only two months, September and October, exhibited increases over the decade for one of the statistics, the 95th percentile, and these increases were only 2.4% and 17.2% by 2022. These 2022 medians were 6.7% and 13.4% below the highest medians of the eleven year period for each month.

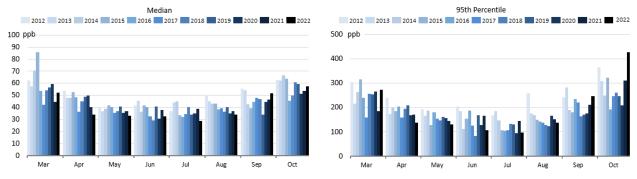


Figure 3-6: Monthly TNMOC Trends in the DFW Nonattainment Area

Diurnal trends in ozone season TNMOC for the DFW area are displayed in Figure 3-7: *Ozone Season Hourly TNMOC Trends in the DFW Nonattainment Area.* Hourly trends in

median TNMOC show a morning peak similar to that of  $NO_x$ , at around 6:00 LST. Hourly trends in 95th percentile TNMOC follow a similar pattern but with greater variability. Since VOC are reactive in the presence of sunlight, higher concentrations are more likely to be measured overnight.

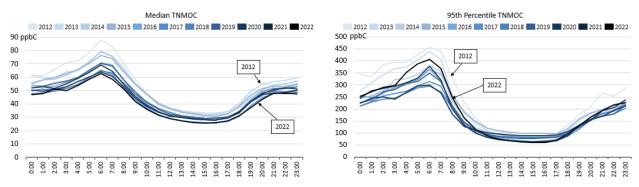


Figure 3-7: Ozone Season Hourly TNMOC Trends in the DFW Nonattainment Area

To determine if area-wide increases occurred throughout the DFW area or only at specific monitors, TNMOC trends by monitor are shown in Figure 3-8: *Ozone Season TNMOC Concentrations by Monitor in the DFW Nonattainment Area.* Results show all but one monitor across the DFW area exhibited decreases in median TNMOC over the eleven-year period. The one monitor with an increase in median TNMOC was Dallas Hinton with a trivial increase of 0.7%. Nine of fifteen auto-GCs observed the lowest median TNMOC concentrations over the period in 2022. The other six all recorded minimum medians in 2017.

Monitor-level trends in 95th percentile concentrations were not as straightforward as trends in medians, with only one monitor, Mansfield Flying L Lane, recording its series minimum in 2022. Five monitors recorded their lowest 95th percentile TNMOC concentrations in 2017, five others in 2020, and four in 2021. All but three monitors recorded decreases in 95th percentile TNMOC over the 2012 through 2022 period. One of these was Dallas Hinton, which recorded an 11.2% increase. Another was Arlington UT Campus with a 2.7% increase. However, one anomalous monitor, DISH Airfield, recorded an 18.2% increase in the 95th percentile TNMOC concentration over the 2012 through 2022 period. The 2022 value, 732.5 ppbC, was 90% higher than the series minimum recorded in 2020, 384.6 ppbC. This monitor typically recorded substantially higher 95th percentile TNMOC concentrations compared to all other auto-GCs in the DFW area.

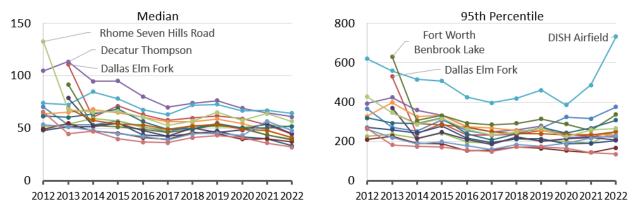


Figure 3-8: Ozone Season TNMOC Concentrations by Monitor in the DFW Nonattainment Area

The conceptual model (Appendix B) for the DFW Moderate Attainment Demonstration SIP (TCEQ, 2023) evaluated the magnitudes of individual ambient VOC species in the DFW area and found that isoprene is the dominant reactive species.

# 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 onroad, 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<sub>x</sub> 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 2022 and beyond, even as daily VMT is estimated to increase. This reduction in on-road NO<sub>x</sub> 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 analysis using the Texas NONROAD (TexN) model. Non-road emissions are estimated to decrease from 1999 through 2022 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<sub>x</sub> Emissions Trends

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 2022 were not available in time to be included in this analysis. The emissions trends analysis uses ten years of data from 2012 through 2021.

Emissions trends by site are displayed in Figure 3-9: *Point Source NO<sub>x</sub> Emissions by Site in the DFW Nonattainment 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<sub>x</sub> emission trends show that the top nine reporting sites accounted for 60% of the total point source NO<sub>x</sub> emissions in the DFW area in 2021. Each of these sites report total NO<sub>x</sub> emissions exceeding 200 tons in 2020. The overall trend in NO<sub>x</sub> emissions is a decline of 26% since 2012.

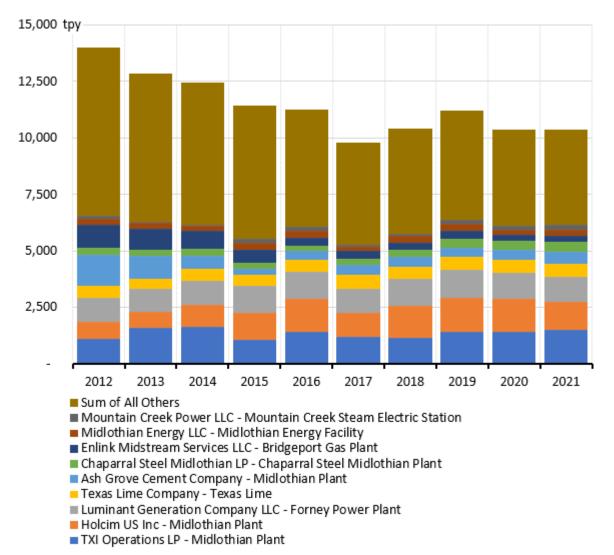


Figure 3-9: Point Source NO<sub>x</sub> Emissions by Site in the DFW Nonattainment Area

Figure 3-10: *Map of 2021 Point Source*  $NO_x$  *Emissions Sources in the DFW Nonattainment 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.

