Texas A&M Transportation Institute

Subtask 3.1

Addressing Dallas Fort Worth VOC-limited and transitional areas in Designated NOx-limited Regions of Ozone Nonattainment

FINAL MEMORANDUM

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Texas A&M Transportation Institute

TECHNICAL MEMORANDUM – FINAL

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Sub-Task 3.1 – TWG Technical Issues Analysis

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ACRONYMS

AMPD	Air Markets Program Data
AQRP	Air Quality Research Program
AQS	Air Quality System
Auto-GC	Auto-Gas Chromatograph
BAU	Business as Usual
BPA	Beaumont-Port Arthur
CAA	Clean Air Act
CAMS	Continuous Air Monitoring Station
CBSA	Core-Based Statistical Area
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CRC	Coordinating Research Council
CSA	Consolidated Statistical Area
DFW	Dallas-Fort Worth
EGU	Electric Generating Unit
ELP	El Paso
EPA	Environmental Protection Agency
HC	Hydrocarbons
HDDM	High-Order Decoupled Direct
HGB	Houston-Galveston-Brazoria
HNO_3	Nitric Acid
HONO	Nitrous Acid
HRVOC	Highly Reactive Volatile Organic Compounds
MIR	Maximum Incremental Reactivity
MOBILE6	Former EPA On-Road Mobile Emissions Model
MOPITT	Measurement of Pollution in the Troposphere
MOPS	Measurement of Ozone Production Sensor
MOVES2014	2014 Version of the Motor Vehicle Emission Simulator
N_2	Nitrogen
NAAQS	National Ambient Air Quality Standards
NH_3	Ammonia
NLEV	National Low Emission Vehicle
NO	Nitrogen Oxide
NO_2	Nitrogen Dioxide

NONROAD	Former EPA Non-Road Mobile Emissions Model
NO_X	Nitrogen Oxides
NO_Y	Reactive Nitrogen Compounds
O_2	Oxygen
O_3	Ozone
OH	Hydroxyl Radical
OMI	Ozone Monitoring Instrument
PAMS	Photochemical Assessment Monitoring Stations
Pb	Lead
PM	Particulate Matter
ppb	Parts per Billion
ppbC	Parts per Billion Carbon
ppbV	Parts per Billion Volume
ppm	Parts per Million
SAN	San Antonio
SCC	Source Classification Code
SIP	State Implementation Plan
SO_2	Sulfur Dioxide
SoCAB	Southern California Air Basin
TCEQ	Texas Commission on Environmental Quality
TexN	Texas NONROAD Model
TNMHC	Total Non-Methane Hydrocarbons
tpd	tons per day
TTI	Texas A&M Transportation Institute
VMT	Vehicle Miles Traveled
VOC	Volatile Organic Compounds

1.0 INTRODUCTION

1.1 BACKGROUND

The overall purpose of this study is to evaluate recent data sets and published literature to investigate the status of ozone (O_3) formation within the Dallas-Fort Worth (DFW) region. DFW is the fourth largest metropolitan area in the U.S. and is currently in nonattainment of the eight-hour ozone standard promulgated by the U.S. Environmental Protection Agency (EPA). Ground-level ozone is formed through a complex interaction of nitrogen oxides (NO_X) and volatile organic compounds (VOC) in the presence of sunlight. The ratio of VOC to NO_X is a critical parameter for determining if a region is VOC limited or NO_X limited with respect to ozone formation. The Texas Commission on Environmental Quality (TCEQ) has characterized ozone formation in the DFW region as primarily NO_X limited, but with some areas in the urban core transitioning from VOC limited to NO_X limited in recent years. One primary goal of this study is to determine if this characterization is correct or needs qualification.

The timing of this study is driven in part by the temporary reduction in vehicular and economic activity that occurred in 2020 due to the COVID-19 pandemic. The COVID-19 "shutdown" led to a temporary reduction in anthropogenic NO_X and VOC emissions, yet high ozone levels were still monitored in DFW during some months of 2020. Another primary goal of this study is to determine if any confounding factors exist that kept the DFW area from significantly reducing ozone levels during the COVID-19 shutdown period. An improved understanding of DFW area ozone formation may allow policy makers to identify additional control strategies that would result in further reduction of NO_X and/or VOC precursor emissions.

1.2 REPORT OVERVIEW

To achieve the primary goals of the study, an overview of the ozone standards promulgated by EPA is provided first. A summary is then given of the current ozone monitoring network in the DFW area, along with peak ozone trends from 1990 through 2021. Details are provided about the form of the ozone standard to demonstrate that it is based on a three-year rolling average of monitoring data. A brief overview is provided of ground-level ozone formation that focuses on NO_X limitation versus VOC limitation, along with the critical importance of reactivity among different VOC species. The

attainment demonstration State Implementation Plans (SIPs) adopted by the TCEQ contain detailed information about NO_X and VOC emissions and concentration trends over time. The SIP documentation also contains detailed descriptions of NO_X versus VOC limited ozone formation within DFW, and these analyses are evaluated. Finally, a literature search of non-SIP documentation shown below was also performed for this study, and pertinent results are discussed:

- TCEQ analysis about air quality impacts of COVID-19 for DFW and other Texas areas.
- A detailed modeling study was done to estimate COVID-19 ozone impacts in the greater Los Angeles area.
- Phoenix area remote sensing study of light-duty vehicle exhaust was performed in 2021 and the results are compared to similar work done in 2006.
- A 2018 study was done that showed how ozone precursor emissions reductions across the U.S. were declining at a faster rate from 2005-2009 than from 2011-2015.
- Two studies from 2011 were performed that equipped the Fort Worth Northwest and Eagle Mountain Lake ozone monitors in DFW with additional instrumentation for characterizing ozone formation.
- In-depth sensitivity analyses were performed on a June 2006 ozone episode in DFW to determine if the region is primary NO_X limited or VOC limited.

After the literature search, a discussion is provided that covers the important points of all sections previously presented. This report ends with conclusions and recommendations for possible further study.

2.0 OVERVIEW OF NATIONAL AMBIENT AIR QUALITY STANDARDS FOR OZONE

Under the authority of the Clean Air Act (CAA), the U.S. EPA has promulgated National Ambient Air Quality Standards (NAAQS) for ground-level ozone, particulate matter (PM), carbon monoxide (CO), lead (Pb), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2). (1) Table 1 provides a brief summary of the 1-hour and 8-hour ozone standards promulgated by EPA from 1979 to 2015 in units of both parts per million (ppm) and parts per billion (ppb). (2)

Table 1. Summary of Ozone Standards from 1997 to 2015

Final Rule Date	Federal Register Reference	Averaging Time	Level (ppm)	Level (ppb)	Form of Standard Using Local Monitoring Site Data
February 8, 1979	44 FR 8202	1 Hour	0.12	124	The number of exceedance days per monitoring site is averaged over the past three calendar years to determine if this average is less than or equal to 1. (3)
July 18, 1997	62 FR 38856	8 hours	0.08	84	For each monitoring site, the three-year average of the fourth-highest daily maximum 8-hour ozone concentration per year should not exceed 84 ppb.
March 27, 2008	73 FR 16483	8 hours	0.075	75	For each monitoring site, the three-year average of the fourth-highest daily maximum 8-hour ozone concentration per year should not exceed 75 ppb.
October 26, 2015	80 FR 65292	8 hours	0.070	70	For each monitoring site, the three-year average of the fourth-highest daily maximum 8-hour ozone concentration per year should not exceed 70 ppb.

Within a metropolitan area such as DFW, multiple regulatory ozone monitors continuously measure ambient ozone concentrations. Under the first form of the ozone standard promulgated in 1979, these concentrations were averaged on an hourly basis for each monitor. An exceedance day would occur if the maximum one-hour ozone concentration for that day was higher than 0.12 ppm. Since current monitors are capable of measuring ozone in units of ppb, the "effective" or "working" level of the one-hour standard was 124 ppb. An ozone concentration of 124 ppb is equivalent to 0.124 ppm, which converts to 0.12 ppm when rounded to two decimal places. An ozone

concentration of 125 ppb is equivalent to 0.125 ppm, which converts to 0.13 ppm when rounded to two decimal places. Thus, a maximum one-hour ozone concentration of 125 ppb at a monitor would be categorized as an exceedance day, but a maximum one-hour ozone concentration of 124 ppb would not.

In 1997, EPA revised the ozone standard to 0.08 ppm averaged over eight hours rather than one hour. EPA also revised how the ozone measurement data are used in relation to the standard for determining the attainment of the NAAQS. For each monitor, a design value is determined by averaging the fourth-highest eight-hour ozone concentration per year over three consecutive years. If this design value is less than or equal to 0.08 ppm, then the monitor is in the attainment of the eight-hour ozone standard. When converted to measurement units of ppb, the effective/working level is 84 ppb since it rounds to 0.08 ppm when converted back to units of ppm and rounded to two decimal places. Thus, a monitor with a design value of 84 ppb or less would be in attainment of the 0.08 ppm eight-hour ozone standard, while a monitor with a design value of 85 ppb or higher would not.

In 2008, the eight-hour ozone standard was revised by EPA to 0.075 ppm, which is equivalent to 75 ppb. In 2015, the eight-hour ozone standard was revised again by EPA to 0.070 ppm, which is equivalent to 70 ppb. For both of these revisions to the eight-hour ozone standard, the determination of the design value is consistent with the methodology for the 0.08 ppm standard where the fourth-highest ozone concentration per year is averaged over three years. In many instances, the 0.08, 0.075, and 0.070 ppm standards are referenced as 1997, 2008, and 2015 ozone NAAQS, respectively. Referring to the standards in this way is certainly accurate, but not always intuitive for a reader that is not well-versed in the regulatory history of these ozone standards. This analysis will primarily refer to the eight-hour ozone standards in the more intuitive forms of 70 ppb, 75 ppb, and 84 ppb. In each case, a design value at or below the level of each standard indicates attainment, while 1 ppb above (e.g., 71 ppb, 76 ppb, and 85 ppb) indicates nonattainment.

A more extensive review of the ozone standards promulgated by EPA is not provided here. An excellent starting point for readers interested in more background is the EPA web page titled *Setting and Reviewing Standards to Control Ozone Pollution*. (4)

3.0 DFW AREA OZONE MONITORING DATA AND TRENDS

3.1 DFW Area Ozone Monitoring Network

Table 2 provides a summary of the 20 ozone monitors currently operated by the TCEQ within the Texas portion of the Dallas-Fort Worth-Oklahoma combined statistical area (CSA). 18 of these 20 ozone monitors are located within the eleven counties that comprise the Dallas-Fort Worth-Arlington core-based statistical area (CBSA): Collin, Dallas, Denton, Ellis, Hunt, Johnson, Kaufman, Parker, Rockwall, Tarrant, and Wise. According to the TCEQ *2021 Annual Monitoring Network Plan*, the 2019 population estimate for the CBSA is 7,573,136 and a minimum of four ozone monitors are required. (5) The two ozone monitors located outside of the CBSA but within the CSA are the Granbury monitor located in Hood County, and the Corsicana Airport monitor located in Navarro County. Figure 2 shows the approximate geographic locations for each of the 20 ozone monitors currently operating throughout the greater DFW area.

Table 2 includes the full monitor names used by the TCEQ, along with the EPA Air Quality System (AQS) (6) code and the Continuous Air Monitoring Station (CAMS) (7) code. The ozone monitors are sorted by activation date stretching from January 1975 to June 2009. As shown, seven of the 20 monitors were activated during the 2000 calendar year: Granbury, Cleburne Airport, Eagle Mountain Lake, Parker County, Grapevine Fairway, Rockwall Heath, and Kaufman. Table 2 (8) does not encompass all of the ozone monitors that ever operated within the greater DFW area. In general, a monitor that was deactivated by TCEQ was replaced by one relatively close by. For example, a monitor named Denton County Airport was deactivated on 11/24/1997, and then Denton Airport South was activated on 2/16/1998. A monitor named Dallas North was deactivated on 11/3/1998, and Dallas North #2 was activated on 11/2/1998.

Table 2. Summary of 20 Ozone Monitors in the Greater DFW Area

TCEQ Monitor Name	AQS Code	CAMS Number	County	Latitude	Longitude	Activation Date
Fort Worth Northwest	484391002	13	Tarrant	32.8058182	-97.3565229	1/1/1975
Keller	484392003	17	Tarrant	32.9225030	-97.2820890	2/11/1981
Dallas Hinton	481130069	60, 161, 401, 3002	Dallas	32.8200660	-96.8601230	1/1/1986
Frisco	480850005	31, 680	Collin	33.1324359	-96.7864066	5/7/1992
Midlothian OFW	481390016	52, 137	Ellis	32.4820856	-97.0268937	11/7/1994
Dallas Redbird Airport Executive	481130087	402	Dallas	32.6764506	-96.8720596	1/1/1995
Denton Airport South	481210034	56, 157, 163	Denton	33.2190529	-97.1963020	2/16/1998
Dallas North #2	481130075	63, 679	Dallas	32.9192125	-96.8085031	11/2/1998
Granbury	482210001	73, 681	Hood	32.4423120	-97.8035418	5/9/2000
Cleburne Airport	482510003	77, 682	Johnson	32.3535988	-97.4367442	5/10/2000
Eagle Mountain Lake	484390075	75	Tarrant	32.9878922	-97.4771706	6/6/2000
Parker County	483670081	76	Parker	32.8687733	-97.9059445	7/26/2000
Grapevine Fairway	484393009	70, 182	Tarrant	32.9842671	-97.0637191	8/4/2000
Rockwall Heath	483970001	69	Rockwall	32.9365214	-96.4592142	8/8/2000
Kaufman	482570005	71	Kaufman	32.5649591	-96.3176968	9/11/2000
Arlington Municipal Airport	484393011	61	Tarrant	32.6563650	-97.0885802	1/17/2002
Greenville	482311006	198, 1006	Hunt	33.1530979	-96.1155692	3/20/2003
Pilot Point	481211032	1032	Denton	33.4110159	-96.9445562	4/4/2006
Italy	481391044	1044	Ellis	32.1754446	-96.8701888	8/21/2007
Corsicana Airport	483491051	1051	Navarro	32.0319335	-96.3991408	6/16/2009

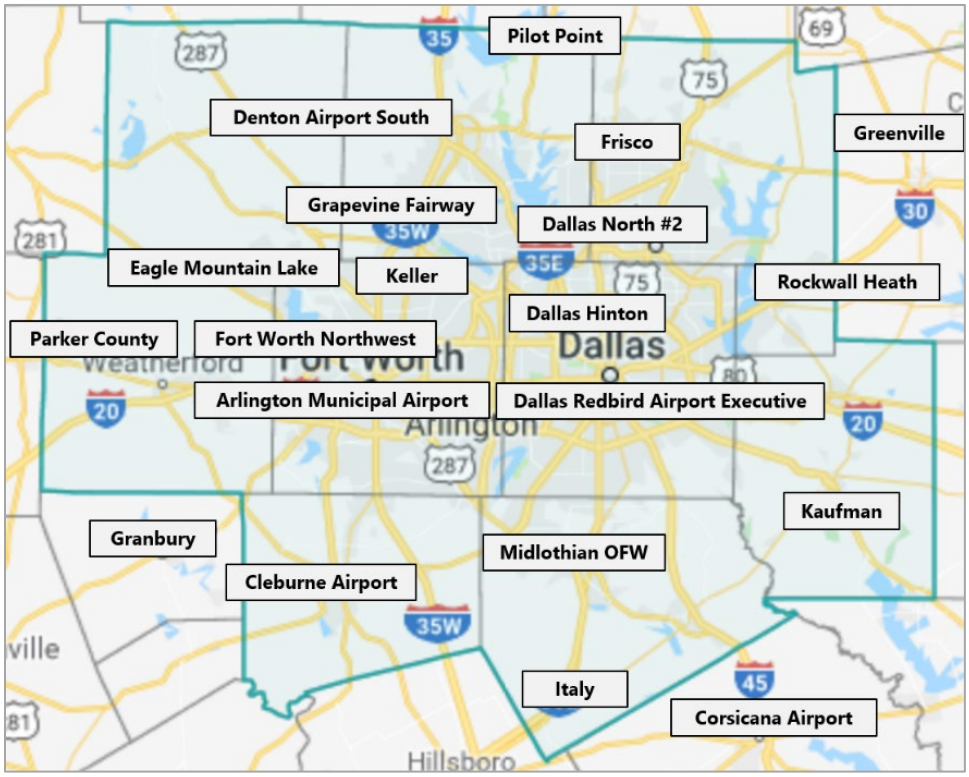

Figure 1. Locations of 20 Ozone Monitors in the Greater DFW Area

3.2 DFW Area Ozone Design Value Trends from 1990 through 2021

Figure 2 presents the number of DFW area ozone monitors with valid design values from 1990 through 2021 (black bar), and the number per calendar year that were above the eight-hour ozone standards of 70 ppb (red bar), 75 ppb (blue bar), and 84 ppb (green bar). The five ozone monitors operating in 1990 were located primarily in the north and northwest portions of DFW to capture the expected highest ozone levels since the primary wind directions during the ozone season are primarily from the south and southeast. In 1990, all five of these monitors had design values above the 70 ppb, 75 ppb, and 84 ppb standards. By 2000, there were eight monitors with valid ozone design values and all were above the 70 ppb, 75 ppb, and 84 ppb standards.

As noted above in Table 1, three years of ozone monitoring data are needed to determine a valid design value. Figure 2 shows that the number of monitors with valid design values increased from nine in 2000 to 16 in 2002. The seven monitors noted above in Table 2 that were activated during 2000 would not have valid design values based on three years of data until 2002, so they do not show up in the 2000 and 2001

data presented in Figure 2. The Rockwall Heath and Kaufman monitors are located in the upwind eastern and southeastern portions, respectively, of DFW where lower ozone concentrations are typically measured and were added in part to better characterize background ozone levels transported into the DFW area.

As shown, all of the 20 ozone monitors currently operating had valid design values starting in 2012. Starting in 2014, none of these 20 monitors were out of compliance with the 84 ppb standard. Of the 17 monitors with valid ozone design values in 2007, all were out of compliance with the 75 ppb standard. As of 2021, only the Pilot Point monitor is out of compliance with the 75 ppb standard as it has a 2021 design value of 76 ppb. Of the 20 monitors with valid ozone design values in 2013, all were out of compliance with the 70 ppb standard. As of 2021, ten of these monitors are out of compliance with the 70 ppb standard.

