APPENDIX D

CONCEPTUAL MODEL FOR THE DFW ATTAINMENT DEMONSTRATION SIP REVISION FOR THE 2008 EIGHT-HOUR OZONE STANDARD

2015-014-SIP-NR

Proposal
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APPENDIX D: 2013 DALLAS-FORT WORTH NONATTAINMENT AREA OZONE CONCEPTUAL MODEL

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0. EXECUTIVE SUMMARY

Ozone formation conceptual models characterize ozone trends, precursors, formation, and transport in a particular geographic area to explain the dynamics of ozone formation in that area. The information is compiled and developed into a comprehensive picture of not only where and when ozone forms, but also how and why ozone forms in a geographic area. Conceptual models are required by the United States (U.S.) Environmental Protection Agency (EPA) to accompany photochemical modeling performed for State Implementation Plan (SIP) revisions (EPA, 2007). This appendix updates the ozone conceptual model for the Dallas-Fort Worth (DFW) nonattainment area.

Conceptual models can be used as tools for selecting representative modeling episodes and for qualitatively evaluating and assessing photochemical modeling results. They are intended to guide modeling efforts conducted in compliance with SIP revision requirements by presenting the state of the science in terms of current understanding of factors that influence ozone formation and transport.

This conceptual model begins with a discussion of the fundamentals of ozone formation photochemistry, followed by more detailed treatment of the characteristics that make the ozone situation in the DFW area unique. This is followed by results of detailed investigations of trends and patterns in ozone and local precursor concentrations. Identifying and assessing trends in ozone and its precursors provide an initial appraisal of the current ozone situation in the DFW area, the magnitude of progress made to date, and the scale of future challenges.

Ozone design values, the statistics used to compare observed ambient ozone levels to the National Ambient Air Quality Standards (NAAQS), have decreased in the DFW area over the past sixteen years. The eight-hour ozone design value in 2013 was 87 ppb at Denton Airport South, a 16% decrease from the 1997 eight-hour ozone design value of 104 ppb. Although the 2013 design value is approaching the 1997 ozone NAAQS of 84 ppb, it must decrease further to reach the 2008 ozone NAAQS of 75 ppb. Examination of design values at individual monitors corroborates these decreases, with all monitors showing a decrease in design values from 1997 through 2013. Despite an increase in the number of monitors located throughout the DFW area, the number of days with eight-hour ozone greater than 75 ppb fell 41%. In addition, while the ozone season was determined to be less severe in recent years, the months in which high ozone occurs, June, August, and September, have not changed over time.

An investigation of geographic patterns in ozone reveals that, while ozone concentrations in the DFW area have been decreasing, the same geographic areas tend to experience the highest ozone concentrations year after year. The highest levels of ozone typically occur in the northwestern part of the region at the Denton Airport South, Grapevine Fairway, and Keller monitors. The location of ozone peaks was not found to differ between high and low ozone days; however, ozone was found to form much later in the day on high ozone days compared to low ozone days. This pattern in peak ozone on high ozone days versus low ozone days indicates slower wind speeds on high ozone days, leading to larger accumulations of ozone. This is corroborated by an analysis of wind patterns that shows surface winds are predominately from the south and southeast, with the majority showing slower speeds from the southeast on high ozone days.

Nitrogen oxides (NO_X) trends from 1997 through 2013 also exhibited decreases, with monitors located in urban areas showing larger decreases compared to more rural monitors. Despite the reductions in severity, regions that observe the highest and lowest concentrations remain roughly the same, with the urban core of Dallas and Tarrant counties experiencing the highest

NO_X concentrations. This indicates that a large portion of NO_X concentrations in the DFW area originates from mobile sources, and that the emissions from these sources appear to be decreasing.

Total volatile organic compounds (VOC) trends decreased from 2001 through 2013; however, the largest decreases in total VOC occurred prior to 2006. Highly reactive VOC (HRVOC) trends indicate that ethylene and propylene have decreased from 2000 to 2012, with most of this decrease occurring from 2000 to 2009. Monitors whose ambient air is dominated by vehicle emissions had the highest concentrations of these two compounds and showed the same pattern of decrease in HRVOC. Similar to NO_X, this suggests that vehicle emissions are the most important source of these two HRVOCs, and that reductions in vehicle emissions are likely the reason for the decrease.