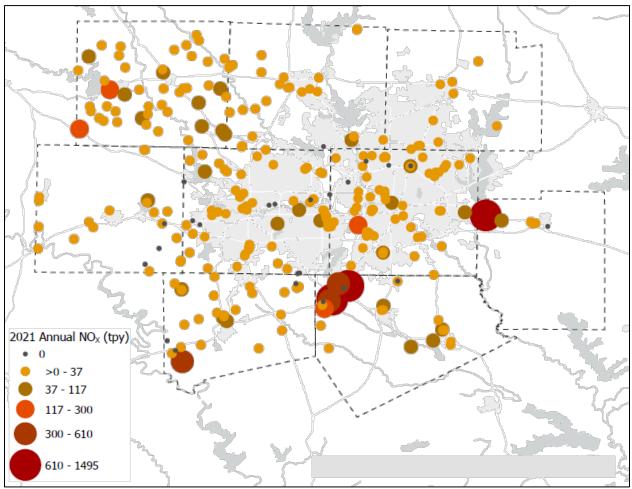


Figure 3-10: Map of 2021 Point Source NO<sub>x</sub> Emissions in the DFW Nonattainment Area

# 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. 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.

Point source VOC emission trends from STARS were also investigated. Figure 3-11: *Point Source VOC Emissions by Site in the DFW Nonattainment 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.

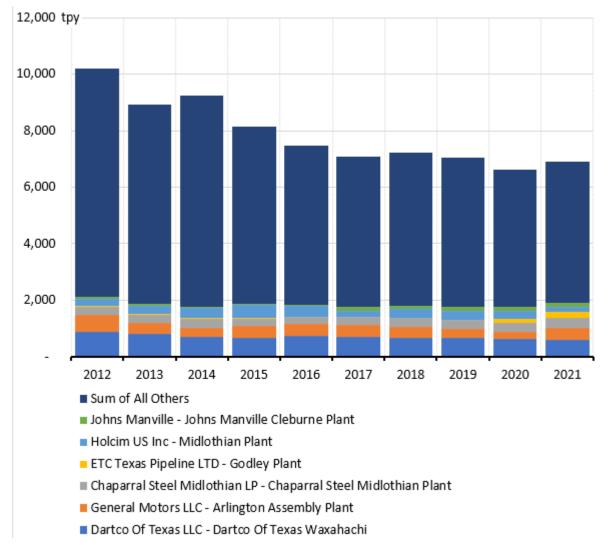


Figure 3-11: Point Source VOC Emissions by Site in the DFW Nonattainment Area

Locations of larger anthropogenic VOC emissions sources are shown in Figure 3-12: *Map of 2021 Point Source VOC Emissions in the DFW Nonattainment 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.

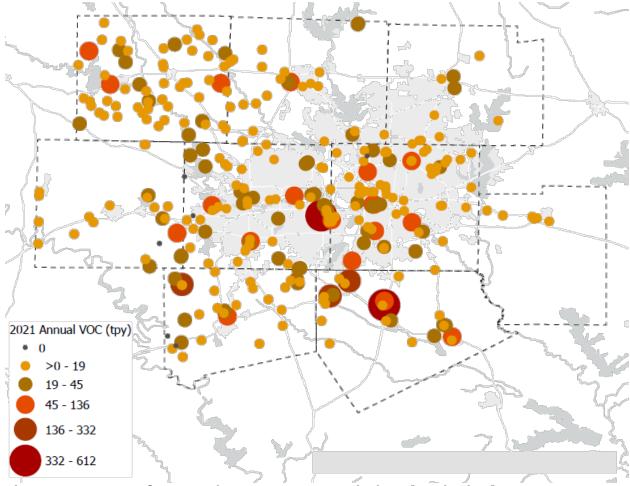


Figure 3-12: Map of 2021 Point Source VOC Emissions by Site in the DFW Nonattainment Area

#### **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<sub>x</sub>) limitations and ozone formation on weekdays versus weekends in the DFW area.

### 4.1 VOC AND NO<sub>x</sub> LIMITATION

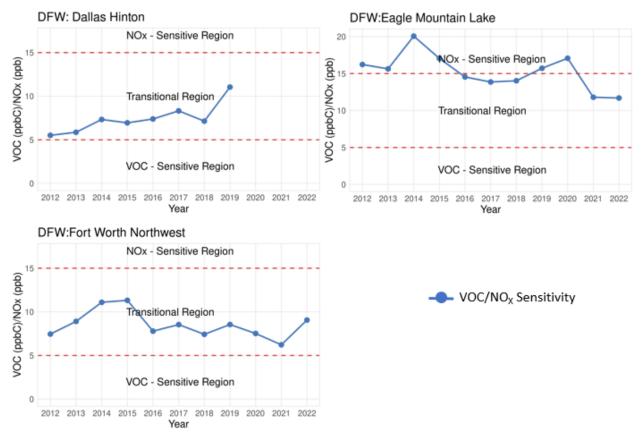
Ozone is formed from precursors in proportions determined by their molecular properties, therefore, unless precursors are present in these exact proportions in an airshed, ozone formation will be governed by whichever precursor is scarcer or limited. If one is in excess in the atmosphere, that excess will be unused in reactions. In this situation, reducing the surplus 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 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 airshed 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 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<sub>x</sub> ratios are calculated by dividing hourly total non-methane hydrocarbons (TNMHC) concentrations in parts per billion-carbon (ppbC) by hourly NO<sub>x</sub> 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<sub>x</sub>-limited, and ratios between 5 ppbC/ppbV and 15 ppbC/ppbV are considered transitional. Our understanding of VOC-to-NO<sub>x</sub> ratios in an airshed is limited by the number of collocated VOC and NO<sub>x</sub> 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<sub>x</sub> monitors: Dallas Hinton, Eagle Mountain Lake, and Fort Worth Northwest.

Figure 4-1: *Median VOC-to-NO<sub>x</sub> Ratios During Ozone Season in the DFW Nonattainment Area* shows the evolving nature of the relationship between these two ozone precursors. Data from March through October 2012 through 2022 were used in creating the figure. 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<sub>x</sub>-sensitive region, dipped briefly into the transitional region from 2016 through 2018, rose back into the NO<sub>x</sub>-sensitive region in 2019 and 2020, then declined back into the transitional region in 2021 and 2022. Eagle Mountain Lake is in an area likely to have ample biogenic VOC and, therefore, is expected to be NO<sub>x</sub> sensitive. Fort Worth Northwest resembled Dallas Hinton, with annual fluctuations but consistent residence in the transitional range.