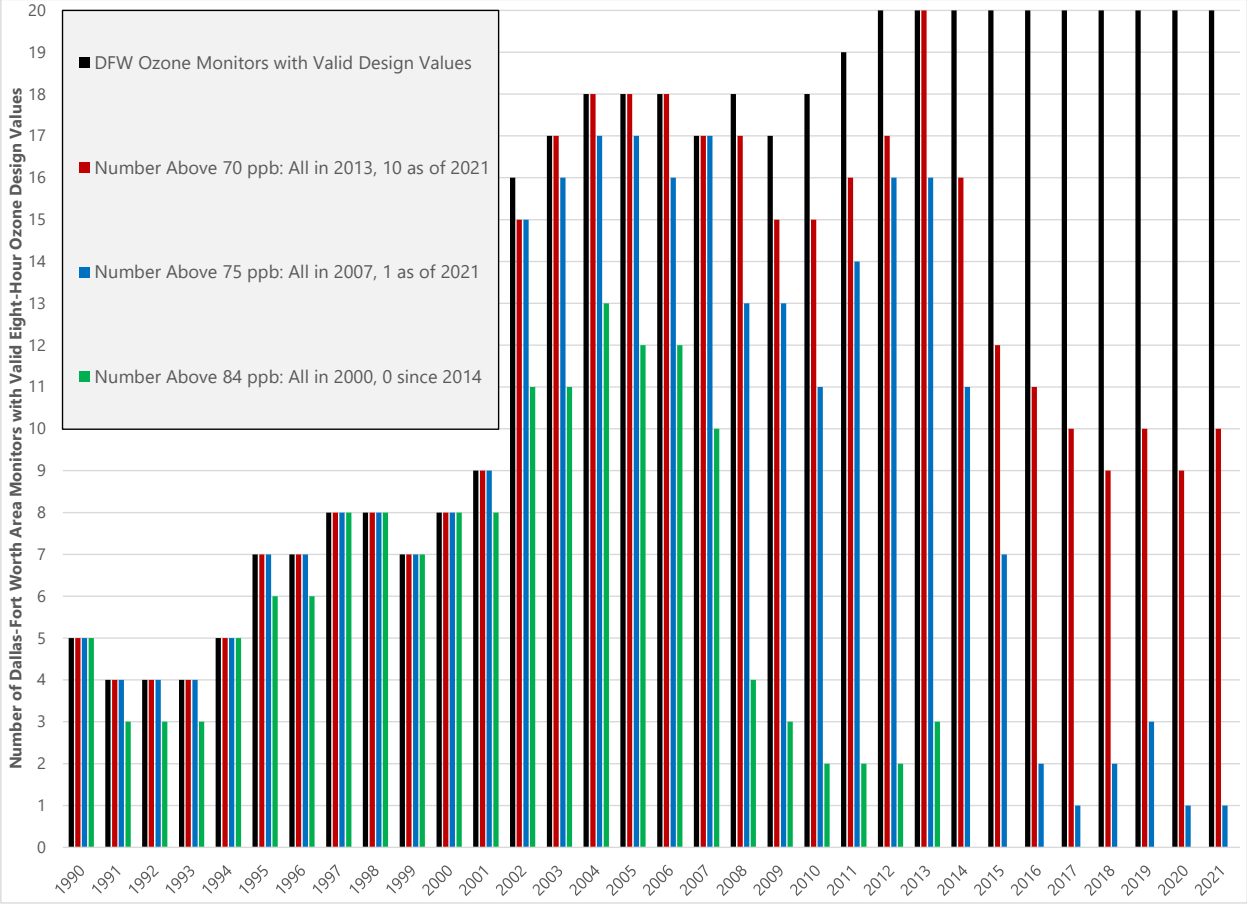

Figure 2. DFW Area Ozone Monitors with Valid Design Values from 1990-2021

A design value is determined annually for each monitor based on the most recent three full years of ozone measurement data. As an example, Table 3 summarizes the design value calculations for the Pilot Point monitor from 2010 through 2021 based on the fourth-highest ozone concentrations from 2008 through 2021. The average of the fourth-highest ozone concentrations of 80 ppb in 2008, 78 ppb in 2009, and 78 ppb in 2010 is 78.67 ppb. This value is truncated (not rounded) to zero decimal places to obtain a 2010 design value of 78 ppb. For 2011, the 2009-2011 fourth-highest ozone concentrations are used. For 2012, the 2010-2012 ozone concentrations are used. This rolling average approach continues for 2021 when 2019-2021 data are used to obtain a 2021 design value of 76 ppb. When the 2022 fourth-highest ozone concentration is available, the 2020-2022 data will be used. Relative to previous years, the fourth-highest value of 85 ppb in 2021 stands out. This value of 85 ppb will be part of the three-year design value calculation through 2023 (using 2021-2023 data), but not for 2024-and-later years.

Table 3. Pilot Point Monitor Design Value Calculations from 2010-2021

Calendar Year	Fourth-Highest Ozone Concentration (ppb)	Average of Most Recent Three Years (ppb)	Eight-Hour Ozone Design Value (ppb)
2008	80		
2009	78		
2010	78	78.67	78
2011	91	82.33	82
2012	78	82.33	82
2013	84	84.33	84
2014	75	79.00	79
2015	79	79.33	79
2016	75	76.33	76
2017	68	74.00	74
2018	74	72.33	72
2019	73	71.67	71
2020	71	72.67	72
2021	85	76.33	76

The Pilot Point monitor was selected as the example for Table 3 since it currently has the highest design value of all 20 ozone monitors within DFW. Within any given year, any of the 20 monitors could have the highest design value, and this peak level becomes the design value for the entire DFW area for that year. Figure 3 provides the peak one-hour and eight-hour ozone design values throughout DFW from 1990 through 2021. As

shown, the highest one-hour design value was 147 ppb in 1992 and it is 98 ppb as of 2021, which is a reduction of 49 ppb over 29 years. The highest eight-hour ozone design value was 106 ppb in 1995 and it is 76 ppb as of 2021, which is a reduction of 30 ppb over 26 years. Figure 3 also shows how the population of the ten-county DFW nonattainment area steadily grew from 3.9 million in 1990 to 7.6 million in 2021, which is a relative increase of 95%.

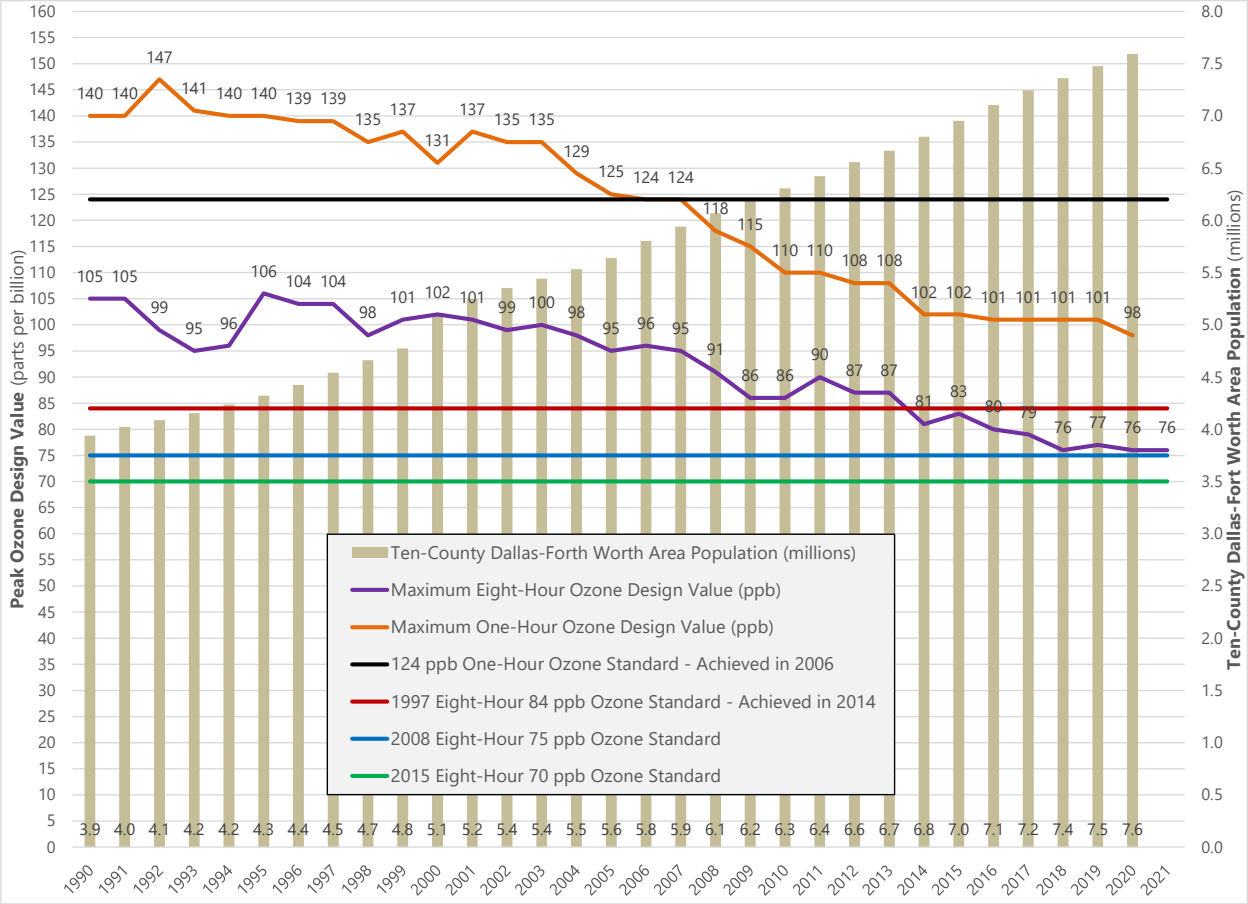

Figure 3. Peak Ozone Design Value Trends in DFW from 1990-2021

An area cannot be classified as attainment of a NAAQS ozone standard until all of the monitors located within the area are compliant, so the focus is appropriately placed on the maximum eight-hour ozone design value within each calendar year. Figure 4 provides the maximum eight-hour ozone design values from 1990-2021 along with the minimum and average design values for each calendar year. As shown, there has been a substantial reduction in regional DFW ozone during this time since the trends for maximum, minimum, and average are all downward. For the minimum design value

(plotted in green), the very large drop from 91 ppb in 1999 (at the Dallas Hinton monitor) to 70 ppb in 2002 (at the Kaufman monitor) could be misinterpreted. As noted above in Table 2, the Rockwall Heath and Kaufman monitors were added in 2000 and are located in the furthest upwind portions of DFW during the ozone season, so lower design values are expected. It was not until 2002 that valid design values could be obtained for these monitors, so the one-time large reduction was due to the expansion of the monitoring network to include monitors with the lowest design values within the DFW area.

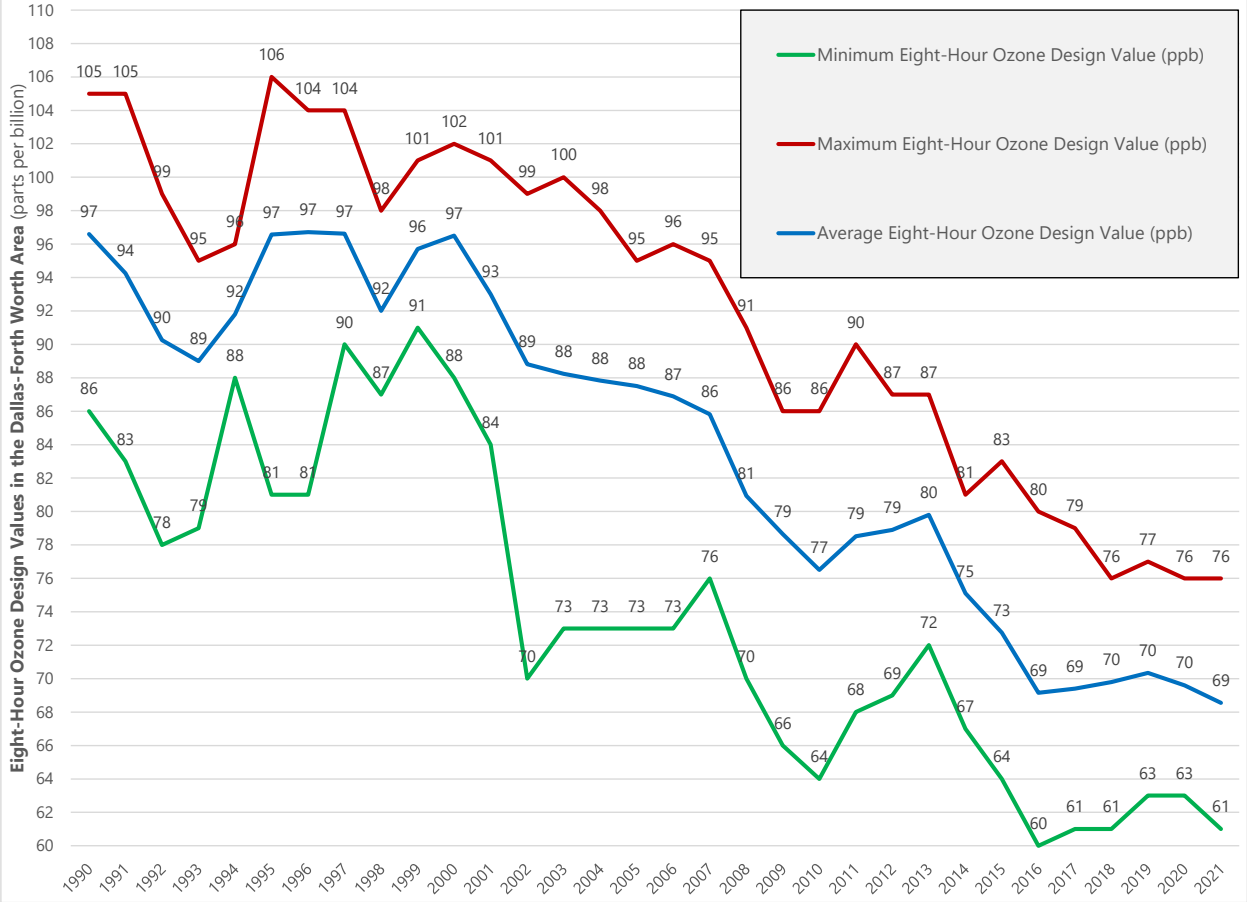

Figure 4. Minimum, Maximum, and Average DFW Design Values from 1990-2021

High ozone concentrations can be monitored on any day of a given year, but days with the highest ozone in DFW tend to occur from May through September, and particularly in the months of June and August. During high ozone periods, the dominant wind directions are from the south and southeast, which leads to monitors in the north and northwest of DFW to measure, on average, the highest ozone concentrations. Table 4

lists the monitor(s) that had the highest eight-hour ozone design values each year from 1990 to 2021. In most cases, only one monitor per year had the highest value, but two monitors shared the highest design value for 2003, 2004, and 2018. Three monitors shared the highest design value for 2005.

Table 4. DFW Ozone Monitors with Highest Design Values from 1990-2021

Calendar Year	Maximum Design Value (ppb)	Monitor(s) with Maximum Eight-Hour Ozone Design Value
1990	105	Keller (activated in 1981)
1991	105	Keller
1992	99	Keller
1993	95	Keller
1994	96	Keller
1995	106	Keller
1996	104	Keller
1997	104	Denton County Airport (deactivated in 1997)
1998	98	Frisco (activated in 1992)
1999	101	Frisco
2000	102	Denton Airport South (activated in 1998)
2001	101	Denton Airport South
2002	99	Denton Airport South
2003	100	Keller, Grapevine Fairway (activated in 2000)
2004	98	Keller, Grapevine Fairway
2005	95	Keller, Fort Worth Northwest (activated in 1975), Eagle Mountain Lake (activated in 2000)
2006	96	Eagle Mountain Lake
2007	95	Eagle Mountain Lake
2008	91	Denton Airport South
2009	86	Eagle Mountain Lake
2010	86	Keller
2011	90	Keller
2012	87	Keller
2013	87	Denton Airport South
2014	81	Denton Airport South
2015	83	Denton Airport South
2016	80	Denton Airport South
2017	79	Denton Airport South
2018	76	Grapevine Fairway, Cleburne Airport (activated in 2000)
2019	77	Dallas North #2 (activated in 1998)
2020	76	Grapevine Fairway
2021	76	Pilot Point (activated in 2006)

Within Table 4, the activation year is noted at the first mention of the monitor. The activation dates are included to provide context. The Keller monitor had the highest

design values from 1990 to 1996, but this is in part because it has been operational since 1981. The Eagle Mountain Lake and Grapevine Fairway monitors are not located far from Keller, but would not have a chance to have the highest design value until 2002 when three years of operational data first became available.

Table 5 summarizes the number of times a specific monitor had the highest design value for a given calendar year from 1990 to 2021. As shown, the Keller and Denton Airport monitors had the highest design values for 13 and 10 years, respectively, while both the Eagle Mountain Lake and Grapevine Fairway monitors had the highest design values for four years. All four of these monitors are located in the northwestern portion of the DFW metropolitan area within 12-24 miles of each other. Of the remaining five monitors that had the highest design values from 1990-2021, four are located in either the north or northwestern portion of the DFW metropolitan area. These are the Frisco, Fort Worth Northwest, Dallas North #2, and Pilot Point monitors. Figure 5 shows the locations of these ozone monitors relative to each other within the north and northwest portions of the DFW area. In 2018, the Grapevine Fairway and Cleburne Airport monitors had design values of 76 ppb, and this is the only year in which a monitor not located in the north or northwest of DFW had the highest design value. Cleburne Airport is located in the southwest portion of the DFW area.

Table 5. Number of Times a DFW Ozone Monitor Had the Highest Design Value

Years at Peak Ozone Design Value	DFW Area Ozone Monitor
13	Keller
10	Denton County Airport / Denton Airport South
4	Eagle Mountain Lake
4	Grapevine Fairway
2	Frisco
1	Fort Worth Northwest
1	Dallas North #2
1	Cleburne Airport
1	Pilot Point

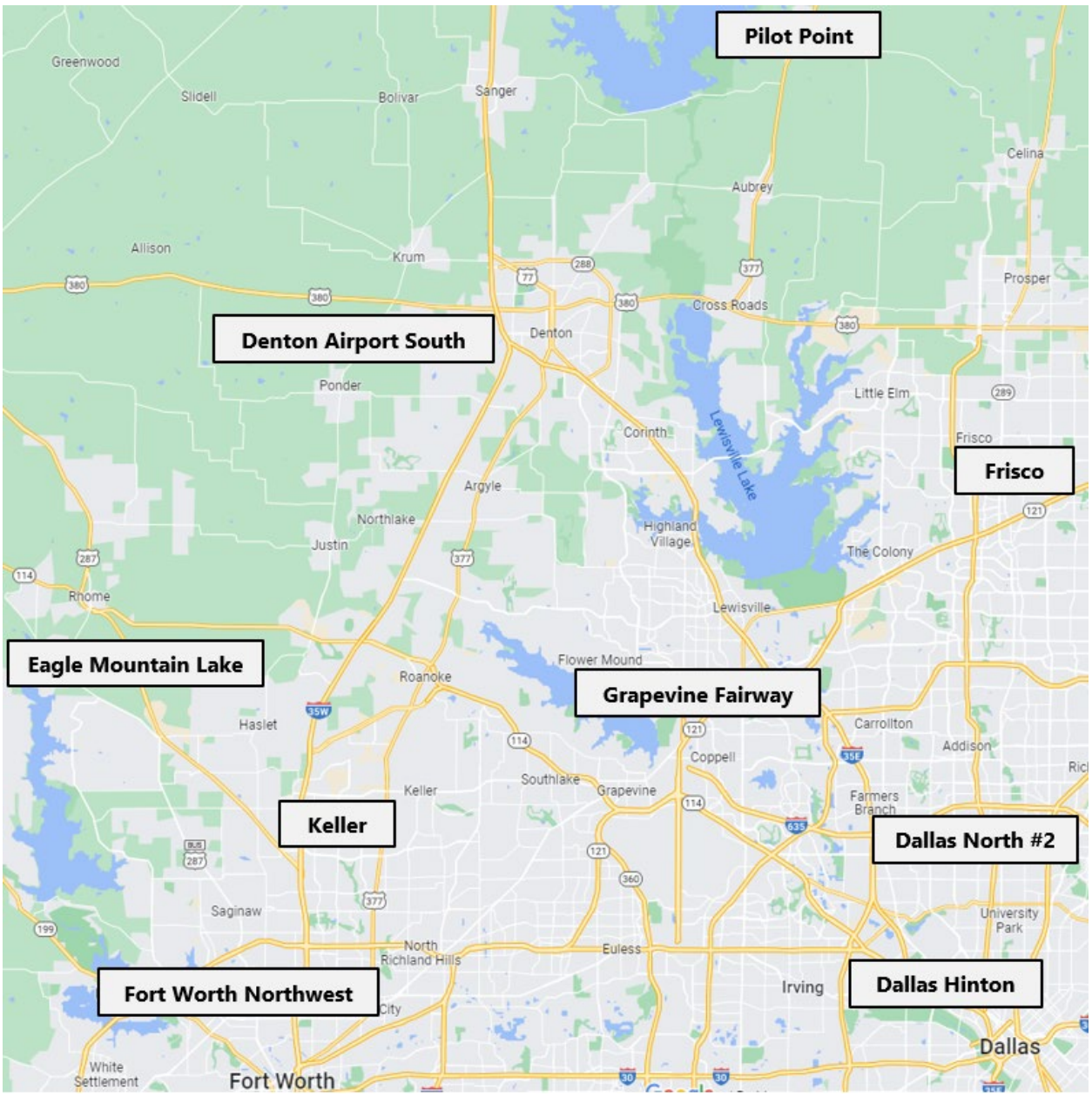

Figure 5. Ozone Monitors in the North and Northwest Portions of the DFW Area

Figure 6 provides the fourth-highest ozone concentrations from 2000-2021 for the four monitors in DFW that have historically had the highest design values: Denton Airport South, Eagle Mountain Lake, Grapevine Fairway, and Keller. The year 2000 was chosen as the starting point since that is the year in which the Eagle Mountain Lake and Grapevine Fairway ozone monitors were activated. At first glance, the fourth-highest ozone concentration for Grapevine Fairway (plotted in green) rapidly increases from 2000 to 2001, but that is because this monitor was not activated until August of 2000, which is the latter part of the ozone season. As shown, the fourth-highest ozone concentration

levels have declined over time from as high as 100-109 ppb in 2002 to as low as 74-81 ppb in 2021. Due to meteorological variability from year-to-year, the fourth-highest ozone concentration per monitor has fluctuated while steadily decreasing.

Figure 7 calculates three-year rolling averages of the fourth-highest ozone concentrations from Figure 6 to show the design value trends for these four monitors. As shown, these have declined from a peak of 100 ppb in 2003 to 75 ppb in 2021. Taking the rolling average of the fourth-highest ozone concentrations in three-year increments has a "smoothing" effect on the downward trends in the design values. The design value trends are certainly not linear, but fluctuate much less than the fouth-highest ozone concentrations per year.

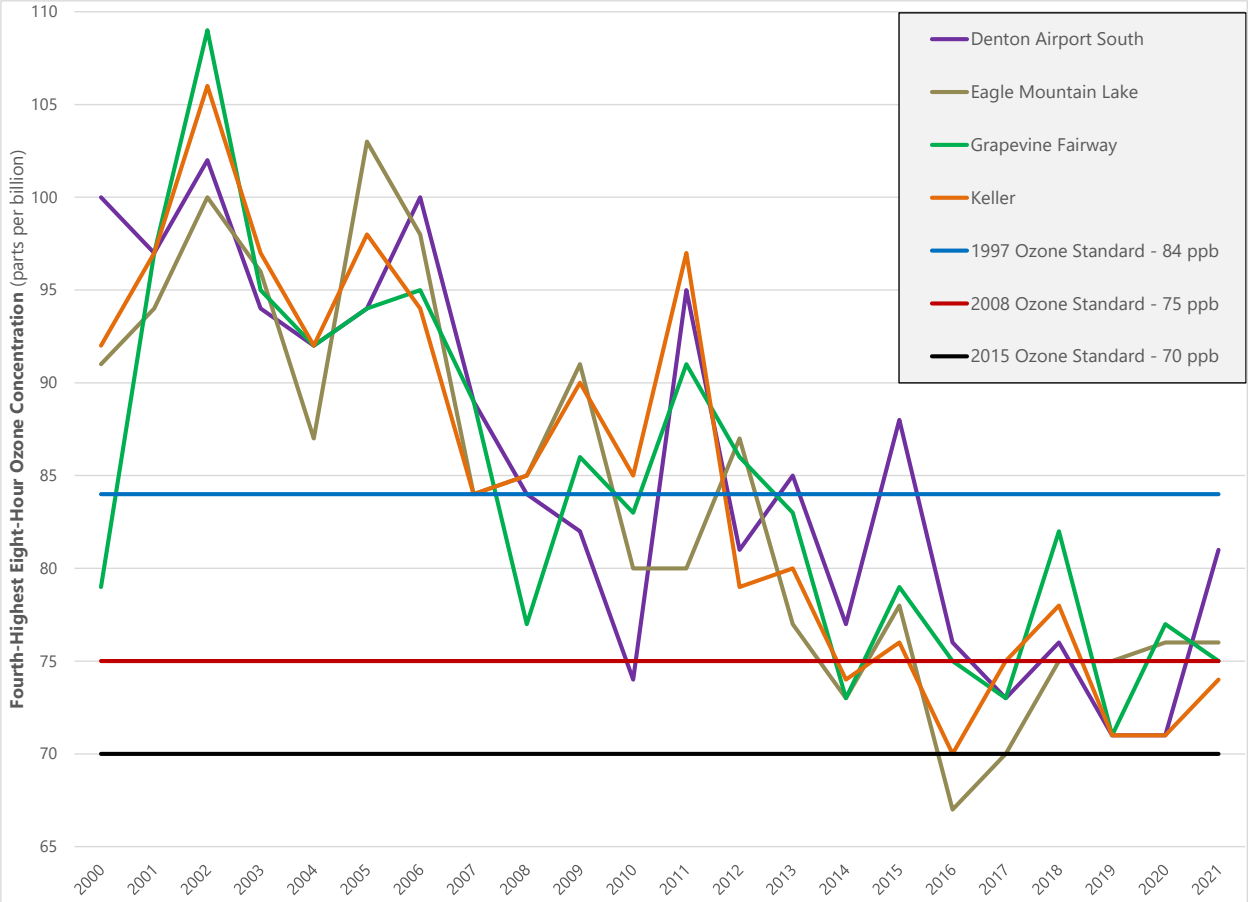

Figure 6. Fourth-Highest Ozone Concentrations at Four Highest DFW Monitors

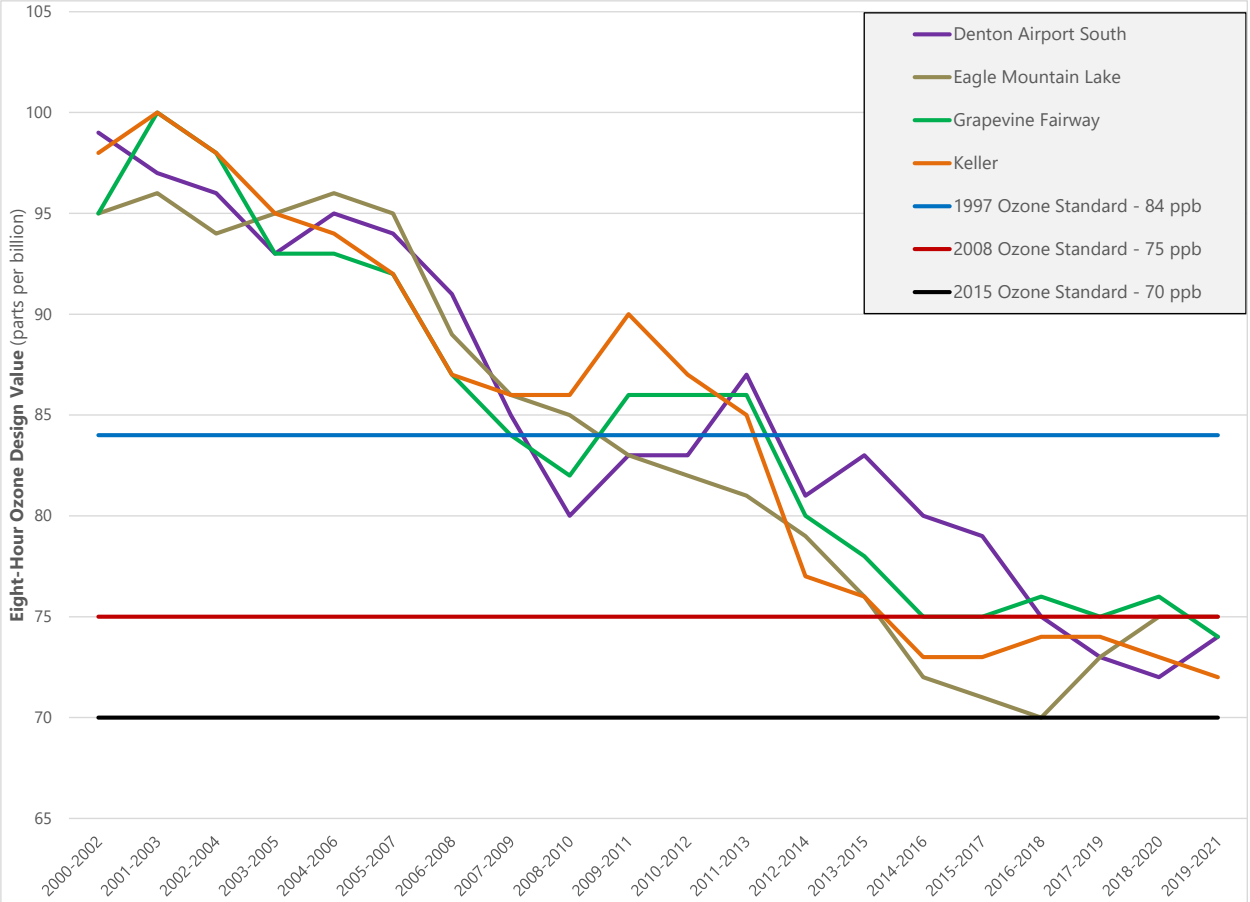

Figure 7. Eight-Hour Ozone Design Values at Four Highest DFW Monitors

High ozone concentrations tend to be measured on the most stagnant days. Since the design value is based on the fourth-highest concentration per year, an ozone season with only three excessively stagnant days can be considered a "low" ozone year, while one with four excessively stagnant days can be considered a "high" ozone year. For example, 2011 stands out as an abnormally high ozone year compared to 2009, 2010, 2012, and 2013. The meteorological conditions that occurred during the drought of 2011 led to multiple stagnant days resulting in high ozone concentrations. An alternative example is 2016 standing out as an abnormally low ozone year compared to 2014, 2015, 2017, and 2018. The meteorological conditions in 2016 led to fewer high ozone days than usual, particularly in August when the largest number of high ozone days historically occurs. These abnormally low and high ozone years are to be expected periodically, and the three-year averaging required by the standard lessens the impact that conditions in any one year will have on the design value for each monitor.

4.0 OVERVIEW OF OZONE FORMATION

4.1 General Background on Ozone Formation

Ground-level ozone formation is a highly complex process, and only a brief overview is provided here. Primary sources of information for this overview are the first (9) and second (10) editions of *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* by John H. Seinfeld and Spyros N. Pandis. Readers interested in more detail are encouraged to review the detailed ozone formation descriptions included with either edition.

Ground-level ozone is formed by a complex interaction of NO_X and VOC in the presence of sunlight. NO_X is a combination of nitrogen oxide (NO) and NO_2. Nitrogen in the form of N_2 comprises roughly 80% of ambient air, is very stable, and is relatively inert. Under the high-temperature conditions associated with fossil fuel combustion, N_2 reacts with oxygen (O_2) to form NO_X. While some NO_X does occur naturally, the primary sources are anthropogenic such as exhaust emitted from gasoline engines in passenger vehicles, from diesel engines in heavy-duty diesel vehicles and equipment, from power plants that burn coal and natural gas, and from various fuel types for industrial, commercial, and residential applications.

In the presence of sunlight, NO_2 forms NO and a free oxygen atom designated as O. This free oxygen atom of O reacts with O_2 in the troposphere to form O_3. Once O_3 is formed, it reacts with NO to form NO_2 and O_2. Provided that sufficient sunlight remains, the newly formed NO_2 forms NO and O, and this cycle continues. As described by Seinfeld and Pandis, "because NO_X gets cycled back and forth between NO and NO_2 in O_3 generation, NO_X can be viewed as the catalyst in O_3 formation" and "ozone formation depends critically on the level of NO_X."

4.2 NO_X Limited versus VOC Limited Ozone Formation

In the highly simplified description of ozone formation described above, NO_X is the catalyst and VOC plays no role. The presence of VOC enhances the ozone formation process by increasing both the magnitude of ozone formed and the rate at which this process occurs. With NO_X playing the role of catalyst in ozone formation, VOC can be viewed as playing the role of both "fuel" (i.e., increases the magnitude of ozone formed) and "accelerant" (i.e., increases the rate at which ozone is formed). There is wide variation in how individual VOC species act as both fuel and accelerant in this process.

Under real-world conditions, a critical role is played by the hydroxyl radical (OH), which Seinfeld and Pandis describe as the "primary oxidizing species in the troposphere" and "the key reactive species in the chemistry of ozone formation." A VOC species reacts with OH to initiate an oxidation sequence. The NO_X and VOC that are present will compete for any OH that is available:

- When the ratio of VOC to NO_X is above roughly 5.5 ("abundant VOC" conditions), OH will react mainly with VOC and this is categorized as NO_X limited ozone formation.
- When the ratio of VOC to NO_X is below roughly 5.5 ("abundant NO_X" conditions), OH will react mainly with NO_X and this is categorized as VOC limited ozone formation.
- When the ratio of VOC to NO_X is at roughly 5.5 (neither NO_X nor VOC is abundant), OH will react with both VOC and NO_X at an approximately equal rate, and this will typically be the ratio at which the peak amount of ozone is formed at a given level of VOC.

One simplified way to understand NO_X limited ozone formation is to visualize an isolated chamber containing an abundant amount of VOC in the presence of sunlight. At first, no NO_X is present but is then steadily added. As additional NO_X is steadily injected into the chamber, the net amount of ozone formed will increase. This initial stage will have high VOC/NO_X ratios and is categorized as NO_X limited ozone formation. Under such conditions where VOC is abundant, the amount of ozone formed will respond to changes in NO_X, but not to relatively small changes in the amount of VOC. If the VOC levels are held constant while NO_X is steadily increased, the VOC/NO_X ratio will eventually decline to a point where ozone will be scavenged in a process known as NO_X titration. Under these VOC limited conditions where NO_X is abundant, the amount of ozone formed will be lowered by either reducing VOC or increasing NO_X.

One simplified way to understand VOC limited ozone formation is to instead visualize an isolated chamber containing an abundant amount of NO_X in the presence of sunlight. At first, no VOC is present but is then steadily added. As additional VOC is steadily injected into the chamber, the net amount of ozone formed will increase provided that no additional NO_X is added since the latter would cause titration to occur. Under this scenario, the VOC/NO_X ratio starts low and is steadily increased until ozone formation eventually transitions from VOC limited to NO_X limited.

4.3 Ozone Formation in Real-World Environments

In real-world environments, ozone formation is complicated by multiple factors. Most of the NO_X emitted is from anthropogenic activity as a result of fuel combustion. VOC is emitted by both anthropogenic sources and biogenic sources such as trees and other vegetation. Densely populated urban areas tend to have a higher spatial concentration of emitted NO_X due to on-road vehicle activity, non-road equipment operation, local airports, etc. These same sources exist in suburban and rural areas but are less concentrated spatially compared to urban areas. In many parts of the central and eastern U.S., naturally occurring biogenic sources of VOC are abundant in suburban and rural areas, but are relatively less abundant in dense urban environments.

The net result is that ozone formation tends to be NO_X limited in suburban and rural areas where biogenic VOC emissions are often abundant and anthropogenic NO_X emissions are not heavily concentrated. In dense urban environments, VOC limited ozone formation is more common since biogenic VOC emissions tend to be lower and anthropogenic NO_X emissions are more spatially concentrated. VOC from anthropogenic sources also tends to be more highly concentrated in urban versus suburban/rural areas.

Over the span of several years, the effects of environmental regulations have generally reduced the total amount of anthropogenic NO_X and VOC emitted, and this has altered the ozone formation chemistry in numerous areas. If ozone formation in a suburban/rural area with abundant biogenic VOC was NO_X limited 20-30 years ago, then ozone formation is likely, even more, NO_X limited today due to reduced NO_X emission levels. If ozone formation in an urban area was VOC limited 20-30 years ago, then ozone formation may still be VOC limited today, or it could be transitioning to being more NO_X limited due to reduced NO_X emission levels. Please note that this description applies to metropolitan areas located within the central and eastern portions of the U.S. Metropolitan areas located within arid climates of the western U.S. (e.g., Los Angeles) tend to have far less biogenic VOC, and ozone formation tends to be more VOC limited than in the less arid cities of the central and eastern U.S.

An additional complicating factor is that the VOC/NO_X ratio at a specific location can also vary by time of day. In general, the meteorological mixing layer resides at a relatively low level during overnight and early morning hours, and this "traps" NO_X emissions from vehicle activity during the morning rush hour. As the land surface is heated by daytime sunlight, the mixing layer height increases which also increases the volume containing the surface-level NO_X emissions. For example, if the NO_X level is held

constant and the volume of space containing it doubles, then the NO_X concentrations are reduced by half. As the day progresses, biogenic VOC emissions increase as a function of solar radiation. This combination of multiple variables changing by hour (e.g., NO_X emissions, VOC emissions, mixing layer height) results in a changing VOC/NO_X ratio throughout the day. With relatively high NO_X and low biogenic VOC emissions in the early morning, a location could have VOC limited ozone formation, but then transition more towards NO_X limitation in the afternoon as biogenic VOC emissions increase. An abrupt change in wind direction during the day will typically bring a different mix of NO_X and VOC emissions, and this can also alter the ozone forming conditions at a specific location.

4.4 Wide Range of Reactivity Among VOC Species

A further complication is that the "tipping point" VOC/NO_X ratio of 5.5 described above is based on an average urban mix of VOC. The OH rate constants vary considerably across different VOC species, so the particular ratio that determines NO_X or VOC limitation can vary considerably depending on the mix of VOC species present at any given time and location. Detailed work performed by William Carter of the University of California, Riverside is an excellent source for understanding the wide range of reactivity among several hundred individual VOC species. (11)

Table 6 contains a summary of the maximum incremental reactivity (MIR) for ozone formation and OH rate constants provided by Carter for 15 VOC species. Seinfeld and Pandis reported that the relative role of a specific VOC species is determined by its concentration and OH rate constant. "A species with a large concentration will not necessarily be an important O_3 precursor if it is unreactive; conversely, another compound with a small concentration can be important if it is extremely reactive. (An example is methane, typically the most abundant VOC in the atmosphere but of negligible importance in producing ozone on urban or regional scales because of its extremely low reactivity.) An airmass can have a large total VOC concentration but a low ozone-producing capacity if the VOCs present are relatively unreactive."

The 15 species in Table 6 were selected as examples because they are commonly found in many environments (e.g., methane and isoprene) and/or have a significant impact on local ozone formation (e.g., isoprene). The purpose here is not to provide a detailed summary of MIR and OH rate constant values for all compounds. Instead, this table is provided to demonstrate the very wide range of reactivity that exists among VOC species involved with local ozone formation. For additional information, interested

readers should consult Carter's detailed speciation work that is available at https://intra.engr.ucr.edu/~carter/.

Table 6. Maximum Incremental Reactivity and OH Rate Constants for VOC Species

VOC Species	MIR (grams O_3/grams VOC)	MIR Relative to Methane	OH Rate Constant (cm^3 molec-1 s-1)	OH Rate Constant Relative to Isoprene
1,3-Butadiene	12.61	877	6.59E-11	66.14%
Propylene (Propene)	11.66	811	2.60E-11	26.12%
Isoprene	10.61	738	9.96E-11	100.00%
1-Butene	9.73	676	3.11E-11	31.18%
Ethylene (Ethene)	9.00	626	8.15E-12	8.18%
Alpha-Pinene	4.51	313	5.18E-11	51.95%
Beta-Pinene	3.52	245	7.35E-11	73.79%
Isopentane	1.45	101	3.60E-12	3.61%
n-Pentane	1.31	91	3.84E-12	3.86%
Isobutane	1.23	86	2.14E-12	2.14%
n-Butane	1.15	80	2.38E-12	2.39%
Benzene	0.72	50	1.22E-12	1.23%
Propane	0.49	34	1.11E-12	1.12%
Ethane	0.28	20	2.54E-13	0.25%
Methane	0.0144	1	6.62E-15	0.01%

For a specific VOC species, the MIR is the highest amount of ozone that can be formed per unit of VOC if a sufficient quantity of NO_X is present and the full reaction is allowed to go to completion (e.g., not halted by loss of sunlight or absence of NO_X). With respect to ozone formation, methane and isoprene are representative "bookends" that demonstrate the wide range of reactivity among VOC species. As shown, the very stable and relatively non-reactive compound of methane has a very low MIR compared with high MIR compounds such as 1,3-butadiene, propylene, and isoprene. For example, if all conditions are held constant in a controlled environment, a gram of isoprene will produce 738 times more ozone than a gram of methane. In the analogy described above where VOC acts as a fuel in the ozone formation process, methane could be considered a very weak fuel and isoprene a very potent one.

The additional critical factor is the OH rate constant. As shown, isoprene has a very fast OH reaction rate relative to other compounds, especially methane. In the analogy described above where VOC is also an accelerant in the ozone formation process,

methane could be considered as a very weak accelerant and isoprene a very potent one. Isoprene is very common in many environments because it is emitted by multiple plant species (e.g., oak and poplar trees) in the presence of sunlight. Seinfeld and Pandis emphasize the critical importance of biogenic VOC in general and isoprene in particular:

- "A great variety of organic compounds are emitted by vegetation. These biogenic compounds are highly reactive in the atmosphere. They are basically alkenes or cycloalkenes, and their atmospheric chemistry is generally analogous to that of alkenes."
- "If one had to single out the most important biogenic hydrocarbon in atmospheric chemistry, it would be isoprene."

As previously noted, many metropolitan areas can be VOC limited in their most densely populated urban cores and NO_X limited in their peripheral suburban and rural portions. This can sometimes lead to the erroneous conclusion that separate ozone reduction strategies should be pursued for individual locations within a larger metropolitan area. Due to local meteorological patterns, the NO_X and VOC precursors emitted at one location (along with the ozone that is formed) will be transported downwind to other locations within a metropolitan area. With respect to reducing ground-level ozone, it is beneficial for the area as a whole to reduce anthropogenic NO_X and reactive anthropogenic VOC emissions as much as possible. In areas where reactive biogenic VOC emissions are abundant, the reduction of anthropogenic VOC with low reactivity will likely have a small impact on ozone formation. Conversely, reducing anthropogenic VOC of high reactivity can have a significant impact on local ozone formation.