**Figure 4-1:** Median VOC-to-NO<sub>x</sub> Ratios During Ozone Season in the DFW Nonattainment Area

Figure 4-2: *Median Hourly VOC-to-NO<sub>x</sub> Ratios During Ozone Season in the DFW Nonattainment Area* plots median VOC-to-NO<sub>x</sub> ratios by hour of the day at the three sites with co-located instruments. Results show that the ratio fluctuates over the course of a day at all three sites, rising into a more NO<sub>x</sub>-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<sub>x</sub>. Ratios rise in the afternoon, before dropping again in late evening.

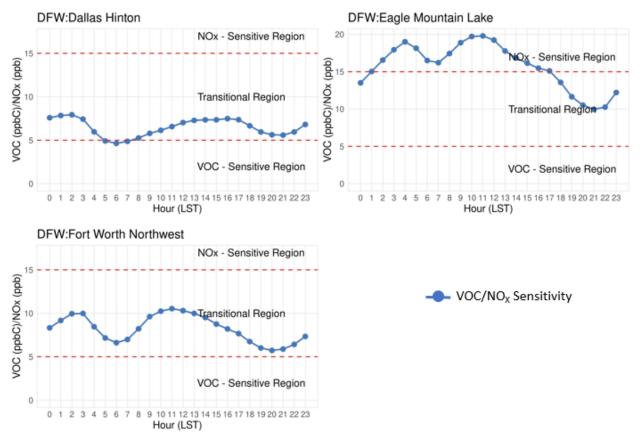


Figure 4-2: Median Hourly VOC-to-NO<sub>x</sub> Ratios During Ozone Season in the DFW Nonattainment Area

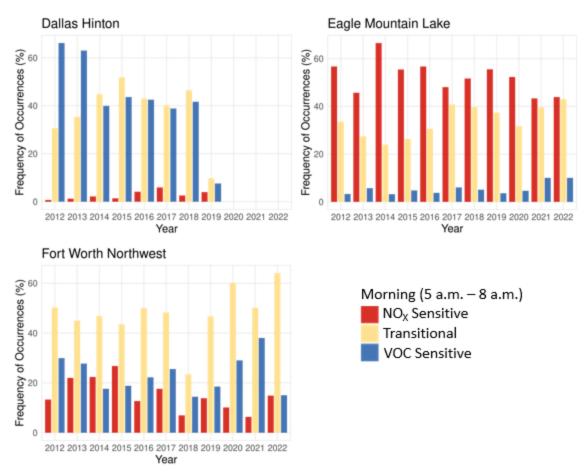
While diurnal patterns are similar across sites, absolute values of the ratios differ substantially, suggesting there are distinct differences in the chemical characteristics of the atmosphere depending on where in the region a site is located. Ratios at Dallas Hinton, located in a heavily urbanized 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<sub>x</sub> 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<sub>x</sub> 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 4-3: *Frequency of VOC-Limited, NO<sub>x</sub>-Limited, and Transitional Regimes During Ozone Season Mornings in the DFW Nonattainment 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<sub>x</sub>-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<sub>x</sub> 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.



**Figure 4-3:** Frequency of VOC-Limited, NO<sub>x</sub>-Limited, and Transitional Regimes During Ozone Season Mornings in the DFW Nonattainment Area

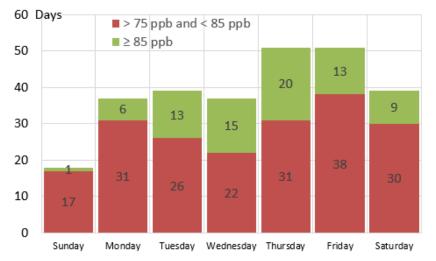
# 4.2 WEEKDAY VERSUS WEEKEND ANALYSIS

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. 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 provide information on impactful sources. A weekend effect can also provide inferences as to whether an area is VOC-limited or NO<sub>x</sub>-limited, providing clues to the efficacy of precursor reductions. A decrease in monitored ozone on weekends compared to weekdays indicates NO<sub>x</sub>-limitation, since weekend NO<sub>x</sub> concentrations are generally lower compared to their weekday counterparts. Conversely, a weekend increase in ozone concentrations can indicate VOC-limitation.

VOC and NO<sub>x</sub> 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<sub>x</sub> limitations found in the DFW area. To determine the effects these limitations

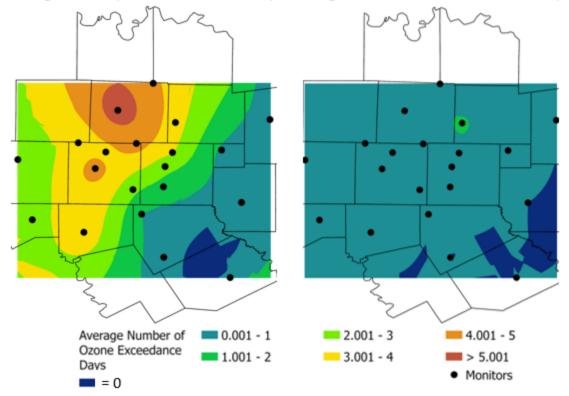
might have on the frequency of ozone events in the area, eight-hour ozone exceedance day counts and peak  $NO_x$  by day of the week were examined from 2012 through 2022. Only the ozone season months were used when looking at the peak  $NO_x$  data.

The number of days with an exceedance of the level of the 2008 ozone NAAQS was found for each day of the week at all available ozone monitors in the DFW area from 2012 through 2022. Figure 4-4: *Number of* Eight-*Hour Ozone Exceedance Days by Day of the Week in the DFW Nonattainment Area* shows how these 272 days over the eleven-year period are distributed by day of the week. The days with the most exceedances were Thursdays and Fridays, with 51 days each, followed by Tuesdays and Saturdays with 39 each. Sundays recorded the fewest exceedance days at 18 days. It appears that lower ozone occurs on the weekends, with the likelihood of experiencing an exceedance increasing over the week.



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

These patterns in eight-hour ozone exceedance days by day of the week suggest that changes in emissions from weekdays relative to weekends influence ozone concentrations in the DFW area. To examine this further, the annual average number of eight-hour ozone exceedance days on weekdays and weekends from 2012 through 2022 was calculated at each monitor location. Those values were then mapped using kriging interpolation to determine if there were any location-based changes in ozone exceedance days on weekdays versus weekends. Only ozone monitors in operation in 2022 and with more than eight years of data were analyzed. Results are presented in Figure 4-5: *Annual Average Number of Ozone Exceedance Days on Weekdays versus Weekends in the DFW Nonattainment Area.* This figure shows that there is a substantial difference between the number of exceedances recorded on weekdays and those recorded on weekends. Further, the number of exceedances in weekdays is higher as a location is more northerly and westerly in the DFW area, while there is little geographic difference observed on weekends.