5.0 DFW AREA STATE IMPLEMENTATION PLAN DOCUMENTS

5.1 Ozone Precursor Emissions Trends

The U.S. EPA promulgated nonattainment designations for:

- the 1997 eight-hour ozone standard of 84 ppb (12) on June 15, 2004;
- the 2008 eight-hour ozone standard of 75 ppb (13) on July 20, 2012; and
- the 2015 eight-hour ozone standard of 70 ppb (14) on August 3, 2018.

Since 2007, the TCEQ has adopted five major attainment demonstration revisions to the SIP for the DFW area under the 84 ppb and 75 ppb eight-hour ozone standards. These five attainment SIP revisions are summarized in Table 7. At this time, an attainment demonstration SIP revision has not yet been proposed or adopted by the TCEQ for the DFW area under the 70 ppb eight-hour ozone standard. All of the SIP revisions adopted from 1972 to the present are available on the TCEQ *Texas SIP Revisions* web page.

Table 7. Attainment Demonstration SIP Revisions for the DFW Area Adopted by TCEQ for Eight-Hour Ozone Standards

SIP Adoption Date	TCEQ Project Number	Applicable Eight-Hour Ozone Standard	Base Case Modeling Year	Future Case Modeling Year
May 23, 2007	2006-013-SIP-NR (*15*)	1997: 84 ppb	1999	2009
December 7, 2011	2010-022-SIP-NR (*16*)	1997: 84 ppb	2006	2012
June 3, 2015	2013-015-SIP-NR (*17*)	2008: 75 ppb	2006	2018
July 6, 2016	2015-014-SIP-NR (*18*)	2008: 75 ppb	2006	2017
March 4, 2020	2019-078-SIP-NR (*19*)	2008: 75 ppb	2012	2020

Each attainment demonstration SIP revision includes detailed anthropogenic emissions inventory estimates for base and future case modeling years by major source category. These attainment SIP revisions are the primary sources for the ozone precursor emissions estimates in units of tons per day (tpd) provided in Table 8 for NO_X and Table 9 for VOC.

Table 8. DFW Area Summer Weekday NO_X Emissions Trends from 1999 to 2020

Anthropogenic Emissions Source Category	1999 NO_X (tpd)	2006 NO_X (tpd)	2012 NO_X (tpd)	2017 NO_X (tpd)	2020 NO_X (tpd)
On-Road	526.26	284.27	216.64	130.77	88.27
Non-Road	131.40	98.06	65.38	45.54	38.18
Off-Road – Airports	16.88	12.78	14.65	12.36	19.21
Off-Road – Locomotives	22.57	20.14	14.96	12.88	11.74
Area Sources	35.00	29.02	18.49	26.55	34.47
Oil and Gas - Drilling/Production	5.68	80.07	25.93	13.87	6.79
Point - Cement Kilns (Ozone Season Average)	25.02	22.08	9.03	8.87	15.21
Point - Electric Generating Units (August Average)	106.31	12.40	9.78	6.97	10.25
Point - Non-EGUs (Ozone Season Average)	19.48	25.84	24.07	23.18	12.83
Ten-County DFW Area Total	888.60	584.66	398.93	280.99	236.95

Table 9. DFW Area Summer Weekday VOC Emissions Trends from 1999 to 2020

Anthropogenic Emissions Source Category	1999 VOC (tpd)	2006 VOC (tpd)	2012 VOC (tpd)	2017 VOC (tpd)	2020 VOC (tpd)
On-Road	201.14	116.50	92.45	64.91	53.05
Non-Road	89.69	64.69	41.82	34.01	28.76
Off-Road – Airports	3.41	4.46	5.61	2.99	3.36
Off-Road – Locomotives	0.91	1.28	0.91	0.67	0.58
Area Sources	229.30	290.46	227.39	236.70	303.98
Oil and Gas - Drilling/Production	1.47	44.88	71.97	32.18	43.14
Point - Cement Kilns (Ozone Season Average)	1.00	1.94	0.86	0.77	1.80
Point - Electric Generating Units (August Average)	2.00	1.03	3.87	0.55	0.45
Point - Non-EGUs (Ozone Season Average)	35.70	47.47	46.88	46.06	27.90
Ten-County DFW Area Total	564.62	572.71	491.76	418.84	463.02

In order to provide appropriate consistency to the emissions trends in Table 8 and Table 9, a few adjustments were needed to the emissions estimates reported in the SIP revisions. For example, the most recent SIP revisions that included emissions estimates for 2006, 2012, 2017, and 2020 relied on EPA's 2014 version of the Motor Vehicle Emission Simulator (MOVES2014) model (*20*) to develop on-road inventories. The 1999 on-road inventories included in the May 2007 SIP revision relied on the MOBILE6 (21) model that was the predecessor to MOVES, which was not initially released until March of 2010. A 2015 study was conducted by the Texas A&M Transportation Institute (TTI) under contract with the TCEQ to develop on-road emissions trends using the

MOVES2014 model for all 254 Texas counties from 1999 through 2050.(*22*) The 1999 on-road emissions estimates from this TTI trends study for the ten-county DFW nonattainment area are the source of the 526.26 NO_X tons per day (tpd) and 201.14 VOC tpd shown in Table 8 and Table 9, respectively.

The electric generating unit (EGU) emissions estimates reported by TCEQ in the attainment of SIP revisions are often averaged over a period of weeks or months, depending on the timeframe of the modeling episode chosen. To provide consistency, the DFW EGU NO_X emissions estimates reported in Table 8 are based on an average of all 31 days in August of each specified year. The source of these EGU NO_X figures is the EPA Air Markets Program Data (AMPD) (*23*) website, which archives the hourly emissions continuously measured at each EGU facility since 1997. August was chosen to be the representative month for the EGU NO_X trends presented here since it tends to be, on average, the hottest month in any given year, and therefore usually has the highest generation load and emission levels.

Table 10 presents the estimated reductions in NO_X and VOC emissions from 1999 to 2020, based on the values in Table 8 and Table 9 above. The change in NO_X from 1999 to 2020 of 652 tpd is a 73% reduction from 1999 levels. The change in VOC from 1999 to 2020 of 102 tpd is an 18% reduction from 1999 levels. As shown, the on-road source category accounts for the largest reductions of NO_X and VOC at 438 tpd and 148 tpd, respectively. The non-road source category accounts for significant NO_X and VOC reductions of 93 tpd and 61 tpd, respectively. The EGUs operating within the DFW area account for 96 tpd of NO_X reductions from 1999 levels.

Table 10. Change in DFW Area NO_X and VOC Emissions from 1999 to 2020

Anthropogenic Emissions Source Category	Change in NO_X Emissions from 1999 to 2020 (tpd)	Change in VOC Emissions from 1999 to 2020 (tpd)
On-Road	-437.99	-148.09
Non-Road	-93.22	-60.93
Off-Road – Airports	2.33	-0.05
Off-Road – Locomotives	-10.83	-0.33
Area Sources	-0.53	74.68
Oil and Gas - Drilling/Production	1.11	41.67
Point - Cement Kilns (Ozone Season Average)	-9.81	0.80
Point - EGUs (August Average)	-96.06	-1.55
Point - Non-EGUs (Ozone Season Average)	-6.65	-7.80
Ten-County DFW Area Total	-651.65	-101.60

The combined NO_X from the on-road, non-road, and EGU source categories in 1999 totaled 764 tpd, which was 86% of the total 889 NO_X tpd for the entire area. These three source categories accounted for 627 (or 96%) of the 652 NO_X tpd of reductions achieved from 1999 to 2020. Since the on-road, non-road, and EGU categories were such dominant NO_X sources in 1999 and have accounted for the large majority of NO_X reductions, additional focus is warranted.

A copy of Figure 5-1 from the DFW attainment SIP revision from March 2020 is provided in Figure 8 showing on-road emissions trends for an average Summer weekday from 1999 through 2050 for the pollutants of NO_X, VOC, and CO. Also included are historical estimates and future year projections of vehicle miles traveled (VMT) for the ten-county DFW area. The source of the data for this chart is the 2015 TTI trends study previously referenced that was done under contract to TCEQ. As shown, total on-road NO_X, VOC, and CO emissions have continuously declined since 1999 even as VMT has steadily increased. This is due to on-road fleet turnover where older high-emitting vehicles leave the fleet due to attrition, and newer much lower-emitting vehicles that meet stringent standards enter the fleet as new purchases. Even with an increase in VMT, the net effect is an ongoing reduction in total on-road emissions for NO_X, VOC, and CO as average vehicle emission rates steadily decline.

For the light-duty portion of the on-road fleet, stringent Tier 2 standards (*24*) were applied from the 2004-through-2016 model years. The operating NO_X, VOC, and CO emission rates for Tier 2 vehicles are roughly 2% of what unregulated vehicles from the 1960s emitted from the tailpipe. Even more stringent Tier 3 standards (*25*) apply for 2017-and-later model year light-duty vehicles. The operating NO_X, VOC, and CO emission rates for Tier 3 vehicles are less than 1% of what unregulated vehicles from the 1960s emitted from the tailpipe. As these Tier 3 vehicles for 2017-and-later model years continue to enter the fleet and older vehicles leave due to attrition, on-road emissions will continue a steady decline until Tier 3 vehicles dominate the light-duty portion of the on-road fleet. Close inspection of Figure 8 indicates that minimum emissions of on-road NO_X and VOC are expected to occur in 2037 and 2042, respectively, absent more stringent emissions standards being promulgated by EPA in the future.

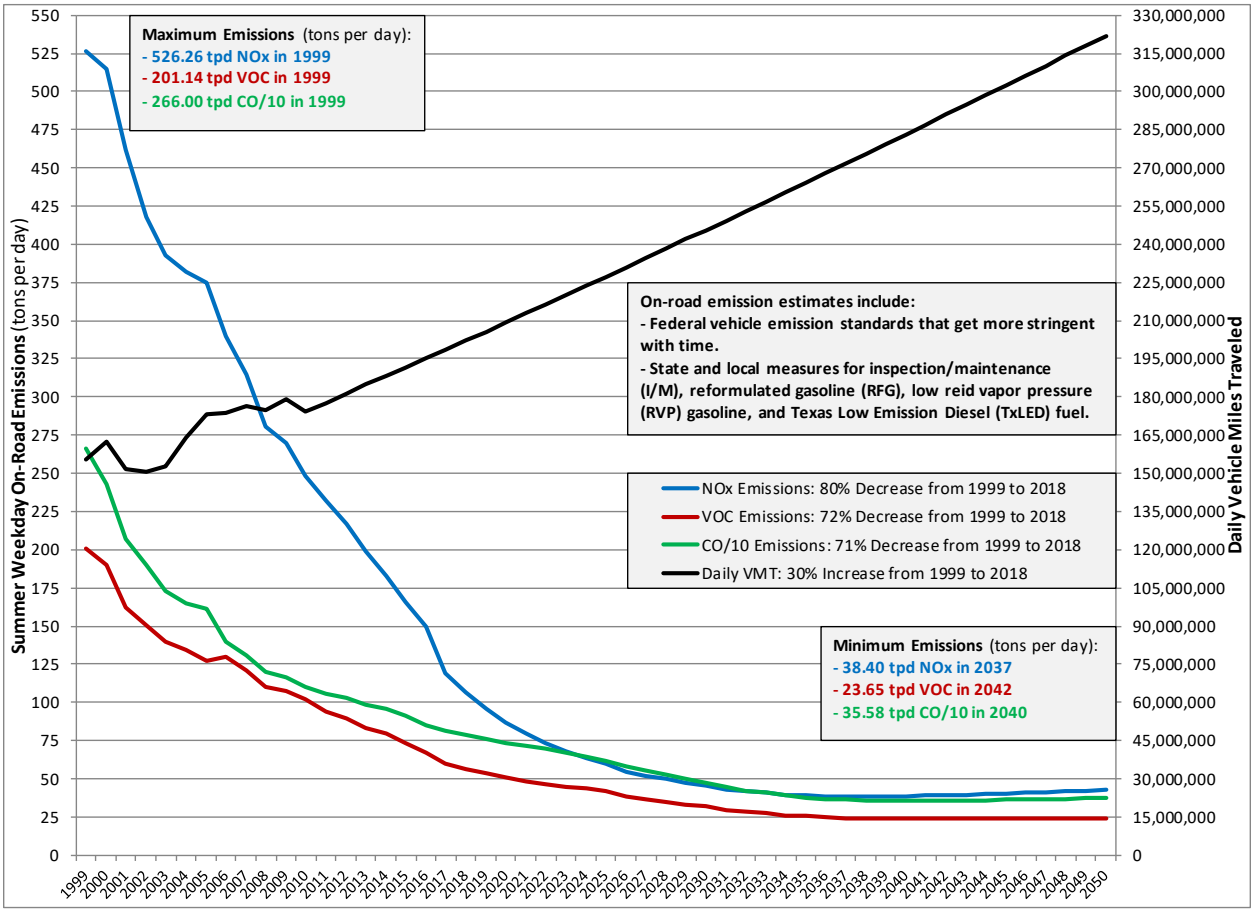

Figure 8. DFW Area On-Road Emissions Trends Reported in TCEQ Attainment SIP

A copy of Figure 5-2 from the DFW attainment SIP revision from March 2020 is provided in Figure 9 showing non-road emissions trends for an average Summer weekday from 1999 through 2050 for the pollutants of NO_X, VOC, and CO. Also included are estimates of the non-road equipment population for each calendar year. The source of the data for this chart are multiple runs of the Texas NONROAD (TexN) model (26) performed by TCEQ staff. As shown, total non-road NO_X, VOC, and CO emissions have continuously declined since 1999 even as the equipment population has steadily increased. Similar to the impacts of on-road fleet turnover, older high-emitting equipment regularly leaves the non-road fleet due to attrition, while newer lower-emitting equipment that meets stringent standards enters the fleet in the form of new purchases. Even with a steady increase in equipment population, the net effect is an ongoing reduction in total non-road emissions for NO_X, VOC, and CO as average equipment emission rates steadily decline. Close inspection of Figure 9 indicates that minimum emissions of non-road NO_X and VOC are expected to occur in 2034 and 2023, respectively, absent more stringent emissions standards being promulgated by EPA in the future.

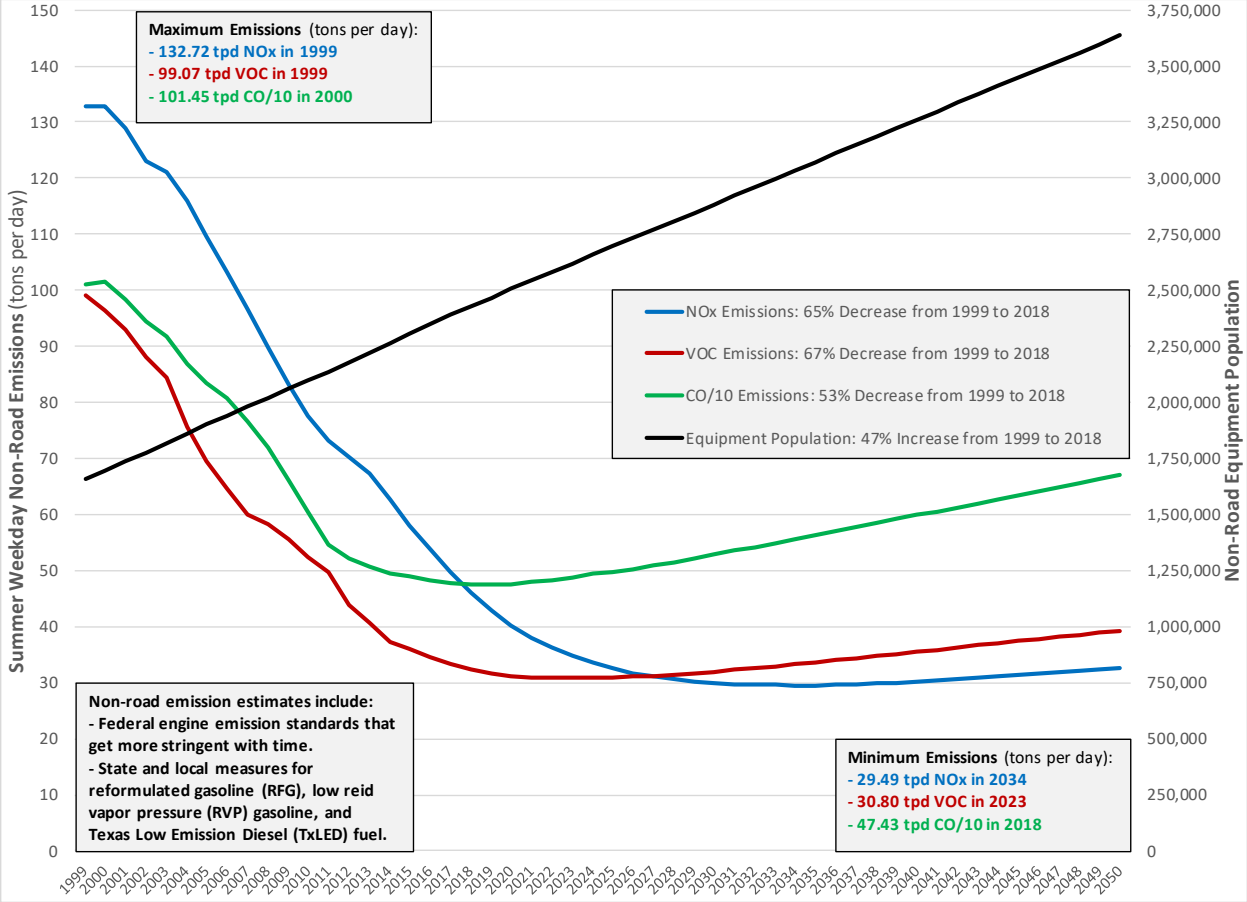

Figure 9. DFW Area Non-Road Emissions Trends Reported in TCEQ Attainment SIP

Figure 10 presents NO_X emissions and electricity generation trends for DFW area power plants from 1997 through 2020. The source of this information is the EPA AMPD website that archives historical hourly EGU emissions, and this chart presents a typical Summer day averaged over the 92 days from June, July, and August of each year. As shown, the 12 power plants that had been operating in DFW from 1997 to 2000 emitted roughly 80 tons of NO_X on an average Summer day, with a notable increase in both generation and NO_X emissions in the Summer of 1998. Substantial reductions in EGU NO_X emissions occurred from 2001 to 2004, and the average amount of EGU NO_X emitted from 2005 to 2020 was typically at or below 10 tons on an average Summer day. Overall, there was an 89% decrease in NO_X emissions from 1997 to 2020 while the amount of electricity generated increased by 21%. Please note that the EGU NO_X emissions presented above in Table 8 are for an August daily average, which is usually higher than the Summer daily average from June, July, and August, as presented in Figure 10.

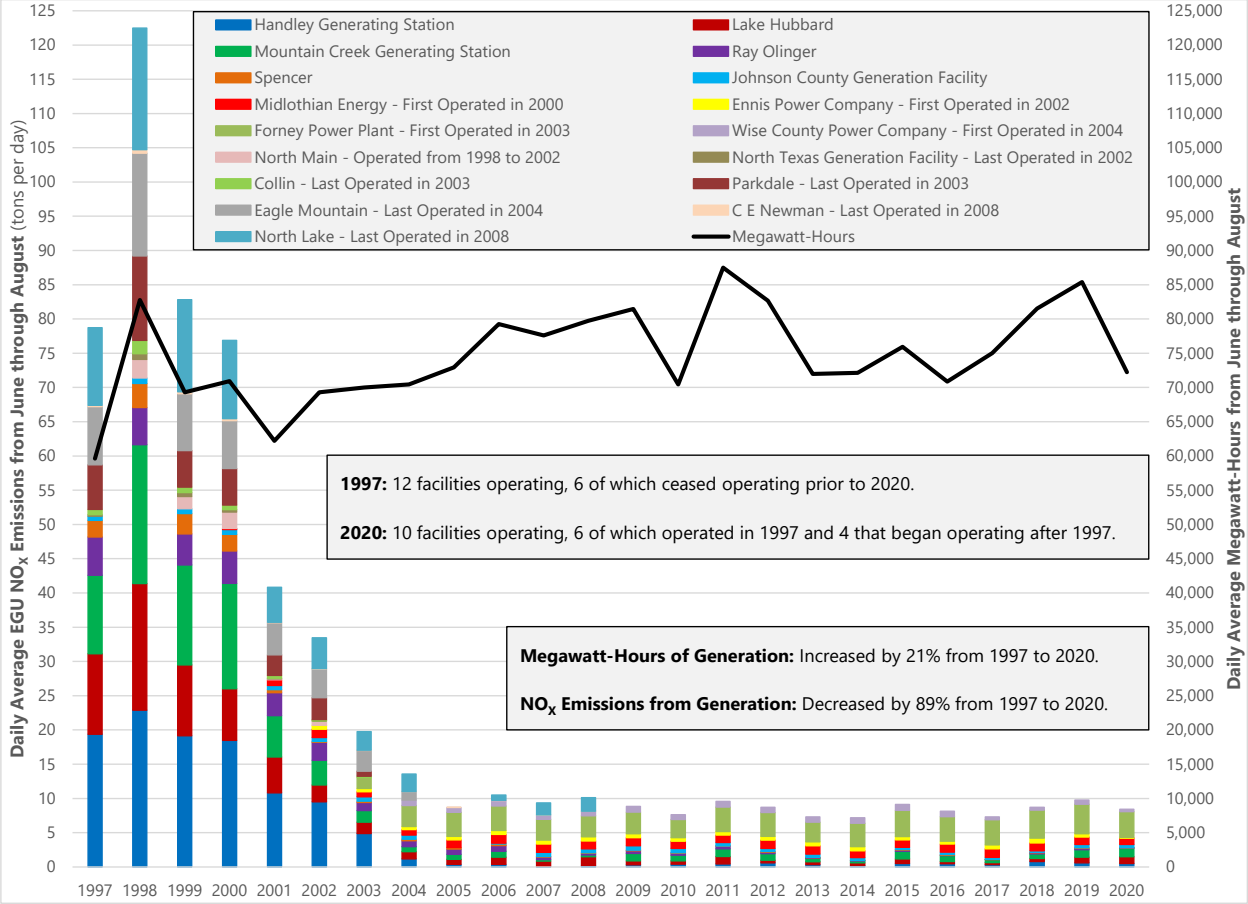

Figure 10. DFW Area EGU NO_X and Electricity Generation Trends from 1997 to 2020

5.2 Trends in Monitored NO_X Concentrations

The DFW attainment SIP revisions adopted by the TCEQ typically include detailed analyses of ozone formation, ozone trends, background and transport of ozone, and trends of NO_X and VOC concentrations over time within DFW. In the DFW attainment SIP revisions presented above in Table 7, this information is included in Chapter 5, *Weight of Evidence*, for the December 2011, June 2015, July 2016, and March 2020 adoptions. In the May 2007 adoption, this information is included in Chapter 4, *Corroborative Analysis*.

In accordance with EPA guidance, each major attainment SIP revision typically includes a conceptual model, which is a comprehensive summary of the "state of the knowledge regarding the influence of emissions, meteorology, transport, and other relevant

atmospheric processes on air quality in the area."(27) In the May 2007 attainment SIP adoption for DFW, the conceptual model was included as Appendix G. For the four subsequent attainment SIP adoptions for DFW from 2011 through 2020, the conceptual model was included as Appendix D.

For the most recent attainment SIP revision from March 2020, a detailed review was conducted of both Chapter 5, *Weight of Evidence*, and Appendix D, *Conceptual Model for the DFW Attainment Demonstration SIP Revision for the 2008 Eight-Hour Ozone Standard*. Similar information is included in the previous DFW attainment SIP revisions from 2007 through 2016, but the March 2020 revision includes more updated monitoring data from recent years in its analyses. It is recommended that interested readers initially review Chapter 5 since it is more condensed, and then Appendix D since it is more detailed and expands on much of the information presented in Chapter 5.

In addition to the 20 ozone monitors presented above in Table 2, the DFW monitoring network also includes 15 NO_X monitors. The TCEQ presented several charts, including Figure 11 shown below that document a steady decline in average monitored NO_X concentrations from 2005 through 2018. Figure 11 is one of these charts showing how peak NO_X concentrations at the 10^{th}, 50^{th}, and 90^{th} percentiles steadily declined from 2005 through 2018 across the DFW area as a whole during the primary ozone season of March through October of each year.

Figure 12 is another of the TCEQ charts showing how the average decline in NO_X concentrations varies across 15 monitors throughout the DFW area. For example, the Kaufman monitor is located in a primarily rural area in the southeast part of DFW that is not surrounded by a high density of NO_X sources, and only a slight decline from roughly 4-5 ppb to 2-3 ppb is observed from 2005 to 2018, respectively, at the 50^{th} percentile. Conversely, the Dallas Hinton monitor is located in a densely populated area immediately northwest of downtown Dallas and adjacent to multiple highways. From 2005 through 2018, the 50^{th} percentile NO_X concentration at Dallas Hinton has steadily declined from roughly 15 ppb to 5-6 ppb. The NO_X trends for other monitors located throughout DFW are included in Figure 12. Historically, the monitors in primarily urban areas (such as Dallas Hinton) have relatively high NO_X concentrations, and they generally saw the sharpest declines in average NO_X concentrations over time. Monitors in more rural areas (such as Kaufman) tended to have relatively low or moderate NO_X concentrations in past years. Thus, while decline in NOx concentrations are still present in more rural areas, the declining rates are not as steep as those of urban monitors.

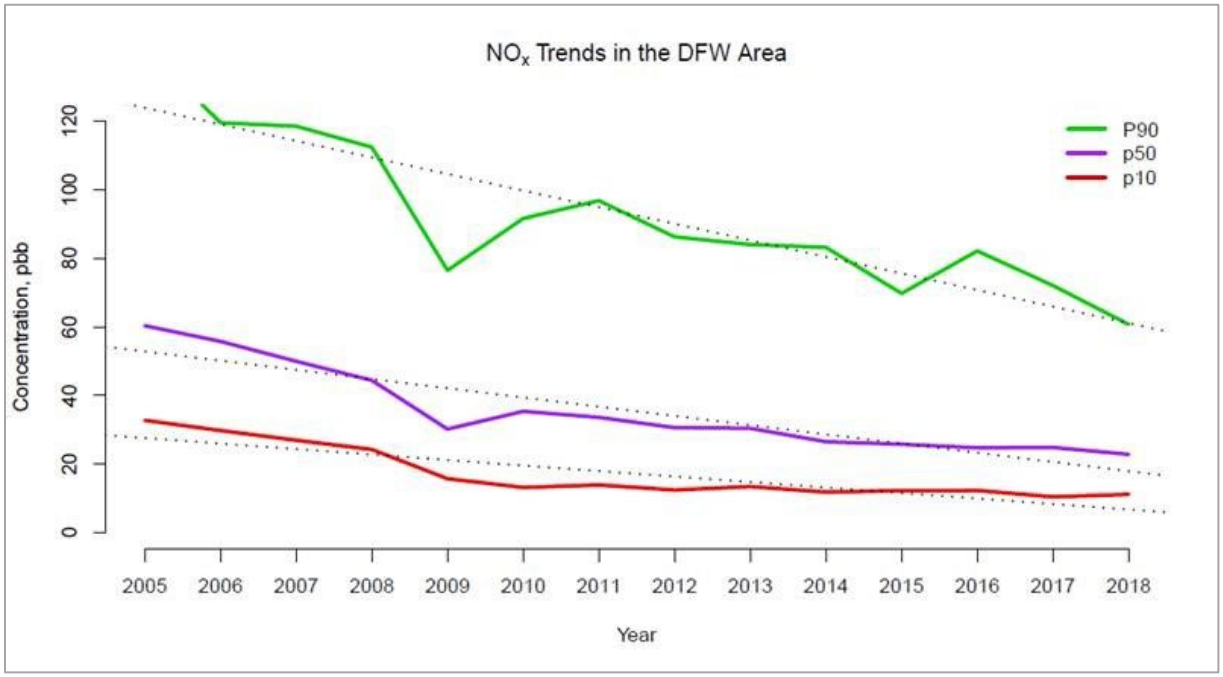

Figure 11. Figure 5-6 from DFW Attainment SIP for Peak NO_X Concentration Trends from 2005 through 2018

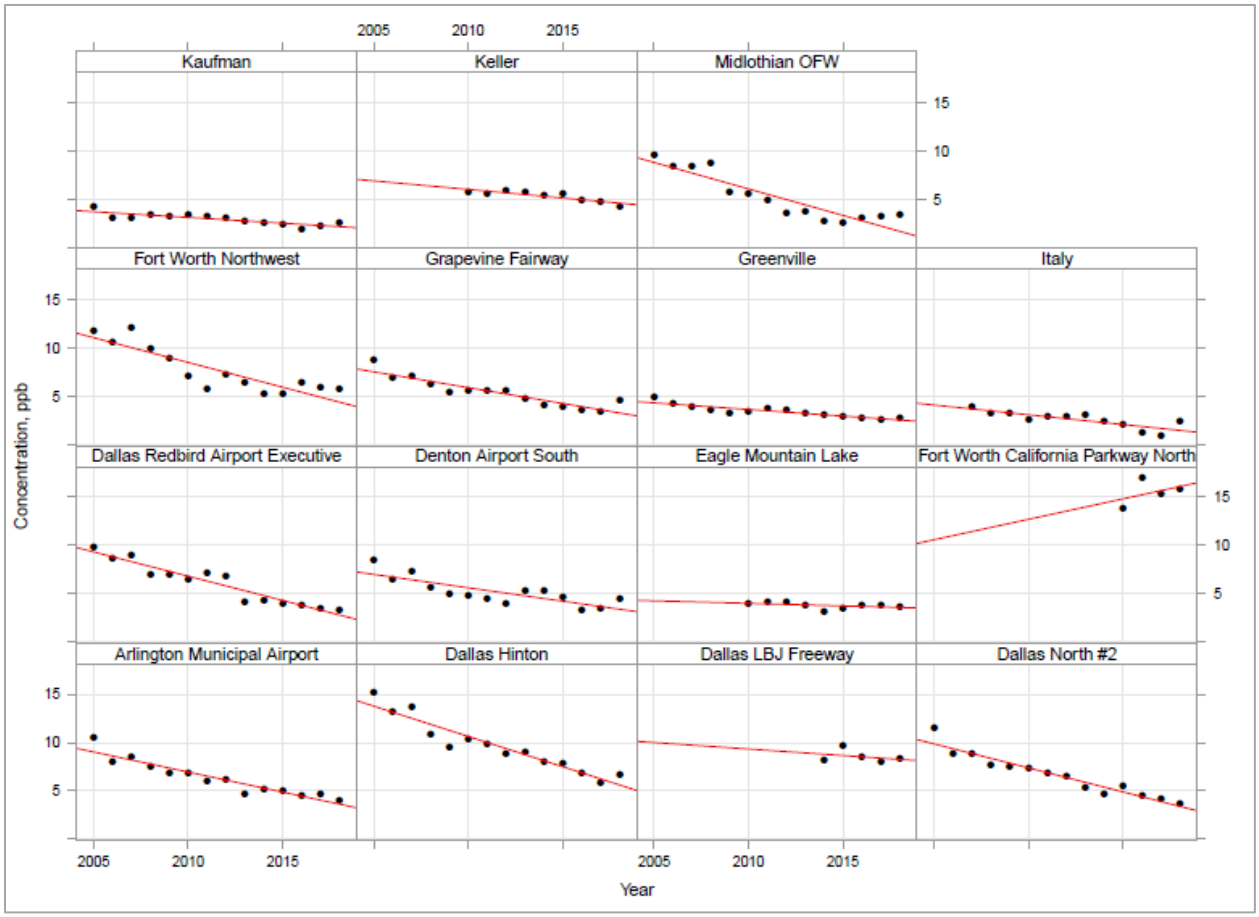

Figure 12. Figure 5-7 from DFW Attainment SIP for 50th Percentile NO_X Concentrations at Fifteen DFW Monitors from 2005 through 2018

TCEQ had included a chart showing a steady decline in NOx concentration for the Dallas Hinton monitor from 1995 to 2018 in their July 2019 presentation (28). The aforementioned chart is in this report as Figure 13. Since the Dallas Hinton monitor has been operational for many years, the historical NOX concentrations are available for earlier years than other newer monitors. Figure 13 shows that average NOX concentrations were reduced by roughly 69-72% from 1995 to 2018, depending on the percentile grouping of the measurements averaged from May through September of each year. Due to its location downwind of multiple highways and downtown Dallas, NOX emissions concentrations measured at the Dallas Hinton monitor are influenced primarily by on-road mobile sources. The steady and continuous decline in average NOX concentrations evident in Figure 13 parallels the steady and continuous decline in on-road NOX emissions presented above in Figure 8.

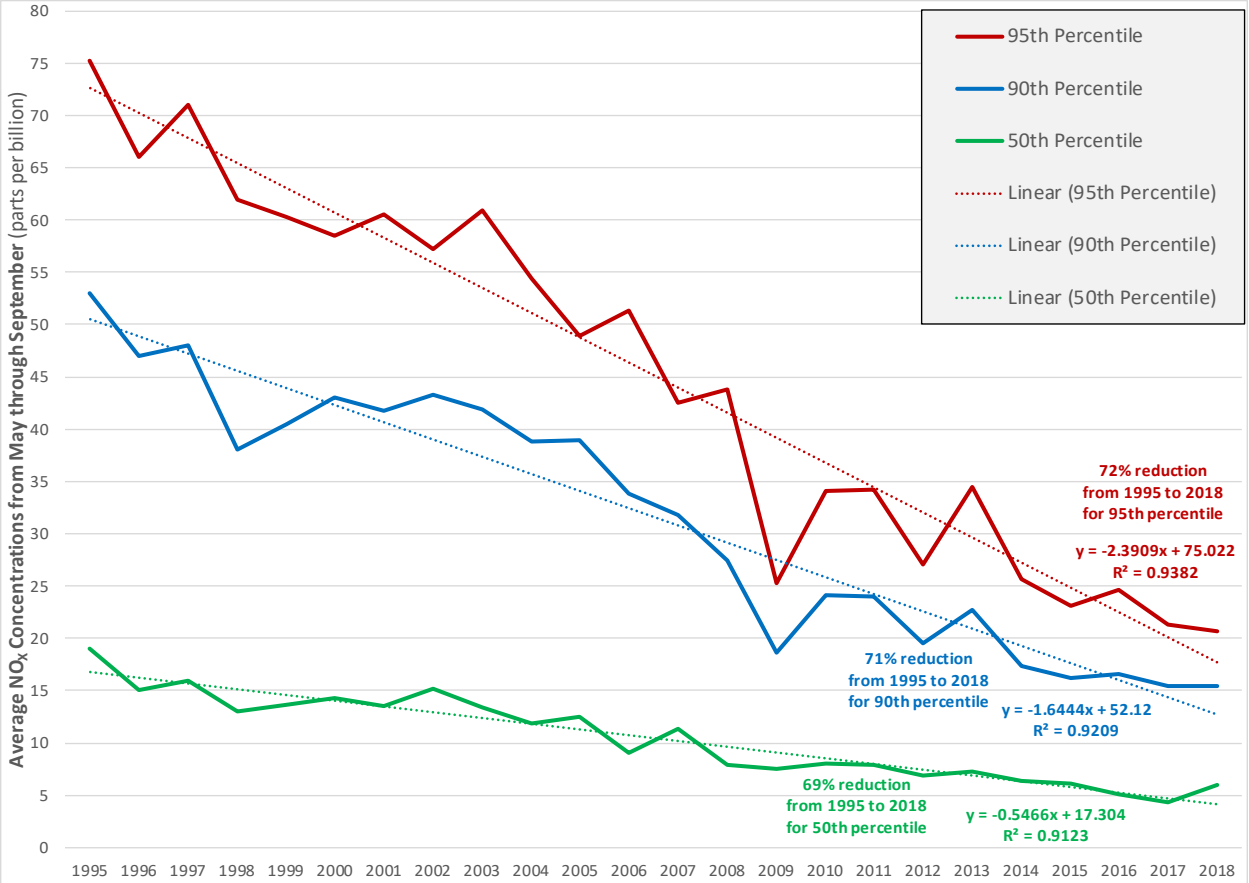

Figure 13. NO_X Concentration Trends at Dallas Hinton Monitor from 1995 through 2018

5.3 Trends in Monitored VOC Concentrations

In addition to the 20 ozone monitors presented above in Table 2, the DFW monitoring network also includes 15 automated gas chromatograph (auto-GC) monitors for VOC. The monitoring datasets include 58 VOC species identified for photochemical assessment monitoring stations (PAMS). (29) Figure 14 is a chart included by TCEQ showing the 50th percentile VOC trends at fifteen DFW area monitors from 2005 through 2018. For the entire period, the overall trend in VOC concentrations is downward at the majority of monitors. The exceptions to this are the Dallas Hinton, Eagle Mountain Lake, and Fort Worth Northwest monitors, all of which show a slightly upward VOC concentration trend when averaged from 2005 through 2018. However, all three monitors show a slightly downward trend if averaged over more recent years from 2014 through 2018.

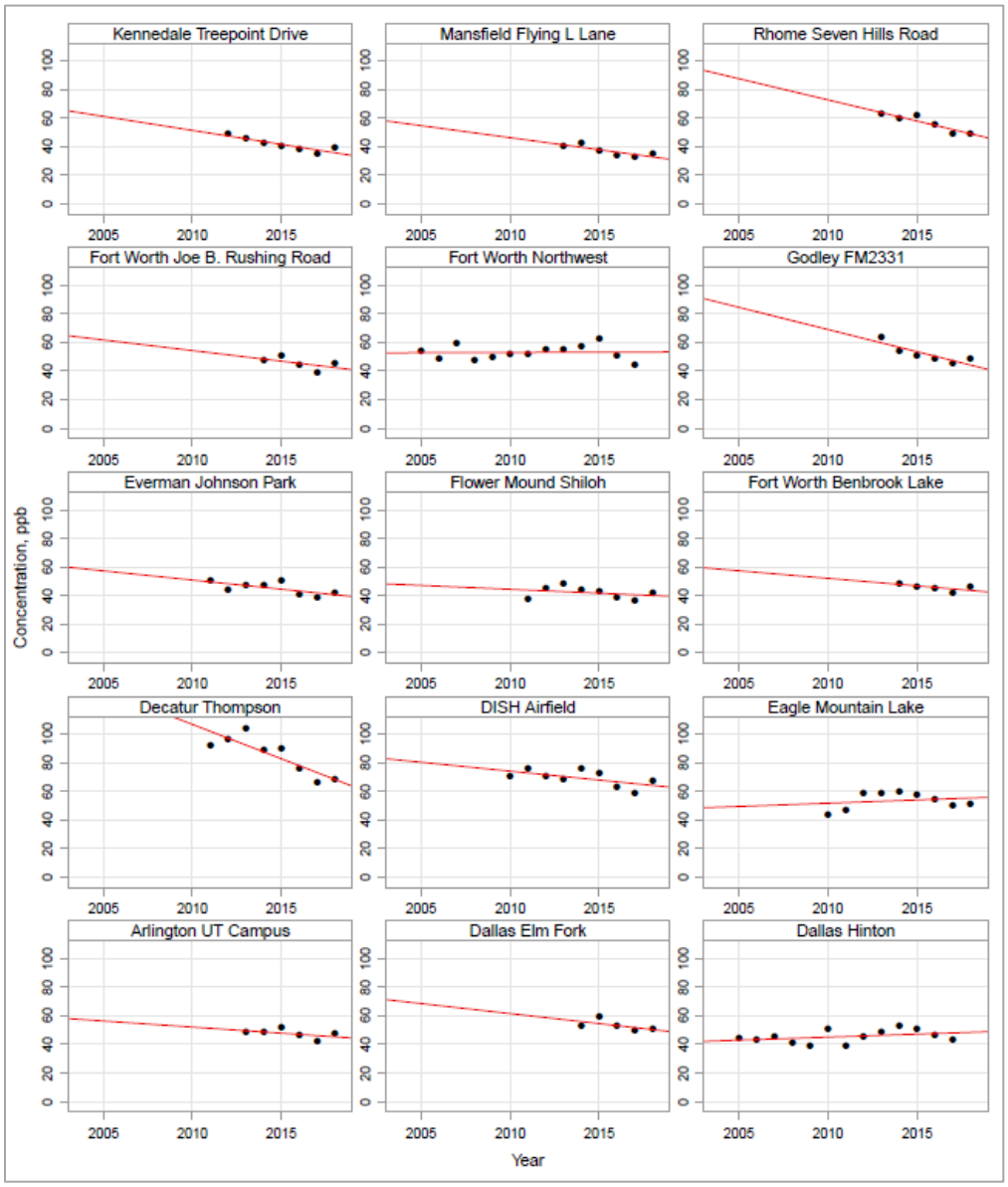

Figure 14. Figure 5-10 from DFW Attainment SIP for 50th Percentile VOC Trends at Fifteen DFW Monitors from 2005 through 2018

Appendix D to the DFW attainment SIP provides analyses of VOC collected with 24-hour gas canisters at twelve locations from 2000 to 2012, and these collection efforts are in addition to the auto-GC measurements. In general, the annual geometric means of VOC concentrations show the sharpest rates of decline prior to 2006, with more shallow rates of decline from 2006 through 2012.