Average Weekday Ozone Exceedance Days Average Weekend Ozone Exceedance Days

Figure 4-5: Annual Average Number of Ozone Exceedance Days on Weekdays versus Weekends in the DFW Nonattainment Area

To examine possible causes for the weekend effect, eight-hour ozone, NO<sub>x</sub>, and TNMOC concentrations were investigated by day of the week. Since it is typically the highest values that change due to the weekend effect, this analysis investigates 95th percentile concentrations. Only valid ozone season days and years from 2012 through 2022 were used in the analysis. A valid day is any day with at least 75% complete data and a valid year is any year with at least 75% valid days during the ozone season. All valid hours for each parameter were used to calculate the 95th percentile values. Results are shown in Figure 4-6: *Ozone Season 95th Percentile Concentrations by Day of the Week in the DFW Nonattainment Area.* All monitors with valid days and years were used in this analysis. Caution should be used when comparing across monitors rather than across days of the week. Weekdays are represented by blue bars in the figures while weekends are represented by red bars.

All DFW monitors exhibit slightly lower 95th percentile MDA8 ozone concentrations on weekends compared to weekdays with Sundays always recording the lowest 95th percentile MDA8 ozone concentration at each monitor. Sunday 95th percentile MDA8 ozone concentrations are roughly 0% to 6% lower than the minimum weekday 95th percentile MDA8 ozone concentration at the same monitor. Saturday 95th percentile MDA8 ozone concentrations are typically comparable to the minimum weekday MDA8 ozone concentration but is not always lower. Weekend (Saturday and Sunday) average 95th percentile ozone concentrations are 1% to 6% lower than weekday (Monday through Friday) average 95th percentile ozone concentrations. The weekend effect is clearly seen when looking at 95th percentile  $NO_x$  concentrations. These  $NO_x$  concentrations are always lowest on Sundays, followed by Saturdays, and often by a wide margin. Weekend (Saturday and Sunday) average 95th percentile  $NO_x$ concentrations range from 18% to 43% lower than weekday (Monday through Friday) average 95th percentile  $NO_x$  concentrations.

Weekend 95th percentile TNMOC concentrations were similarly lower than weekday 95th percentile TNMOC concentrations at most monitors. Weekend (Saturday and Sunday) average 95th percentile TNMOC concentrations are 5% to 20% lower than weekday (Monday through Friday) average 95th percentile TNMOC concentrations. Only one of the fifteen auto-GC monitors, Godley FM 2331, recorded a 95th percentile TNMOC concentration that was lower on a weekday (Friday, 241 ppb) than either Sunday (253 ppb) or Saturday (248 ppb). This monitor is located in a largely rural area southwest of the DFW metropolitan area in Johnson County.

Overall, it appears that ozone in most of the DFW area decreases on weekends, which is driven largely by reductions in  $NO_x$  concentrations. The change in ozone levels on weekends is much smaller than the change in  $NO_x$ . This indicates that changes in ozone are not proportional to changes in precursor concentrations.

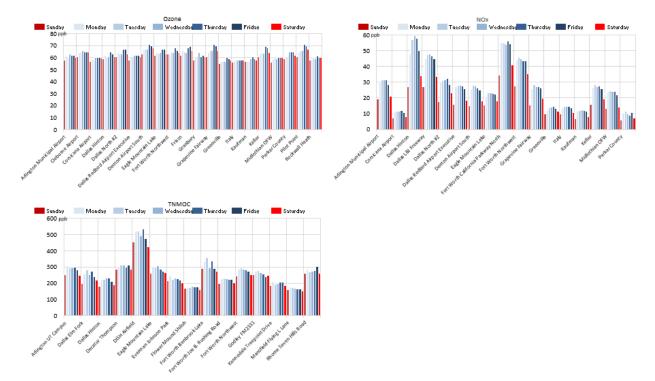


Figure 4-6: Ozone Season 95th Percentile Concentrations by Day of the Week in the DFW Nonattainment Area

## 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 Nonattainment 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 75 parts per billion (ppb) and temperatures less than 80 degrees Fahrenheit (°F). However, there were many days with temperatures above 100° F that did not exceed 75 ppb, suggesting that temperature is not determinative of high ozone but only one of several indicators of ozone conducive prevailing meteorology. There were 17 days over the eleven-year period when MDA8 ozone exceeded 75 ppb while daily maximum temperature was between 80° F and 90° F. However, most exceedances occur when daily temperatures exceed about 90° F.

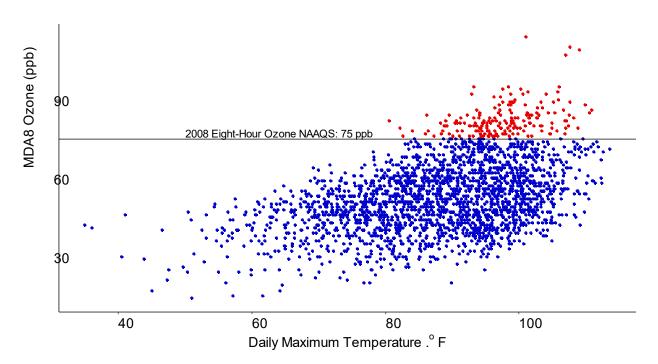


Figure 5-1: Ozone Season Daily-Maximum Temperature versus MDA8 Ozone in the DFW Nonattainment Area

## 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 correlate negatively with ozone concentrations. Low relative humidity indicates less moisture in the air. This negative correlation suggests that as the air is more saturated with moisture, less ozone is formed. 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; Rappenglück 2008). Therefore, low relative humidity is another meteorological factor that suggests conditions are conducive to ozone formation.

Four regulatory sites in the DFW area measure both relative humidity and ozone (Denton Airport South, Italy, Kaufman, and Grapevine Fairway). Average mid-day (10:00 LST through 15:00 LST) relative humidity was compared to the MDA8 ozone value for each monitor with at least eight years of valid ozone season data from 2012 through 2022. A mid-day time scale was chosen because this time was shown to have a larger correlation with ozone concentrations (Wells et al. 2021). A day was considered valid when at least 75% of hours had a relative humidity value. Results are displayed in Figure 5-2: *Ozone Season Average Mid-Day Relative Humidity versus MDA8 Ozone in the DFW Nonattainment Area.* This plot shows the negative correlation between average mid-day relative humidity and daily maximum eight-hour ozone. Ozone exceedance days are highlighted in red. The wide range of relative humidity even on exceedance days illustrates the earlier assertion that relative humidity is not determinative but can be suggestive of ozone conducive meteorology.