5.4 Ethylene and Propylene Trends Measured with Gas Canisters

Appendix D to the DFW attainment SIP includes a discussion on the highly reactive VOC (HRVOC) compounds of ethylene and propylene. The measurements used in this discussion were retrieved from 2000 through 2012 at the auto-GC monitors and with 24-hour canisters. The general finding is that the DFW area as a whole experienced decreased concentrations in both ethylene and propylene from 2000 through 2012. The most substantial decrease in ethylene and propylene occurred between 2000 and 2009. The declines in these compounds were most pronounced at the Dallas Hinton and Fort Worth Northwest monitors, both of which are influenced by on-road activity from nearby highways.

Table 11 is a summary of the ethylene and propylene content of the VOC profiles used to speciate the on-road VOC emissions for the DFW area. The profiles are identified in a set of emissions processing message files for a 2020 calendar year inventory provided by TCEQ. (30) The EPA SPECIATE database is the source of the nine profiles listed. (31) Each of the nine profiles individually contains between 83 and 121 hydrocarbon species, and all nine profiles combined contain 242 individual hydrocarbon species. As shown, ethylene and propylene are primarily by-products of engine combustion rather than fuel evaporation. For diesel engines, both propylene and ethylene are relatively large contributors for 2006-and-earlier model year vehicles, but the contribution is reduced for 2007-and-later model year vehicles. For gasoline engines, both propylene and ethylene are relatively large contributors for vehicle cold start operation, but the contribution is reduced for hot stabilized exhaust operation. Figure 8 summarized significant reductions in DFW area on-road VOC emissions due to fleet turnover. As the total on-road VOC emissions have steadily declined in DFW, it is highly probable that the ethylene and propylene components of on-road emissions have also declined, and this is the most likely cause of these reductions identified at the Dallas Hinton and Forth Worth Northwest monitors.

Table 11. Ethylene and Propylene Content in VOC Speciation Profiles for DFW Area On-Road Emissions

Profile Code	EPA Profile Description	Weight % Ethylene	Weight % Propylene
5552	Diesel Exhaust - Low Aromatic Diesel - Cold Start	4.94%	1.82%
8774	Diesel Exhaust Emissions from Pre-2007 Model Year Heavy-Duty Diesel Trucks	20.45%	5.87%
8775	Diesel Exhaust Emissions from 2007 Model Year Heavy-Duty Diesel Engines with Controls	3.07%	0.94%
8839	86°F Static Permeation Evaporative Emissions from Gasoline Vehicles Using 10% Ethanol at 7 Reid Vapor Pressure (RVP)	0.00%	0.00%
8851	Dynamic Permeation Evaporative Emissions from Gasoline Vehicles Using 10% Ethanol at 7 RVP	0.19%	0.00%
8867	Gasoline Headspace Vapor - 10% Ethanol (E10), 15% Aromatics	0.00%	0.00%
8888	Gasoline - 10% Ethanol (E10), 15% Aromatics	0.00%	0.00%
8917	Gasoline Exhaust - E10 Gasoline, Summer Grade, LA92 Cycle - Stabilized Exhaust	0.81%	1.62%
8923	Gasoline Exhaust - E10 Gasoline, Summer Grade, LA92 Cycle - Cold Start	2.78%	6.31%

5.5 NO_X and VOC Limitation of Ozone Formation Analyzed with Monitoring Data

The TCEQ included a detailed discussion of NO_X versus VOC limitation in ozone formation in the most recent DFW attainment SIP documentation from March 2020. Since the anthropogenic and biogenic emission sources throughout DFW are not evenly distributed, the monitored concentrations of NO_X and VOC can vary significantly, particularly between urban and rural areas. Therefore, any analysis of NO_X and VOC limitations must be done on a monitor-specific basis before drawing conclusions about the DFW area as a whole.

The TCEQ reported that "VOC to NO_X ratios are calculated by dividing hourly total non-methane hydrocarbon (TNMHC) concentrations in parts per billion by carbon (ppbC) by hourly NO_X concentrations in parts per billion by volume (ppbV). Ratios less than 5 ppbC/ppbV are considered VOC limited, ratios above 15 ppbC/ppbV are considered NO_X limited, and ratios between 5 ppbC/ppbV and 15 ppbC/ppbV are considered transitional."(32)

Figure 15 is a chart included by TCEQ in the DFW Attainment SIP, which showed the trends in VOC to NO_X ratios at the Dallas Hinton, Eagle Mountain Lake, and Fort Worth Northwest monitors from 2005 through 2018 based on auto-GC data. From 2005 through 2009, the Dallas Hinton and Fort Worth Northwest monitors had VOC to NO_X ratios below 5 ppcC/ppbV and would be characterized as primarily VOC limited. Since roughly 2010, both of these monitors have shown an upward trend in their VOC to NO_X ratios and are now characterized as transitional monitors. If VOC is held constant over time while NO_X steadily decreases, then the VOC to NO_X ratio will increase. The NO_X concentration trends over time presented above in Figure 12 and Figure 13 show steady declines for the Dallas Hinton and Fort Worth Northwest monitors, while the VOC concentrations over time presented above in Figure 14 show relatively little change for these monitors. The expected effect is to transition towards a more NO_X limited environment due to lowering NO_X while VOC remains relatively constant.

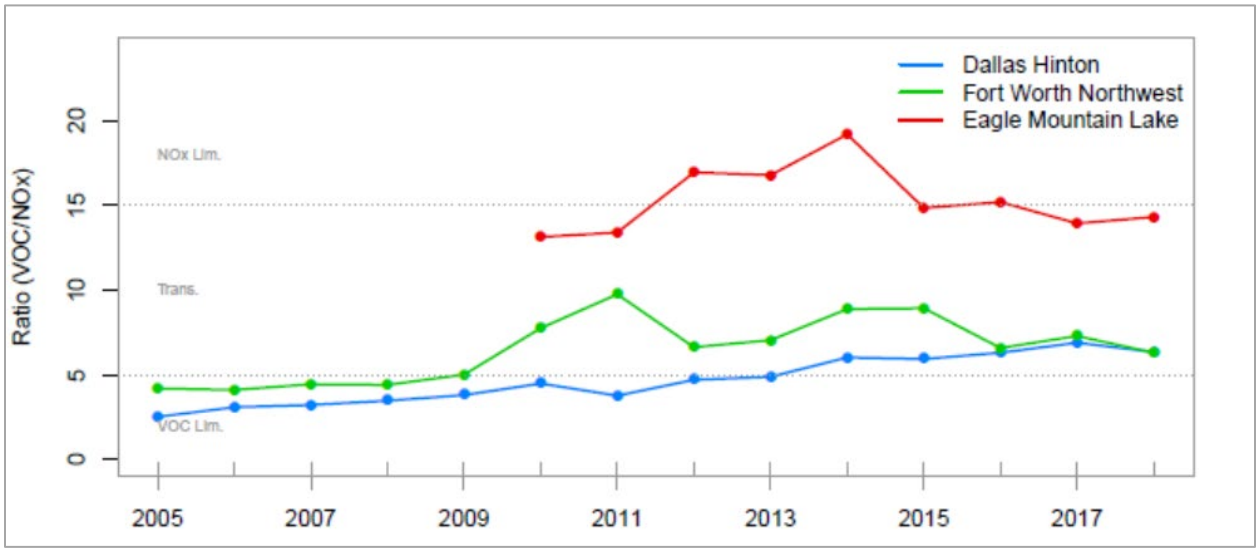

Figure 15. Figure 5-8 from DFW Attainment SIP for Trends in VOC to NO_X Ratios at Three Monitors from 2005 through 2018

Additional discussion about NO_X versus VOC limitation of ozone formation is included in Appendix D of the DFW Attainment SIP. An analysis of 24-hour canister data from 2000 through 2013 in Appendix D showed that the Denton Airport South, Kaufman, Midlothian, and Italy monitors are solidly in the NO_X limited range, while the Dallas Hinton, Fort Worth Northwest, and Grapevine Fairway monitors are in a transitional range. The results using canister VOC data do not identically match with the results

presented above using auto-GC VOC data as the former are 24-hour measurements collected every six days while the latter is continuous measurements.

Information is presented by TCEQ to show how the VOC to NO_X ratio can vary by hour of the day. In the morning hours, the lower mixing height keeps anthropogenic emissions closer to the surface, and morning NO_X emissions are contained beneath this mixing layer. Biogenic VOC emissions such as isoprene are just starting to be emitted in early morning hours as solar radiation becomes present. It is not until later morning hours and mid-day that the heating of the earth's surface raises the mixing layer while biogenic emissions simultaneously increase due to increased solar radiation. During later afternoon hours, biogenic emissions begin decreasing due to lower overhead solar radiation, and then become markedly reduced during overnight hours. The net effect from various sources emitting at different rates throughout the day is variable VOC to NO_X ratios by the hour at many locations. The primary conclusions drawn by TCEQ are:

- the majority of monitors in the suburban and rural portions of DFW are primarily NO_X limited; and
- some monitors in more urban areas of DFW used to be VOC limited, but are now transitional and trending towards NO_X limitated as average NO_X concentrations continue to decrease.

5.6 NO_X Limitation Predicted by Weekday/Weekend Effect

Figure 16 is a chart from the DFW attainment SIP that shows the peak NO_X concentrations by day of the week at 15 monitors from 2005 through 2018. The variation is most pronounced at monitors dominated by on-road mobile sources, such as Dallas Hinton, where NO_X concentrations are lowest on Sundays when VMT activity is lowest and highest during weekdays when VMT activity is at its peak.

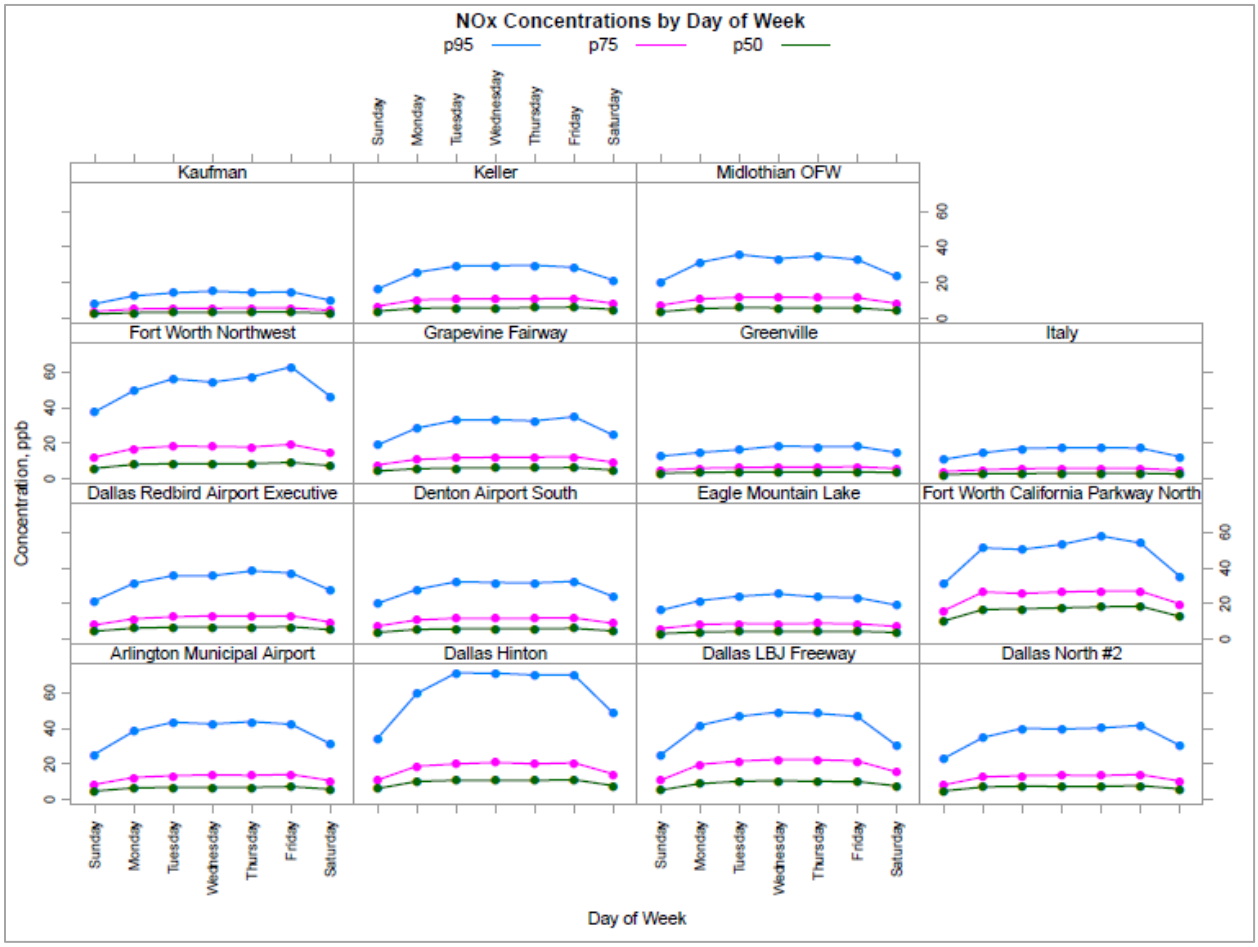

Figure 16. Figure 5-9 from DFW Attainment SIP for Peak NO_X Concentrations by Day of Week from 2005 through 2018

This variation in NO_X concentrations by day of week results in a useful test for determining NO_X or VOC limitation. The meteorological conditions that lead to high ozone concentrations are randomly distributed by day of week, but the precursor NO_X emissions are not. In a NO_X limited environment, reduced NO_X emissions on weekends would on average lead to lower ozone levels than on weekdays. In a VOC limited environment, reduced NO_X emissions on weekends would lead to less titration and therefore higher ozone levels than on weekdays.

An analysis is included in the *Weight of Evidence* chapter of the DFW attainment SIP showing the number of high eight-hour ozone days by day of week from 2005 through 2018. Sunday had the lowest number of high ozone days at 30, while there were 75 high ozone days on a Thursday and 71 on a Friday. A similar analysis is included in Appendix D for the years from 1997 through 2013. The same pattern as the previous analysis was evident where Sunday had the fewest number of high ozone days at 85 while Thursday

and Friday had the highest numbers at 120 and 137, respectively. The primary conclusion is that there is a pronounced weekday/weekend ozone effect in DFW due to varying NO_X emissions from on-road sources, and that the reduced number of high ozone days on weekends versus weekdays indicates a primarily NO_X limited environment.

6.0 LITERATURE REVIEW OF STUDIES RELATED TO OZONE FORMATION AND PRECURSORS

This section reviews some recent studies related to ozone formation and precursors.

The Effects of COVID-19 Activity Changes on Air Quality in Texas, Texas Commission on Environmental Quality (TCEQ), November 18, 2020. (33)

Based on monitoring data available in late 2020, the TCEQ investigated the possible impacts of COVID-19 activity changes on air quality in DFW, El Paso (ELP), Houston-Galveston-Brazoria (HGB), San Antonio (SAN), and Beaumont-Port Arthur (BPA). The TCEQ evaluated monitoring data for ozone, NO_X, and HRVOC over the six months of April through September 2020, and compared them with previous years. The TCEQ emphasizes that "the complexity of urban air pollution means it is difficult to determine with certainty if observed differences are due to COVID-19 activity changes, meteorology, or other causes." For the DFW area, the TCEQ noted that the eight-hour design values in 2020 decreased up to 4 ppb at some monitors and increased up to 2 ppb at others. They also noted that the NO_X and HRVOC levels during 2020 in DFW indicated mixed results with some monitors showing decreases in concentrations while others showed increases. The TCEQ emphasized that "these mixed results may be due to typical year-to-year variability observed in ozone and its precursors."

Based on data obtained from the University of Maryland *COVID-19 Impact Analysis Platform*, (34) the TCEQ included a summary of weekly miles traveled per person within each of the five Texas metropolitan areas during 2020, and the weekly trends matched well among the areas. These rates of miles traveled began falling in early March, reached their lowest point in early April, and then steadily increased until reaching the pre-pandemic levels by mid-June where they roughly stabilized in subsequent months.

Ability of Models to Reproduce the Observed Changes in Ozone in the South Coast Air Basin (SoCAB) Due to Emissions Reductions from COVID-19, Ramboll US Consulting, Coordinating Research Council (CRC) Report Number A-126, March 2022. (35)

The primary purpose of this study was to estimate the ozone impacts throughout the greater Los Angeles area of the anthropogenic emissions reduced due to the temporary reduction of activity that occurred in the early phases of the COVID-19 pandemic. The author Ramboll noted that the largest reduction in transportation activity and associated on-road emissions due to COVID-19 occurred in late March and April of 2020, with the

reduction impacts lessening in subsequent months. Ramboll also noted that evaluating time periods such as late March and April are too early in the year because the highest ozone levels that drive the design values for the SoCAB are typically monitored in the hotter Summer months from May through August. Ideally, all four months of May, June, July, and August could be included in such an analysis, but Ramboll emphasizes that meteorological conditions in both May and August of 2020 were much more conducive to ozone formation than previous years, so comparisons with recent non-COVID-19 years would prove difficult. If the historically high ozone months of 2020 had relatively similar meteorological conditions to recent years, then it would be more straightforward to evaluate the "natural experiment" of a sudden reduction in anthropogenic emissions due to an episode like COVID-19.

Ramboll noted the difficulties of performing such an analysis, particularly in comparison to attainment demonstrations where the meteorological conditions for a base case episode are held constant for modeling both the base case and future emissions scenarios. For such attainment analyses, a model performance evaluation is performed on the base case to determine its suitability for estimating the ozone impacts of the reduced emissions levels that are expected in the future year(s). However, to fully evaluate impacts from an episode like COVID-19, it is impossible to perform proper model performance evaluations on both COVID-19 and non-COVID-19 emissions scenarios because they do not simultaneously occur under identical meteorological conditions.

Ramboll elected to focus on the months of June and July of both 2019 and 2020. 2019 was chosen because it was the closest year to 2020 with respect to "business as usual" (BAU) levels of anthropogenic emissions. Ramboll compared the meteorological conditions for June 1-July 31 of both years and found them to be different, but similar enough that ozone impacts from COVID-19 could be approximated. Ramboll estimated that overall anthropogenic NO_X was reduced by 13% from BAU levels during this time due to COVID-19. For the entire two-month period, it was estimated that these NO_X emissions reductions resulted in the following domain wide impacts in eight-hour ozone: maximum increase of 0.81 ppb in VOC limited areas, and a maximum reduction of 1.33 ppb in NO_X limited areas.

Ramboll noted that not only does the western portion of SoCAB have the highest population density in the region, but it is also part of the Pacific coastal area, which can "inhibit ozone formation by trapping fresh NO_X emissions within a shallow surface marine layer producing more VOC-sensitive ozone formation conditions." The

combination of high population density, close proximity to the coast, and the absence of a large amount of naturally occurring vegetation typically leads to VOC limited ozone formation where reductions in NO_X will tend to cause local increases in ozone. In general, the NO_X limited portions of the larger SoCAB region are located further east away from the coast and in areas of high population density. Overall, 2020 ozone levels in the SoCAB were higher than in 2019, and Ramboll states that "meteorology played the major role in the increases in ozone between 2019 and 2020."

On-Road Remote Sensing of Automobile Emissions in the Phoenix Area: Spring 2021, Gary A. Bishop, University of Denver, Coordinating Research Council (CRC) Report Number E-119-3, March 2022. (36)

The primary purpose of this study was to estimate in-use tailpipe emissions of the light-duty on-road fleet in Phoenix using remote sensing equipment. The University of Denver had done similar work in the Phoenix area in 1998, 1999, 2000, 2002, 2004, and 2006. Across five days in April of 2021, a total of 18,294 vehicle records were obtained. The ratios to carbon dioxide (CO_2) were measured for the following six tailpipe pollutants: CO, hydrocarbons (HC), NO, NO_2, ammonia (NH_3), and SO_2. Bishop reported that the SO_2 levels measured were negligibly small and below the instrument detection limits. The Tier 3 regulations that began with the 2017 model year require a phase-in through 2020 to get gasoline sulfur levels down to 10 ppm from the level of 30 ppm that applied during the Tier 2 model years from 2004 through 2016. Prior to the Tier 2 requirements, gasoline sulfur levels averaged roughly 300 ppm.

Bishop compared the 2006 and 2021 results and estimated that the overall reductions in light-duty NO, HC, and CO were 52%, 15%, and 15%, respectively. During 2006, the light-duty on-road fleet would be dominated by Tier 1 vehicles from the 1994-through-2000 model years and national low emission vehicles (NLEVs) from the 2001-through-2003 model years. Vehicles meeting more stringent Tier 2 standards did not start entering the fleet until the 2004 model year, and this phase-in would not be completed until the 2007 model year. So, a 2006 sample would not capture many in-use vehicles meeting Tier 2 standards. Compared to 2006, a 2021 sample would capture far fewer vehicles meeting Tier 1 and NLEV standards because many of these would have left the fleet due to attrition. Instead, the 2021 sample would be dominated by the Tier 2 vehicles from the 2004-through-2016 model years and the even more stringent Tier 3 vehicles that began phasing into the fleet with the 2017 model year.

Bishop notes that the NO and HC emission levels for Tier 2 vehicles "are low and vary little even with age." Bishop stated that, compared to Tier 2 vehicles, even lower emissions levels are detected in the NO and CO readings from Tier 3 vehicles, but the reductions are "small on an absolute basis" and that "the lowest emitting segments of the fleet continue to approach zero emissions." These results make sense since Tier 2 emission rates for these pollutants are roughly 2% of the unregulated levels of emissions from vehicles of the 1960s, while Tier 3 emission rates for these pollutants are less than 1% of unregulated levels.

Bishop reported that the pattern of fleet mean emissions being dominated by a small percentage of high emitting vehicles is similar to the results of previous remote sensing studies. In the 2021 Phoenix data set, the highest emitting 1% of the measurements (99th percentile) accounted for 32% of the NO, 49% of the NO_2, 19% of the HC, 28% of the CO, and 19% of the NH_3. Bishop also noted a vehicle age anomaly in the 2021 data set where fewer 2020 and 2021 model year vehicles were identified compared to what would be expected under non-pandemic conditions. Bishop stated that remote sensing studies performed after the 2008 financial crisis also revealed fewer 2009 and 2010 model year vehicles than what would be expected under non-recession conditions.

Unexpected Slowdown of U.S. Pollutant Emission Reduction in the Past Decade, Jiang et al., Proceedings of the National Academy of Sciences (PNAS), May 15, 2018. (37)

The primary purpose of this study was to evaluate the rate of NO_X and CO reductions that occurred throughout the U.S. from 2011 to 2015 compared to those from 2005 to 2009. Satellite data from the Ozone Monitoring Instrument (OMI) were used for NO_2, along with surface measurements from the EPA AQS datasets. They found a general agreement in the NO_2 measurements between the OMI and AQS datasets. The combination of the different datasets indicated that overall U.S. NO_X emissions were reduced from 2005 to 2009 at a rate of 7% (+/- 1.4%) per year. From 2011 to 2015, the rate of NO_X reduction had slowed to 1.7% (+/- 1.4%) per year.

CO measurements of the same time period were obtained from the Measurement of Pollution in the Troposphere (MOPITT) and the AQS datasets. The rates of reduction in CO were estimated at 7% from 2005 to 2009 and 4.6% from 2011 to 2015. The authors noted that trends of CO reductions in gasoline vehicles were highly correlated with trends in VOC reductions. They also noted that the slowdown in the rate of NO_X, VOC, and CO reductions is expected since three-way catalytic converters in gasoline vehicles

have already provided substantial reductions and it is inevitable that a point of diminishing returns will be reached.

The authors stated that as on-road emissions had been steadily declining, the relative contribution to total NO_X emissions from industrial, area, and off-road sources had increased. However, they did note that overall industrial, area, and off-road NO_X emissions showed a roughly similar pattern to on-road sources in that the rate of reduction for these sectors were higher from 2005 to 2009 than from 2011 to 2015. The authors emphasized that the reduction in power plant NO_X emissions, which started in the late 1990s, had steadily progressed during the time period of evaluation.

Dallas Measurement of Ozone Production Sensor (MOPS), Barry Lefer (University of Houston), William Brune (The Pennsylvania State University), Air Quality Research Program (AQRP) Project Number 10-034, December 1, 2011. (38)

The primary purpose of this study was to deploy ozone production sensors from August to October 2011 at the Fort Worth Northwest and Eagle Mountain Lake monitoring sites. The data collection at the Fort Worth Northwest site was more complete than at the Eagle Mountain Lake monitor because some technical problems were encountered at the latter. At the Fort Worth Northwest monitor, Lefer found that ozone production was significant during mid-morning with peak production rates of 40-60 ppb per hour on sunny days with southerly winds. Ozone production was less than 10 ppb per hour on cloudy days. The days with the highest ozone production at Fort Worth Northwest coincided with the highest morning NO concentrations, which were very likely from morning rush-hour activity since this monitor is located in an urbanized area close to highways. Lefer also found that the ozone production at Fort Worth Northwest generally exceeded the observed ozone, which indicated that this is a source region where some of the ozone produced was transported away to downwind locations. The preliminary data collected at Eagle Mountain Lake showed that less ozone was produced in the vicinity of this location, with peaks only exceeding 40 ppb per hour on a few occasions.

Surface Measurements and One-Dimensional Modeling Related to Ozone Formation in the Suburban Dallas-Fort Worth Area, Robert Griffin (Rice University), Jack Dibb (University of New Hampshire), Barry Lefer (University of Houston), Allison Steiner (University of Michigan), Air Quality Research Program (AQRP) Project Number UTA10-000875-RICE-RP24-TO2, December 16, 2011. (39)

A primary purpose of this study was to install additional air quality monitoring equipment at the Eagle Mountain Lake monitor from May 30 to June 30, 2011. An

additional primary purpose was to perform computational modeling with the generated data. The initial round of data collection and analysis indicated that the "air quality at the Eagle Mountain Lake site is determined by being a receptor of aged and processed air from the DFW metropolitan area." The research team was able to draw this conclusion by identifying a relatively small NO to NO_Y ratio in the measurements. NO_Y refers to a broad mix of reactive nitrogen compounds that includes NO, NO_2, nitric acid (HNO_3), nitrous acid (HONO), organic nitrates, and particulate nitrates. (40) A large NO to NO_Y ratio would imply that the NO was more "fresh" and likely to have been emitted locally. A smaller NO to NO_Y ratio indicates that more reaction products are present, which is evident of more aged and processed air from upwind urbanized locations.

The researchers found that biogenic VOC, mostly in the form of isoprene, are the main reactive species during daylight hours. Meteorological measurement equipment was also deployed, which allowed the research team to determine that "boundary layer heights ranged between an average of 500 meters at night and 2,000 meters during the day", from which it could be determined that "any emissions that occur locally during the day would expect to be diluted by a factor of four compared to any local emissions overnight." Even though Eagle Mountain Lake was primarily identified as a receptor site, the researchers noted that local sources would intermittently influence monitored air quality. One-hour ozone readings over 75 ppb were identified on June 6, 7, 22, and 23, which were the four days that had lower than average wind speeds along with lower overnight heights for the planetary boundary layer.

Constraining Ozone-Precursor Responsiveness Using Ambient Measurements, Antara Digar, Daniel S. Cohan, Xue Xiao, Kristen M. Foley, Bonyoung Koo, Greg Yarwood, Journal of Geophysical Research: Atmospheres, 2013. (41)

The primary purpose of this study was to perform a series of Monte Carlo modeling simulations to identify factors that strongly influenced ozone formation in the DFW area during an episode from May 31 through July 1, 2006 using the high-order decoupled direct (HDDM) method. 17 of 33 days in this ozone episode had meteorological conditions conducive to ozone formation, which made it an excellent candidate period for analysis. As indicated in Table 7 above, this episode was also used in three attainment demonstration SIPs adopted by the TCEQ from 2011 through 2016.

Attainment demonstration modeling typically requires a deterministic approach using the best available emissions inputs and model formulations. In this study, a probabilistic approach was taken that resulted in 4,000 model simulations where NO_X and VOC

emissions sensitivities were applied to four different structural changes for the modeled boundary conditions, chemical mechanism, biogenic inputs, and dry deposition scheme. The magnitude of the NO_X and VOC emissions adjustments that were applied were constrained by observed data from 11 DFW area monitors to keep them within the range of uncertainty and avoid highly unrealistic modeling simulations.

The research team identified the best-performing modeling simulations from the total sample of 4,000. From these results, they determined that afternoon ozone formation in DFW is primarily NO_X limited with ozone roughly an order of magnitude more sensitive to anthropogenic NO_X than to anthropogenic VOC. While some VOC limited ozone formation occurs in different areas at different times of day, the researchers found that NO_X limited conditions persisted for daily maximum eight-hour ozone, even in the urban centers where VOC limited ozone formation is more common.

The report also provided detailed results for the Denton Airport South monitor, and noted that similar trends were observed at the other sites. On a per ton basis, the researchers found that NO_X reductions were roughly 7.9 times more effective than VOC reductions for reducing average eight-hour ozone concentrations. The results from the full ensemble of modeling scenarios estimated a 93% likelihood that ozone formation in DFW is more sensitive to anthropopgenic NO_X than to anthropogenic VOC.

7.0 DISCUSSION

7.1 Form of the Eight-Hour Ozone Standard

As shown in the overview of the NAAQS, the ozone standard has become more stringent over time. The former one-hour standard of 124 ppb was strengthened to successive eight-hour standards of 84 ppb, 75 ppb, and the current 70 ppb level. For each ozone monitor within a given area, the form of the eight-hour standard is based on averaging the fourth-highest measured ozone level per year over the three most recent years. Changes in meteorological conditions and precursor emission levels are common from year to year, so this three-year averaging approach has the effect of smoothing out fourth-highest ozone levels that may be abnormally high or low within a given year.

For example, assume economic and transportation activity temporarily drop for a full calendar year due to a deep recession or episode like COVID-19, and this results in the fourth-highest ozone level being abnormally low for that year. Unless this reduced economic and transportation activity persists for three full years, the other two years in the design value calculation will likely have higher fourth-highest ozone levels, and this will keep the design value from becoming abnormally low. A contrary example is when meteorological conditions are unusually favorable for ozone formation within a single year, resulting in an abnormally high fourth-highest ozone level. Unless these unusual meteorological conditions persist for full three years, data from the other two years will keep the design value from becoming abnormally high.

7.2 DFW Area Ozone Trends

As shown above in the overview of ozone trends in DFW, the peak eight-hour ozone design value of 106 ppb has been reduced by 30 ppb from 1995 to the 2021 level of 76 ppb. The overall DFW population had increased significantly during this time, almost doubling from 1990 to 2020. There are 20 ozone monitors currently operating in the greater DFW area, and the majority of these monitors have operated continuously in their current locations for over two decades. The overall trend in the eight-hour ozone design values for all 20 monitors is downward. Starting in 2014, none of the 20 monitors were out of compliance with the 84 ppb standard. All 17 monitors operating in 2007 were out of compliance with the 75 ppb standard, and only one monitor is out of compliance as of 2021. All 20 monitors operating in 2013 were out of compliance with

the 70 ppb standard, and 10 are out of compliance as of 2021. As these trends show, eight-hour ozone levels have been steadily reduced across the DFW area over time.

Due to the dominant south/southeasterly wind direction in the DFW area during ozone season months, the highest ozone design values tend to be found at the monitors in the north and northwest portions of DFW. The historical pattern has been that the ozone monitors located in the south and east portions of DFW achieve design values below a standard (e.g., 84 ppb, 75 ppb, 70 ppb) sooner than the ones in the north and northwest portions do. Provided that the dominant wind directions during ozone season do not change in DFW, this historical pattern will likely remain.

As shown above in the overview of ozone formation, it is a complex process of NO_X and VOC reacting in the presence of sunlight. The large majority of NO_X emissions are from anthropogenic activity, while VOC emissions are emitted from a combination of anthropogenic and biogenic sources. There is a very wide range of ozone forming reactivity among individual VOC species, with highly reactive isoprene from biogenic sources playing a notably critical role. Overall, NO_X limited ozone formation is typically found in suburban and rural areas, while VOC limited ozone formation is more common within dense urban cores.

7.3 Reductions in DFW Ozone Precursor Emissions

From 2007 through 2020, the TCEQ has adopted five attainment demonstration SIP revisions for the eight-hour ozone standards of 84 ppb and 75 ppb. NO_X and VOC emissions estimates for base and future years from 1999 through 2020 were included with these SIP revisions. Total anthropogenic NO_X emissions are estimated to have been reduced by 652 tpd (73%) from 889 tpd in 1999 to 237 tpd in 2020. Total anthropogenic VOC emissions are estimated to have been reduced by 102 tpd (18%) from 565 tpd in 1999 to 463 tpd in 2020. The large bulk of the NO_X emissions reductions have come from the source categories of on-road, non-road, and power plant EGUs. The majority of the VOC emissions reductions have come from the on-road and non-road source categories.

The primary reason for the on-road and non-road emissions reductions is fleet turnover where older high-emitting vehicles/equipment leave the fleet due to attrition and are replaced by newer low-emitting ones. The newer vehicles/equipment have emission rates low enough to more than offset the effects of population and activity growth in vehicles and equipment. The fleet turnover trend is expected to yield further reductions

of NO_X and VOC from on-road sources, and further reductions of NO_X from non-road sources. Changes in powerplant regulations were the primary reasons for the EGU NO_X emissions reductions. These changes in regulations resulted in DFW EGU NO_X dropping from roughly 80 tpd in the late 1990s to hovering between 7-10 tpd on an average Summer day from 2005 through 2020.

Due to the significant reductions in NO_X and VOC emissions that have occurred since the 1990s, temporary reductions in economic activity (e.g., from a recession or episode like COVID-19) are going to have less of an air quality impact than they would have in the past. For example, assume that temporary reductions in economic and transportation activity happened during all of 1999 and all of 2020, and the effect in both years was a 10% across-the-board cut in NO_X emissions from all source categories. In 1999, the 10% reduction would result in 88.9 NO_X tpd reduced from the 889 NO_X tpd total. In 2020, the 10% reduction would result in 23.7 NO_X tpd reduced from the 237 NO_X tpd total. Under this scenario, the NO_X emissions reduction impact in 1999 would be almost four times higher than the impact in 2020. For hypothetical scenarios of 20% or 30% reductions in emissions, these figures can be multiplied by factors of 2 and 3, respectively.

During the peak period of the COVID-19 shutdown, the primary reduction in activity was likely from on-road sources in late March and early April, as indicated by the TCEQ in their COVID-19 impacts study. Table 8 from above includes DFW on-road area NO_X emissions estimates for 1999 through 2020. If a 10% across-the-board reduction in on-road activity occurred in 1999, the 10% reduction would result in 52.6 NO_X tpd reduced from the 526 NO_X tpd total. In 2020, the 10% reduction would result in 8.8 NO_X tpd reduced from the 88 NO_X tpd total. For on-road sources, the NO_X emissions reduction impact in 1999 would be roughly six times higher than the impact in 2020. As shown, a 10% reduction from a fleet composed of lower-emitting vehicles is going to have much less of an impact than a 10% reduction from a fleet composed of higher-emitting vehicles. This same general pattern applies to the non-road and EGU source categories. As with on-road, the non-road and EGU NO_X emission rates per unit of activity in 2020 were much lower than they were in 1999. Therefore, incremental activity reductions of 10%, 20%, 30%, etc. are going to have much less of an overall emissions impact for sources with relatively low emission rates.

7.4 Trends in NO_X and VOC Concentrations

In its attainment demonstration SIP from March 2020, the TCEQ summarized trends in NO_X concentrations from multiple monitors throughout DFW from 2005 through 2018. The overall trend is downward, with relatively shallow rates of decline for rural NO_X monitors and more pronounced rates of decline for urban NO_X monitors such as Dallas Hinton and Fort Worth Northwest which are heavily impacted by nearby on-road activity. These pronounced NO_X reduction trends at urban locations parallel the on-road NO_X emissions reduction trends identified in the attainment SIP documentation.

The TCEQ also summarized VOC concentration trends at auto-GC monitors from 2005 through 2018, and from 24-hour gas canisters from 2000 through 2012. VOC concentration trends are downward at the majority of monitors, but are flat or slightly upward at a few monitoring locations depending on the time period under review. The TCEQ identified reductions in the HRVOC species of ethylene and propylene across the DFW area from 2000 to 2012, with the most pronounced reductions occurring from 2000 to 2009 at the urban monitors of Dallas Hinton and Fort Worth Northwest. Since these monitors were the most impacted by on-road activity, and on-road VOC is known to contain ethylene and propylene, it is likely that on-road fleet turnover accounted for these reductions in HRVOC. As shown in Figure 8, fleet turnover is expected to result in additional VOC reductions from the on-road source category, so some additional reductions in ethylene and propylene can be expected in future years.

7.5 NO_X versus VOC Limitation of Ozone Formation

Within its SIP documentation, the TCEQ included an analysis of NO_X versus VOC limitation at multiple DFW area monitors by evaluating trends in VOC/NO_X ratios. In 2005, the core urban monitors of Dallas Hinton and Fort Worth Northwest had VOC/NO_X ratios below 5 and were VOC limited. However, the VOC/NO_X ratio at both monitors slowly trended upward and towards NO_X limitation through 2018, and they can now be characterized as transitional monitors. The remaining DFW monitors, for which VOC/NO_X ratios were available, showed characteristics of being either transitional or fully NO_X limited. These results matched with the basic understanding of ozone formation, where monitors in heavily urban areas tend more towards VOC limitation, while those in more suburban and rural locations tend towards more NO_X limitation. Also, with NO_X reductions being more pronounced over time than VOC reductions, increase in VOC/NO_X ratios and an overall trend toward more NO_X limited ozone formation are to be expected.

As part of its NO_X versus VOC limitation analysis, the TCEQ presented a summary of the high ozone days that have occurred on weekdays versus weekend days from 1997 to 2013, and from 2005 to 2018. Weekday/weekend analyses are excellent tests of NO_X versus VOC limitation for a specific area. While the meteorological conditions leading to high ozone are randomly distributed over time across all days of the week, NO_X emissions on weekends are significantly lower than on weekdays due primarily to reduced on-road activity. In a VOC limited environment, ozone would tend to increase on weekends because there would be less NO_X available to titrate ozone. In a NO_X limited environment, the reduced weekend NO_X would lead to less ozone. The ozone monitoring data in DFW show a significantly reduced number of high ozone days occurring on weekends versus weekdays. Sundays tend to have the lowest amount of NO_X in the week, and the fewest number of high ozone days in DFW have occurred on Sundays compared with other days of the week. This analysis further supports characterizing ozone formation in the greater DFW area as primarily NO_X limited.

Based on the primarily NO_X limited ozone formation characteristics of DFW, the reductions in NO_X emissions were the primary cause of the reduced eight-hour ozone levels in DFW from the peak in 1995 through today. The estimated emissions and monitored concentration data indicated that reductions in anthropogenic VOC had also occurred during this time, but not to the same degree as anthropogenic NO_X. If large portions of DFW remained primarily VOC limited, some monitors would show a noticeable increase in ozone design values at some point. The ongoing reduction in NO_X emissions would have inevitably led to short-term increases in monitored ozone due to decreased ozone titration. Instead, when evaluated over multiple years, each monitor had shown an overall downward trend in peak ozone with expected fluctuations from year-to-year based on varying meteorological conditions.

7.6 Literature Review of COVID-19 Studies

The literature review section documents various recent studies on COVID-19 impacts. The TCEQ compared ozone, NO_X, and HRVOC concentration data from DFW and other Texas areas for April-September in 2020 to previous years, and primarily found that the data were within the normal range of year-to-year variability, so a discernible COVID-19 impact could not be determined with high confidence. The TCEQ noted that reduction in on-road activities began in early March for all areas, reached its lowest point in early April, and began steadily increasing again until reaching pre-pandemic levels by mid June of 2020, and leveling off in subsequent months. During 2020 in DFW, the number

of days monitored with eight-hour ozone above 70 ppb were four in May, five in June, and ten in August. No days were monitored above 70 ppb in the nine other months.