During the eleven years under consideration, average mid-day relative humidity was never less than 17%. On exceedance days, relative humidity ranged from 22% to 79%, although the one day with 79% relative humidity (May 31, 2019) appeared to be an outlier since the next highest relative humidity on an exceedance day was 69% (July 7, 2020). While 48% of exceedance days occurred when relative humidity was less than 40%, only twelve days measured relative humidity less than 22% and none of those days exceeded the 2008 ozone NAAQS. On only eight exceedance days did relative humidity exceed 60%,

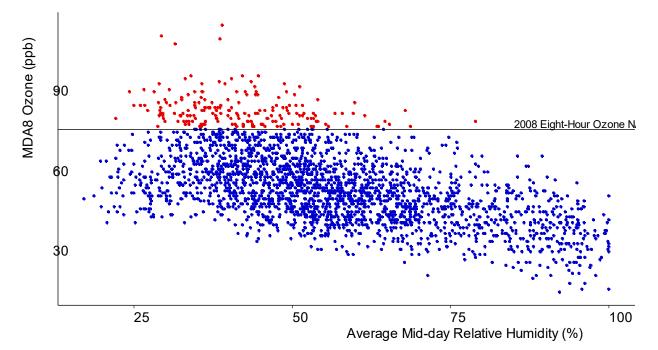


Figure 5-2: Ozone Season Average Mid-Day Relative Humidity versus MDA8 Ozone in the DFW Nonattainment Area

## 5.3 SOLAR RADIATION

Since ozone requires sunlight to form, solar radiation, which is a measure of the energy emitted by the sun, and its correlation with ozone concentrations was investigated. To summarize solar radiation values, average solar radiation during daylight hours was investigated. The hours used, 10:00 LST through 17:00 LST, are hours that would typically go into an MDA8 ozone value. Only ozone season data from monitors with at least eight-years of valid solar radiation data from 2012 through 2022 were used. A day was considered valid when at least 75% of hours had a solar radiation value. Results are displayed in Figure 5-3: *Ozone Season Average Daytime Solar Radiation versus MDA8 Ozone in the DFW Nonattainment Area.* Results show the positive correlation between solar radiation. No exceedances occurred on the 375 days when solar radiation as less than 0.67 Langleys/minute or the nine days when solar radiation exceeded 1.20 Langleys/minute.

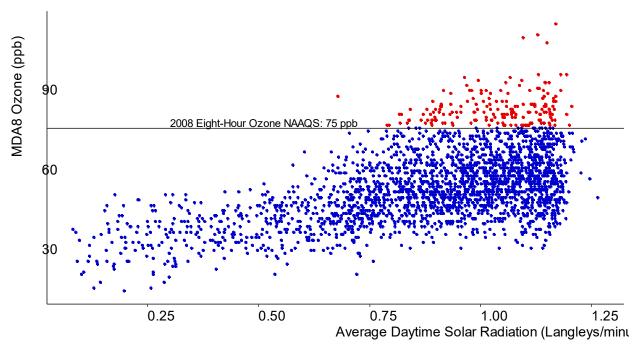


Figure 5-3: Ozone Season Average Daytime Solar Radiation versus MDA8 Ozone in the DFW Nonattainment Area

# 5.4 WINDS

Winds are a crucial factor in ozone formation as they can contribute to ozoneconducive 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. This section will investigate the characteristics of the winds in the DFW area and determine how those winds affect ozone and its precursors.

# 5.4.1 Wind Speed

Typically, higher ozone concentrations are observed on days with lower winds speeds. Lower wind speeds, many times due to a surface-level high-pressure system in the area, give ozone precursors more time to mix and react, and ozone can quickly accumulate due to limited dispersion. High wind speeds ventilate an area, essentially diluting ozone and its precursors.

To determine the effect of wind speeds on ozone formation, the average morning (07:00 LST through 10:00 LST) resultant wind speed in miles per hour (mph) was calculated from all monitors with at least eight years of valid ozone season days from 2012 through 2022. Morning hours were used because these hours were shown to have a larger correlation with ozone concentrations (Wells et al. 2021). As a morning average, it is a rough proxy of how fast winds were during the critical morning period when ozone formation begins each day. A day was considered valid when at least 75% of hours had a relative humidity value and a year was considered valid when it had at

least 75% of valid days. Wind speeds were then compared to the MDA8 ozone from the DFW area.

Figure 5-4: *Ozone Season Average Morning Resultant Wind Speed versus MDA8 Ozone in the DFW Nonattainment Area* shows the relationship between wind speed and ozone. 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 75 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 generally prevents ozone from forming and accumulating in higher concentrations, those above about twelve miles per hour, except in a few rare cases.

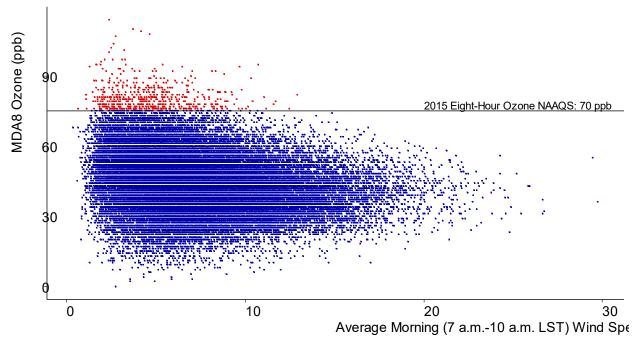
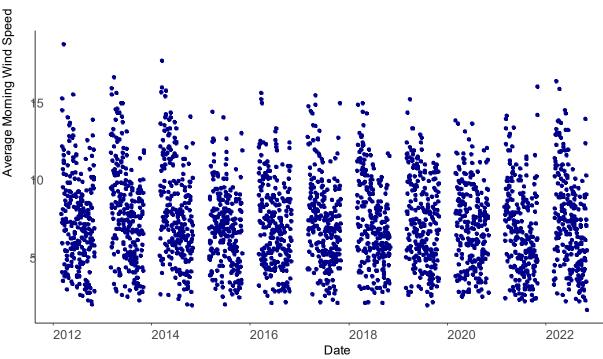
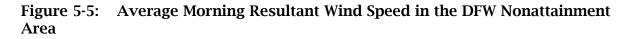


Figure 5-4: Ozone Season Average Morning Resultant Wind Speed versus MDA8 Ozone in the DFW Nonattainment Area

Typically, meteorological patterns do not show trends over time but there have been recent worldwide declines in surface winds speeds, a phenomenon known as terrestrial stilling (Deng et al. 2022). To investigate if this is occurring in the DFW area, the average morning resultant winds speeds for the ozone season, as calculated above, were plotted according to date. Results are shown in Figure 5-5: *Average Morning Resultant Wind Speed in the DFW Nonattainment Area.* When plotted by date, it appears that it is possible that there is a slow decline in average morning resultant wind speeds from 2012 through 2020, possibly through 2022. Since slow winds are correlated with higher ozone concentrations, further analysis is required to determine definitively how terrestrial stilling might impact the DFW area.



Source: TAMIS.



## 5.4.2 Surface Winds on High Ozone Days

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 2022 were examined.

Figure 5-6: *Ozone Season Wind Roses on High and Low Ozone Days in the DFW Nonattainment Area* shows that low ozone days record a high frequency of winds from the south (18%), south-southeast (15%), southeast (8%), and south-southwest (9%), with other directions reported at much lower frequencies. Typically, when winds arrive from these direction, they are greater than 5 miles per hour (mph) (81%).

On high ozone days, winds are more varied directionally, and predominantly arrive with about equal frequencies from the southeast (13%), east-southeast (12%), south-southeast (12%), and east (10%). Winds on high ozone days also arrive with slightly lower frequencies from the south (10%) and east-northeast (8%), though all directions are represented. Winds on high ozone days are typically much slower than on low

ozone days, often not exceeding 5 mph (44%), which are considered stagnant wind conditions. Also, a lower frequency of winds over 10 mph (3%) is apparent.

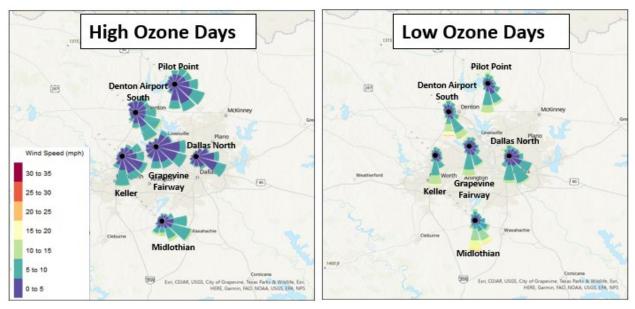


Figure 5-6: Ozone Season Wind Roses on High and Low Ozone Days in the DFW Nonattainment Area

Surface-level backward trajectories were calculated using a Lagrangian model that calculates the location of an air parcel using inverse distance square weighted wind speed and wind direction. This model uses no vertical mixing in calculations of trajectories. The trajectory calculation uses five-minute resolution meteorological data from all available Texas Commission on Environmental Quality (TCEQ) ground-based meteorological monitors in the DFW area, essentially putting the trajectory height at 10 meters above ground level (mAGL).

For this analysis, surface-level backward trajectories were calculated for every ozone exceedance day (MDA8 ozone greater than 75 ppb) at four monitors in the DFW area from 2017 through 2022. The monitors investigated were Dallas North 2, Denton Airport South, Keller, and Pilot Point. These monitors were chosen because they recorded the highest annual fourth highest MDA8 ozone concentrations in 2022. Trajectories were calculated starting at the hour of maximum one-hour ozone for the day at each respective monitor and then were run backwards for four hours. Some exceedance days may have missing meteorological data so not all exceedance days may have a corresponding trajectory.

Surface-level backward trajectories are displayed in Figure 5-7: *Surface-Level Back-Trajectories on Ozone Exceedance Days at Four Monitors in the DFW Nonattainment Area.* Red dots on the map represent estimated locations of each air parcel at five-minute intervals. Although these monitors show varying wind patterns on ozone exceedance days, they all show slow wind speeds, as indicated by short travel distances over the modeled four hour periods. Dallas North #2 and Denton Airport South show that winds arrive exclusively from directions ranging from southeast to southwest, except for one anomalous trajectory from the north-northeast at Denton

Airport South. Exceedance days at Keller found trajectories arriving from the eastsoutheast, while those days at Pilot Point saw trajectories predominantly from the south. All of these directions indicate the more urbanized areas of the DFW area as sources of air parcels on days when MDA8 ozone concentrations exceeded the 2008 NAAQS of 75 ppb.

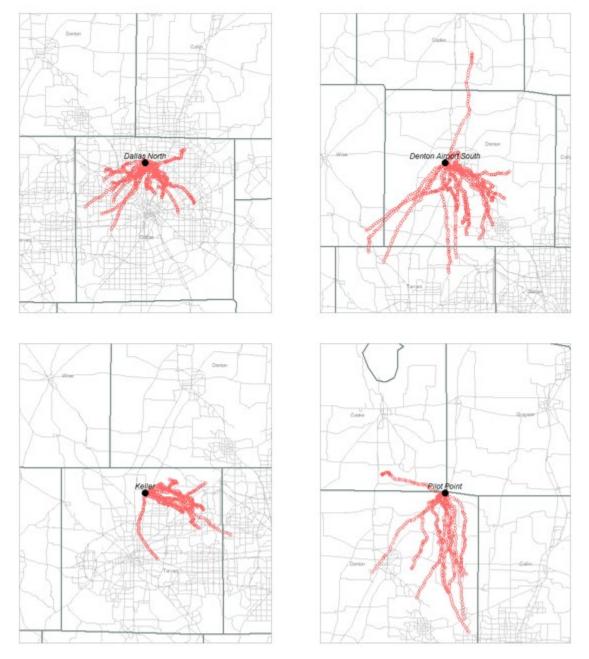


Figure 5-7: Surface-Level Back Trajectories on Ozone Exceedance Days at Four Monitors in the DFW Nonattainment Area

## 5.4.3 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.

Trajectories with similar patterns were then combined to distinguish mean transport patterns into the DFW area. This analysis used a HYSPLIT clustering algorithm to group multiple trajectories based on trajectory size and shape. The total spatial variance (TSV) was used to determine twelve clusters for the DFW area. To further investigate which transport patterns lead to high or low ozone in the DFW area, various ozone statistics were calculated for each trajectory cluster.