Ramboll performed an in-depth analysis to estimate the impacts of reduced activity in 2020 due to the COVID-19 pandemic on the ozone formation in the Los Angeles area. Since 2019 was the closest year to 2020 with respect to anthropogenic emissions, it was used as a reference case. In the report from March 2022, Ramboll noted that the reductions in activity from COVID-19 were most pronounced during late March and April of 2020; however, peak ozone in the area typically occurs from May through September. This is somewhat analogous to DFW and other Texas cities, such as Houston, where the highest ozone levels tend to occur in June and August. In previous years, low or moderate ozone levels are typically seen throughout Texas in March and April, with only occasional high ozone days occurring.

In its comparison of 2019 and 2020 ozone formation for Los Angeles, Ramboll noted that the months of May and August in 2020 had meteorological conditions much more suitable for ozone formation than May and August of 2019. Therefore, these months had to be ruled out for comparison purposes and the months of June and July of both years were studied instead, even though anthropogenic activities were returning to normal from the peak shutdown impact in March/April. While there were some notable differences in the meteorology in June/July of 2019 compared to 2020, Ramboll stated that the conditions were similar enough to draw approximate estimates of ozone impacts. An overall NO_X emissions reduction of 13% was estimated due to COVID-19, and the peak modeled ozone impacts were a 1.33 ppb reduction in NO_X limited areas of Los Angeles and an 0.81 ppb increase in VOC limited areas. Ramboll added the important qualification that "meteorology played the major role in the increases in ozone between 2019 and 2020."

This Ramboll analysis for greater Los Angeles is highly instructive in that it focused on the importance of evaluating meteorological conditions as an integral part of any COVID-19 impacts analysis. At any given levels of anthropogenic NO_X and VOC emissions, high ozone can be formed provided that sufficient sunlight and stagnant winds persist throughout the day. Any analysis of COVID-19 versus non-COVID-19 impacts from different years should first take meteorological conditions into account.

Since April of 2020 was the peak month for reduced activity from COVID-19, comparisons have been made for various areas of the U.S. between April of 2019 and April of 2020 to estimate pollutant impacts. The Grapevine Fairway monitor in DFW had

the highest eight-hour design value in 2020, at 76 ppb, so it was chosen as an example to demonstrate that hourly average wind speeds during April of 2020 were noticeably lower than in the three previous years of 2017, 2018, and 2019. This is demonstrated in Figure 17. At the same level of emissions, lower average wind speeds will cause pollutant concentrations to increase. Under identical meteorological conditions, a reduced level of anthropogenic emissions will cause pollutant concentrations to decrease. However, the results get mixed when lower average wind speeds (e.g., April 2020 versus April 2019), which caused concentrations to increase, were coupled with reduced emissions from a one-time event such as COVID-19 (e.g., April 2020), which caused concentrations to decrease. This combination makes it very difficult to confidently estimate and isolate the impacts that the COVID-19 shutdowns have had on pollutant concentrations in DFW during the peak shutdown month of April 2020.

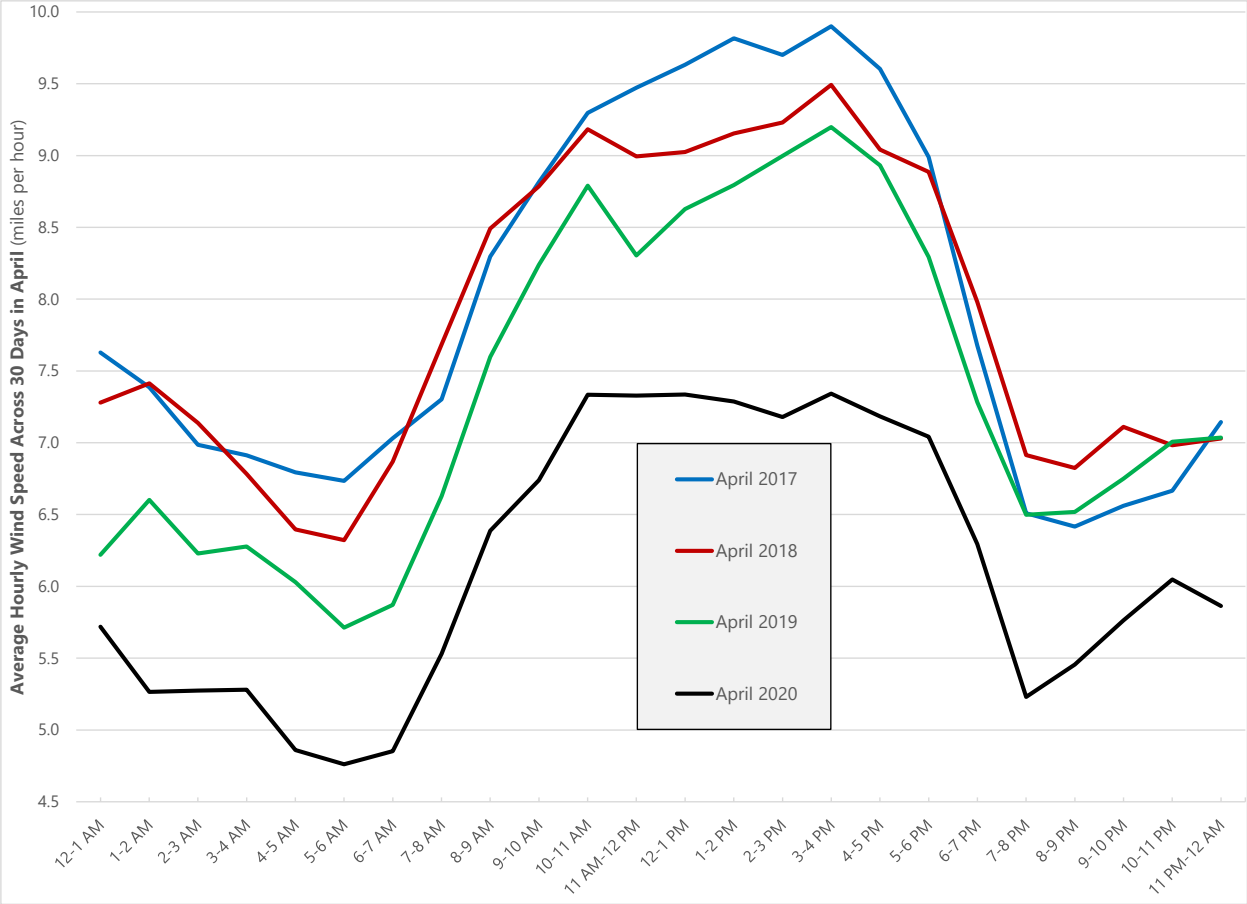

Figure 17. Hourly Average April Wind Speeds at the Grapevine Fairway Ozone Monitor from 2017 through 2020

Further evidence of the crucial importance of meteorological conditions was demonstrated by reviewing the DFW ozone monitoring data from July, August, and September of 2020. During July and September of 2020, none of the 20 ozone monitors measured eight-hour ozone values at or above 70 ppb. However, eight-hour ozone levels above 70 ppb were measured on ten days in August of 2020. There were no indications that the levels of NO_X and VOC precursor emissions during July and September of 2020 were significantly different than during August of 2020. Instead, the meteorological conditions during August were more conducive to ozone formation than during July and September.

August is typically the month when the highest ozone levels are measured in DFW and other major Texas cities. If the peak shutdown impacts of COVID-19 during 2020 had occurred during August instead of March/April, it is likely that less ozone would have been formed due to decreased levels of precursor emissions. Since the eight-hour ozone standard is based on the fourth-highest ozone level measured during the year, it

is the high ozone days (e.g., those occurring in August) that drive the design value rather than the low or moderate ozone days (e.g., those occurring in March or April).

Reduced levels of anthropogenic NO_X and VOC emissions alone cannot guarantee that high ozone days will not occur. However, reduced levels of anthropogenic NO_X and VOC emissions will reduce the frequency with which high ozone days occur. This becomes evident by evaluating day of week emissions estimates with the weekday/weekend analyses documented by TCEQ from 1997 through 2018. The TCEQ SIP documentation typically reports NO_X and VOC emissions for a Summer weekday since that is the most representative day of the week for ozone modeling applications. Chapter 3 and Appendix B of the March 2020 attainment SIP also detailed how on-road, non-road, and area source emissions were expected to differ on weekdays versus weekends.

For the 2020 emissions documented by TCEQ, the Sunday versus weekday NO_X and VOC emissions for DFW are provided in Table 12 and Table 13, respectively. As shown, Sunday NO_X and VOC are estimated to be reduced from their weekday levels by roughly 27% and 20%, respectively. Assuming that a similar pattern of relative reductions had existed over time in DFW, the TCEQ weekday/weekend analysis demonstrated that reduced levels of precursor emissions on a Sunday do not eliminate the chance of high ozone days occurring, but the reduced levels certainly lower the frequency with which they occur.

Table 12. 2020 Weekday versus Sunday NO_X Emissions in DFW

Anthropogenic Emissions Source Category	Weekday NO_X (tpd)	Sunday NO_X (tpd)	NO_X Impact (tpd)	Relative NO_X Change
On-Road	88.27	59.53	-28.74	-32.6%
Non-Road	38.18	23.16	-15.02	-39.3%
Off-Road – Airports	19.21	19.21		
Off-Road – Locomotives	11.74	11.74		
Area Sources	34.47	13.78	-20.69	-60.0%
Oil and Gas - Drilling/Production	6.79	6.79		
Point - Cement Kilns (Ozone Season Average)	15.21	15.21		
Point - EGUs (August Average)	10.25	10.25		
Point - Non-EGUs (Ozone Season Average)	12.83	12.83		
Ten-County DFW Area Total	236.95	172.5	-64.45	-27.2%

Table 13. 2020 Weekday versus Sunday VOC Emissions in DFW

Anthropogenic Emissions Source Category	Weekday VOC (tpd)	Sunday VOC (tpd)	VOC Impact (tpd)	Relative VOC Change
On-Road	53.05	48.22	-4.83	-9.1%
Non-Road	28.76	37.21	8.45	29.4%
Off-Road – Airports	3.36	3.36		
Off-Road – Locomotives	0.58	3.36		
Area Sources	303.98	106.83	-197.15	-64.9%
Oil and Gas - Drilling/Production	43.14	43.14		
Point - Cement Kilns (Ozone Season Average)	1.8	43.14		
Point - EGUs (August Average)	0.45	43.14		
Point - Non-EGUs (Ozone Season Average)	27.9	43.14		
Ten-County DFW Area Total	463.02	371.54	-91.48	-19.8%

7.7 Literature Review of Ozone Precursor Emission Studies

An informative study from March 2022 was reviewed where the University of Denver collected over 18,000 remote sensing measurements of light-duty vehicle exhaust in the Phoenix area during 2021 and compared the results to previous work from 2006. The researchers found that light-duty NO_X, HC, and CO had reduced by 52%, 15%, and 15%, respectively, over the 15-year span. In 2006, only a small number of vehicles meeting Tier 2 standards would have been present in the fleet; however, the light-duty fleet in 2021 would have a large number of Tier 2 vehicles that were sold through the 2016 model year and Tier 3 vehicles that started entering the fleet with the 2017 model year.

The pattern of on-road NO_X reductions being larger than on-road VOC reductions agrees with both the TCEQ emissions estimates and monitored concentration data from DFW. The researchers emphasized that exhaust emission levels from Tier 2 vehicles are quite low, and that Tier 3 exhaust emission levels are even lower, though the absolute magnitude of difference between Tier 2 and 3 vehicles is small. These results are in agreement with the Tier 2 and Tier 3 rules promulgated by EPA, along with the emission rates incorporated into the MOVES model. Tier 2 vehicles emit roughly 2% of unregulated levels of NO_X and VOC, while Tier 3 vehicles emit less than 1% of unregulated levels. The NO_X and VOC emission rates for newer light-duty vehicles are very low and appear to be reaching a point of diminishing returns.

A May 2018 study that analyzed satellite and AQS data across the continental U.S. from 2005-2009 and 2011-2015 was reviewed. The authors found that the annual rate of overall NO_X reduction from 2005-2009 was roughly 7%, but they were only 1.7% from 2011-2015. The results for CO were roughly 7% from 2005-2009 and 4.6% for 2011-2015. The authors note the CO and VOC emissions from gasoline vehicles are highly correlated. They noted that some of this slowdown in the annual rates of reduction is expected since a significant number of very low-emitting light-duty vehicles are now present in the fleet, thus not allowing for the same magnitude of reductions from this sector that occurred in previous years. This finding agrees with the Phoenix remote sensing results that identified very low emission rates for Tier 2 and 3 light-duty vehicles.

7.8 Literature Review of DFW Ozone Monitoring and Modeling Studies

The reports of two AQRP projects conducted in the DFW area during 2011 were reviewed. In the first, the Fort Worth Northwest and Eagle Mountain Lake monitors were equipped with ozone production sensors. The results at the Fort Worth Northwest monitor showed that the highest levels of ozone production typically occur during mid-morning as a result of rush hour NO_X emissions. The researchers found that the amount of ozone produced at Fort Worth Northwest generally exceeds the amount of ozone observed at this location, which indicates that this area is a source region from which some ozone is transported downwind. This makes sense because Fort Worth Northwest is in a more urbanized area with a greater density of ozone precursor emissions. Problems were encountered with the ozone production sensors at the Eagle Mountain Lake site, but the preliminary data showed less ozone produced there than observed, which indicates that the Eagle Mountain Lake area is more of a receptor region for ozone than a source one.

The second AQRP study was an excellent companion to the first because it equipped the Eagle Mountain Lake monitor with additional measurement equipment. Analyses of the measured data confirmed that while some ozone were produced in the vicinity of Eagle Mountain Lake, it is primarily a receptor region for transported ozone. This was determined by measuring the concentrations of aged reaction products, with a greater portion of aged products indicating that the ozone was formed upwind. This makes sense because Eagle Mountain Lake is in a more rural area with a lower density of ozone precursor emissions. It should be noted that all regions are both a source and a receptor

to some degree as wind patterns will inevitably transport ozone and its precursors to-and-from that region. As transported and emitted pollutants continuously mix and get transported, regions with high activity will tend towards being sources and regions of low activity will tend towards being receptors. The researchers also found that isoprene was the dominant reactive VOC species present during daylight hours, and this finding was expected.

The final study for review performed a series of 4,000 Monte Carlo modeling simulations on a 33-day DFW area ozone episode that occurred from May 31 to July 1, 2006. 17 of the 33 episode days had high ozone, so this was an excellent candidate period for analysis. The magnitude of the NO_X and VOC changes in the modeling simulations were constrained to avoid highly unrealistic scenarios, and then the best performing runs were chosen for review. The researchers found that ozone formation in DFW was roughly an order of magnitude more responsive to anthropogenic NO_X than to anthropogenic VOC. They also found that daily maximum ozone was dominated by NO_X even at the more urban monitors that have VOC limited ozone formation at different times of the day. The researchers concluded with a 93% confidence level that the DFW area is NO_X limited with respect to ozone formation. This finding about NO_X limitation is in agreement with the TCEQ analyses of VOC/NO_X ratios and the weekday/weekend effect for high ozone days.

8.0 CONCLUSION AND RECOMMENDATION

A primary goal of this study was to investigate the ozone formation characteristics of the DFW area to determine if it was primarily NO_X or VOC limited. The results show that the DFW area is overall NO_X limited, with some portions in the urban core in a state of transition from VOC limitation towards NO_X limitation. This conclusion is primarily supported by a review of the NO_X and VOC monitored concentration data, analyses of the weekday/weekend ozone effect, and an in-depth modeling sensitivity study that found NO_X reductions in DFW are much more effective than VOC reductions at reducing ozone. This conclusion does not mean that additional VOC reduction strategies should be ignored. Even in NO_X limited areas, reduction of anthropogenic VOC can certainly result in ozone benefits, particularly if VOC species with high reactivity are reduced.

Another primary goal of this study was to determine if any confounding factors exist that kept the DFW area from significantly reducing ozone levels during the COVID-19 shutdown period. Timing is the primary reason why 2020 peak ozone levels in DFW were not strongly influenced by the reduced economic and transportation activity from COVID-19. The reduced activity from COVID-19 was most pronounced in late March and early April, but these are times when high ozone rarely occurs in DFW. The DFW monitoring data indicate that August was the month in 2020 with meteorological conditions most conducive to high ozone, and this is consistent with high ozone measured in past years. Eight-hour ozone above 70 ppb was measured on ten days in August of 2020. If the reduced activity from COVID-19 had been most pronounced during August of 2020 rather than March/April, it is likely that reduced ozone levels would have been measured on these ten days in August.

Even if the shutdown from COVID-19 occurred during August and ozone levels were reduced, the effect on the long-term ozone design value trends would be temporary. The design value for determining attainment is based on a three-year rolling average of the fourth-highest ozone measurement per year. Thus, even if the fourth-highest ozone reading at each of the 20 DFW monitors was abnormally low in 2020, the levels from two additional years would tend to average out the design values. For example, the 2020 design value per monitor averages the fourth-highest ozone reading from 2018, 2019, and 2020. Similarly, the 2020 fourth-highest ozone level is part of the 2021 and 2022 design value calculations. By 2023, the 2020 fourth-highest ozone level is no longer part of the design value calculation for each monitor since 2021-2023 data will be used.

8.1 Recommendations for Further Research

The ozone reductions that have been achieved in the DFW area since the 1990s are substantial, especially considering the large population growth that has occurred. DFW was once nonattainment for the one-hour and 84 ppb eight-hour ozone standards, and both have been attained. Currently, only one DFW monitor is out of compliance with the 75 ppb eight-hour ozone standard, with a 76 ppb design value. The 73% NO_X and 18% VOC reductions achieved in DFW from 1999 to 2020 have been substantial, and have contributed to the reductions in the eight-hour ozone design value from 101 ppb to 76 ppb during this time. Chapter 4 of the March 2020 attainment demonstration SIP summarized the federal, state, and local measures that have enabled these reductions to occur.

Some of the research discussed in this study has identified a slowing down in the rate of NO_X and VOC reductions across the U.S. in recent years, which suggests that a phase of diminishing returns has been reached. Achieving the 70 ppb eight-hour ozone standard at all 20 DFW monitors will be challenging for the fourth largest metropolitan area in the U.S. The following additional NO_X and VOC reductions are expected from fleet turnover based on the TCEQ emissions trends charts included previously:

- 50 tpd of on-road NO_X reductions from 2020 through 2037;
- 29 tpd of on-road VOC reductions from 2020 through 2042; and
- 9 tpd of non-road NO_X reductions from 2020 through 2034.

These additional reductions will help in lowering DFW ozone levels over the next 10-20 years, but additional detail by source category may assist policymakers in identifying areas for more NO_X and VOC emissions reductions. The TCEQ periodically includes source apportionment modeling results in its attainment demonstrations, such as in Chapter 3 of Appendix C to the March 2020 DFW SIP. The source apportionment tool "tags" specific sources by geographic area and category to estimate their respective ozone contributions to the future year design value. For example, the 2020 results in Table 3-5 on page C-75 indicated that DFW on-road sources contribute 8.61 ppb to the 72.37 ppb design value modeled for the Grapevine Fairway monitor. Values for seven other DFW source categories are also included for Grapevine Fairway, and then full results are included for the remaining 19 DFW area monitors. The detailed source apportionment datasets break down these ozone contributions into separate NO_X and VOC components. A detailed review of these NO_X and VOC results for each DFW area monitor help identify how each major source category impacts the monitors with the highest design values.

The modeling inventories developed by TCEQ for the DFW area include NO_X and VOC emissions estimates for over 1,300 source classification codes (SCCs) from the primary source categories of on-road, non-road, off-road, area, oil-and-gas, and point. The most recently available modeling inventories could be analyzed and sorted to separately determine the highest-to-lowest sources of NO_X and VOC emissions. The VOC emissions reported for each SCC must be speciated into distinct reactivity categories for photochemical model input. These speciated emissions could be sorted to determine the SCCs with the highest-to-lowest reactivity for ozone formation. As emphasized in the discussion on ozone formation, a VOC source with high concentration and low reactivity may have little impact on ozone formation, but a VOC source with low concentration and high reactivity can have a significant impact. Identifying the most reactive VOC sources may assist policymakers in strategically targeting additional ozone reductions.

Finally, a study focussing on the ozone exceedence days in DFW monitors would be benefical to understand the cause of exceedences. This study will aim at building models by gathering and assessing the meteorology, demographic, commute patterns, incidents, and other soci-ecomomic changes over time. The study results for selective monitor(s) will help identify how each parameter impacts the monitored values.

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