The top panel of Figure 5-8: *Mean of 72-Hour HYSPLIT Back Trajectory Clusters and Ozone Exceedance Days for the Ozone Season in the DFW Nonattainment Area* plots hourly coordinates of HYSPLIT 72-hour backward 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 2017 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.

The bottom panel of Figure 5-8: *Mean of 72-Hour HYSPLIT Back Trajectory Clusters and Ozone Exceedance Days for the Ozone Season in the DFW Nonattainment Area* presents box and whisker plots of one-hour ozone concentrations at the receptor monitor for all trajectories included in each computed HYSPLIT trajectory cluster. These plots display distributions of one-hour ozone values as rectangles, or "boxes", encompassing the middle fifty percent of values, from the 25th percentile to the 75th percentile, known as the interquartile range (IQR). The median, or 50th percentile, of each box is noted as a horizontal line. Lines extending from the boxes, the "whiskers", reach 1.5 times the width of each box (the IQR) both above and below the bounds of the boxes. Individual outliers beyond the whiskers are plotted, as well. This figure shows that the highest one-hour ozone concentrations were recorded for cluster 12 which arrived on a curving trajectory from the east with very slow wind speeds as noted by the short trajectory length. Other clusters with high medians include cluster 4, 5, and 8.

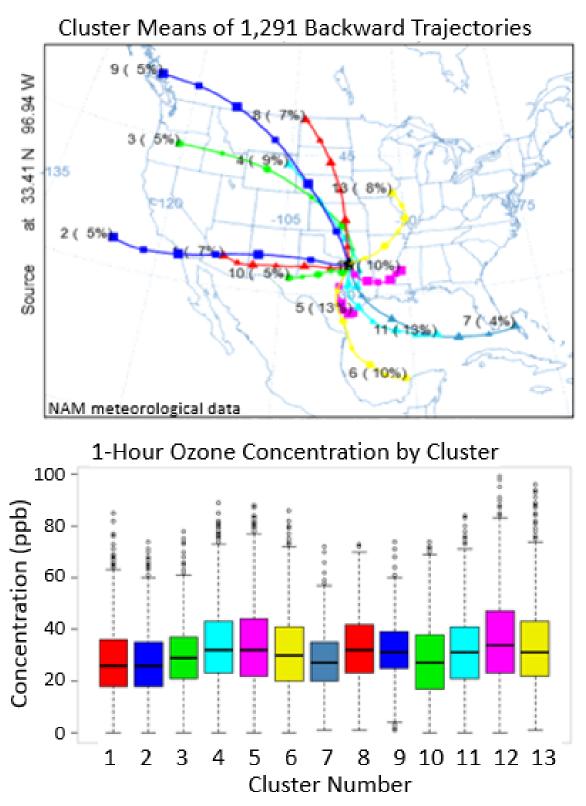


Figure 5-8: Mean of 72-Hour HYSPLIT Back Trajectory Clusters and Ozone Exceedance Days for the Ozone Season in the DFW Nonattainment Area

Cluster statistics are presented in table form in Table 5-1: DFW Area Ozone Statistics from Cluster Analysis. The table reports 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.

| Statistic             | 1† | 2† | 3† | 4† | 5† | 6† | 7† | 8† | 9† | 10† | 11† | 12† | 13† |
|-----------------------|----|----|----|----|----|----|----|----|----|-----|-----|-----|-----|
| Minimum <sup>††</sup> | 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  |
| Maximum††             | 63 | 60 | 61 | 73 | 77 | 72 | 57 | 70 | 60 | 69  | 71  | 83  | 74  |

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

†Cluster Number

††Values of data points that lie beyond the extremes of the whiskers

# 5.5 METEOROLOGICALLY-ADJUSTED OZONE CONCENTRATIONS

Meteorological conditions play an important role in ozone formation. Year-to-year variability in meteorological conditions in turn cause variability in ozone concentration trends. Although design values consider this variability by averaging the fourth-highest

MDA8 ozone over three-years, this is often not enough to account for years with extreme meteorological conditions such as low wind speeds, drought, or extremely high temperatures. Investigating meteorological influences on ozone trends allows analysis of how ozone concentrations respond to changes in emissions rather than changes in meteorology.

Meteorologically-adjusted MDA8 ozone values estimate what ozone would have been if meteorological effects on ozone concentrations were removed. Without the influence of meteorology, changes observed in ozone concentrations are more likely due to emissions changes rather than extreme meteorological events. The Environmental Protection Agency (EPA) developed statistical models that incorporate local meteorology and other factors to predict meteorologically-adjusted ozone concentrations at each monitor (Wells et al. 2021). These models compute meteorologically-adjusted annual average, 90th percentile, and 98th percentile MDA8 ozone concentrations from May through September which can be compared to similar raw or meteorologically-unadjusted values (EPA 2023). Although results for all available statistics were examined, only 98th percentile trends will be discussed in this document since this statistic most closely matches with annual fourth highest ozone concentrations that are used in design value calculations. The 98th percentile is approximately the eighth highest MDA8 value for a year but is the fourth highest for the May through September period. Since annual fourth-highest MDA8 values typically occur during the May through September period, the two measures are practically identical.

Trends at four monitors with the highest 2022 fourth-highest MDA8 ozone were first investigated. Results are shown in Figure 5-9: Meteorologically-Adjusted 98th Percentile MDA8 Ozone for May through September at Select Monitors in the DFW Nonattainment *Area.* This figure demonstrates that each year, meteorology can affect monitors differently. All four locations reported lower annual 98th percentile MDA8 ozone concentrations in 2017 than would be expected if meteorology had been typical. Over the eleven-year period, Cleburne Airport typically observes either no difference in ozone or even lower ozone than it would have if meteorology were considered. This suggests that meteorology typically has been unfavorable to ozone formation at this location at least until 2021. Similarly, Denton Airport South reports either no difference or lower ozone than it would have if corrected for meteorology every year except 2015. Fort Worth Northwest fluctuates between higher and lower reported ozone, with ozone conducive meteorology likely observed in 2016, 2017, 2019, and 2021. Finally, observed and adjusted annual 98th percentile MDA8 ozone concentrations at Granbury track each other very closely except for likely unfavorable ozone meteorology in 2016 and 2017 and ozone conducive meteorology in 2022.

The four monitors show that there is little trend in adjusted or unadjusted ozone concentrations from 2012 through 2022.

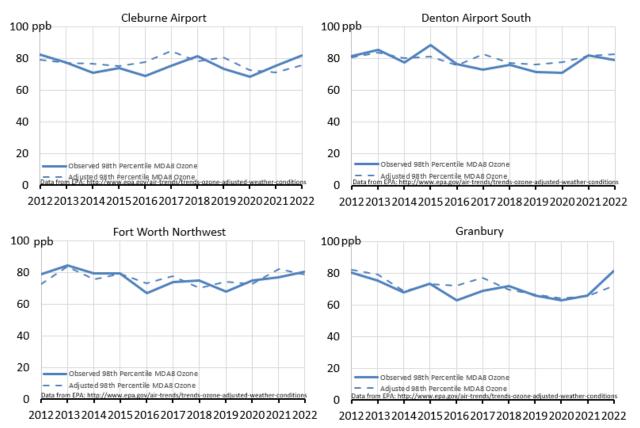


Figure 5-9: Meteorologically-Adjusted 98th Percentile MDA8 Ozone for May through September at Select Monitors in the DFW Nonattainment Area

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.

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 5-10: *Meteorologically-Adjusted Ozone Trends for May through September in the DFW Nonattainment 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. The largest 2022 adjustment to a 98th percentile MDA8 ozone concentration predicted to be necessary to correct for meteorology was 9.7 ppb at Granbury, which would have brought that value from 81.5 ppb to 71.8 ppb. The median 2022 adjustment to the 98th percentile MDA8 ozone concentration was 1.9 ppb. Since there were an even number of monitors evaluated, that value lies midway

between predicted adjustments of 1.8 ppb at Eagle Mountain Lake and 2.0 ppb at Frisco.

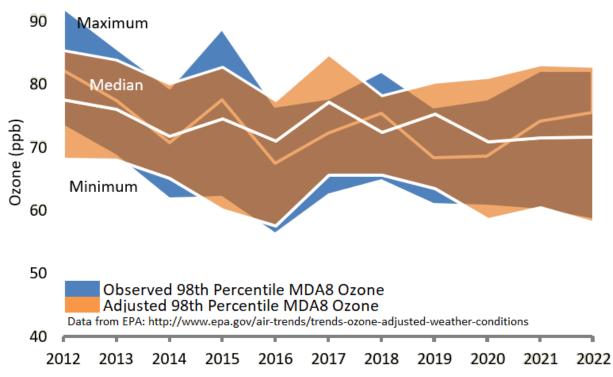


Figure 5-10: Meteorologically-Adjusted Ozone Trends for May through September in the DFW Nonattainment Area

Another way to investigate meteorologically-adjusted ozone trends is to examine the difference between the observed and predicted, meteorologically-adjusted 98th percentile MDA8 ozone for each year. After computing the difference at each monitor, the maximum, median, and minimum difference was found for the area. Positive differences suggest that ozone that year was likely higher due to ozone-conducive meteorology while negative differences suggest that ozone that year was lower due to favorable meteorology. Results are shown in Figure 5-11: *Difference Between Meteorologically-Adjusted and Observed 98th Percentile MDA8 Ozone Concentrations from May through September in the DFW Nonattainment Area.* 

Results show that 2012 was predicted to have the largest adjustments to ozone due to meteorology, meaning that if corrected for meteorology, reported ozone in that year would have been lower. Reported ozone in 2018 and 2022 also appeared to be influenced positively by meteorology. Years 2016, 2017, and 2019 were predicted to have experienced meteorology that was less favorable for ozone formation suggesting that reported ozone in those years could have been worse if meteorology had been typical. Years such as 2013, 2014, 2015, 2020, and 2021 reported about the same number of upward and downward corrections for meteorology, suggesting those years had typical meteorology. Every year and every monitor will have some degree of

prediction error, but if positive and negative adjustments mostly balance, the year was likely close to typical.

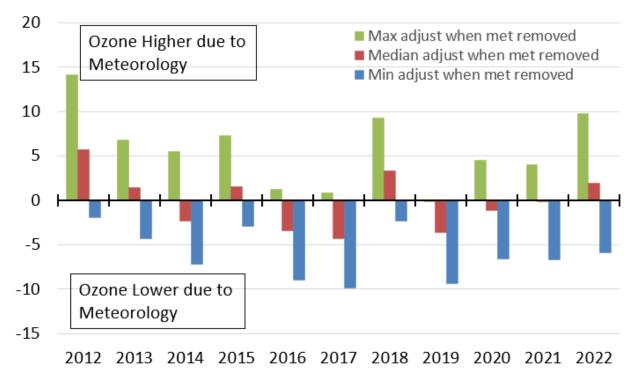


Figure 5-11: Difference Between Meteorologically-Adjusted and Observed 98th Percentile MDA8 Ozone Concentrations from May through September in the DFW Nonattainment Area

#### **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 75 parts per billion (ppb). Most of the analyses in this conceptual model focus on eleven years of ozone season data, 2012 through 2022. 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 2022, eight-hour ozone design values in the DFW area have decreased 11.5%. The area monitors attainment of the 1997 eight-hour ozone standard of 84 ppb but was designated as nonattainment of the 75 ppb 2008 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 75 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 could 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 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 dailymaximum 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 have not changed much over the past eleven 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 combining with local ozone production while the late-summer ozone season is characterized by more local ozone production.

Ozone is 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 eleven years, peak  $NO_x$  has decreased across the DFW area. Comparing only monitors that were in operation for the full eleven years, median  $NO_x$  concentrations dropped 15.7% from 4.0 ppb to 3.3 ppb, while 95th percentile  $NO_x$ 

concentrations fell 4.5% from 20.0 ppb to 19.1 ppb. Two near-road monitors deployed in 2014 and 2015 now record among the highest NO<sub>x</sub> values, underscoring the importance of motor vehicle emissions in the DFW airshed.

Median ambient total nonmethane organic compounds (TNMOC) concentrations dropped by 24.5% over the eleven-year period, 2012 through 2022, while 95th percentile ambient concentrations fell 27.2%. Isoprene, ethylene, toluene, and propylene, all VOC with high ozone formation potential, and ethane, propane, and nbutane, 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 ozone formation potential. The VOC with lower reactivities have such large concentrations in the DFW area that they still contribute a large portion to total VOC ozone formation potential composition even when weighted by their lower 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 2022,  $NO_x$  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. VOC 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 weekends 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 urban area emissions and then transported downwind.

Overall, high ozone days in the DFW area occur most frequently 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 from sources 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 greater than 75 ppb. Ozone chemistry on these days appears to be  $NO_x$  limited to transitional. Because the dominant VOC 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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