Analysis of VOC composition determined that the geometric mean total VOC concentration was higher in the Barnett Shale area compared to other areas in DFW, with the difference due to higher concentrations of ethane, and to a lesser extent propane, at the monitors in the Barnett Shale. When these concentrations were multiplied by a conversion factor based on maximum incremental reactivity (MIR), the monitors located in the urban core of the DFW area had total concentrations equal to or greater than most of the Barnett Shale monitors. The relative increases in MIR-weighted concentrations at urban monitors versus rural ones was due to the greater concentrations of more reactive VOC, such as aromatics and HRVOC, at the two urban core monitors. Although high VOC concentrations were observed in the Barnett Shale region, those concentrations have not been shown to affect ozone concentrations in the DFW area.

Investigation of VOC- and NO_X-limitations reveals a varying pattern across the DFW area, indicating that different photochemical processes likely dominate in different regions. Until recently, urban monitors tended to record VOC-limited conditions; however, in the past few years, the urban core of DFW has trended to a transitional regime. The change in VOC- to NO_X-limitation in the urban core could be due to NO_X decreases in the area. Monitors to the northwest and on the periphery of the DFW area were NO_X-limited, indicating NO_X controls would be more effective at controlling ozone in these areas.

Examining ozone by day of week corroborates the VOC- to NO_X-limitation findings. Ozone on Sundays was significantly lower compared to other days of the week while ozone on Fridays was higher compared to other days of the week. Investigation of NO_X by day of the week showed the lowest NO_X concentrations observed were on Sundays and the highest NO_X concentrations were on Fridays when vehicle miles traveled (VMT) from on-road activity is at its weekly peak. This indicates that decreasing levels of NO_X would in turn decrease levels of ozone.

The need to quantify background ozone, or ozone transported from outside the DFW area, in addition to quantifying local ozone production, is essential given that a large metropolitan area such as DFW regularly generates enough local ozone to exceed the standard when starting from a high background. Investigation of Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model back trajectories identified likely transport of ozone into north Texas on days following elevated ozone episodes in the eastern U.S. Back trajectories indicate that on high ozone days winds are slower and from the east and southeast, while on low ozone days winds were much faster and from the south.

Studies of regional background one-hour ozone in the DFW area show that regional background one-hour ozone is high on days with high eight-hour ozone. On high eight-hour ozone days, background one-hour ozone was found to range from 58 ppb to 61 ppb to the east, and 59 ppb

from the south. Regional background one-hour ozone often exceeds 50 ppb and is especially pronounced on high ozone days in the DFW area. On high ozone days, background is about 1.4 times higher than the EPA estimated 40 ppb. These background and transport analyses show that efforts focused solely on controlling local emissions may be insufficient to bring the DFW area into ozone attainment given that, on many days, background estimates are well over half the eight-hour ozone NAAQS of 75 ppb.

Combining results from these various analyses gives a general picture of how high ozone is formed in the DFW area. High ozone is typically formed in the DFW area on days with slower wind speeds out of the east and southeast. These prevailing winds also lead to higher background ozone levels entering into the DFW area. High background ozone concentrations are then amplified as an air mass moves over the urban core of Dallas and Tarrant counties, which both contain large amounts of NO_X emissions, primarily from mobile sources. Those emissions are then transported across the DFW area to the northwest, where the highest eight-hour ozone concentrations are observed. Analyses revealed that controlling NO_X would lead to the most effective controls for ozone in the DFW area. Due to the prevailing winds, VOC emissions from the Barnett Shale rarely affect ozone concentrations in the DFW area.

1. OZONE FUNDAMENTALS

Ozone formation conceptual models characterize ozone trends, precursors, formation, and transport in a particular geographic area to explain the dynamics of ozone formation in that area. This information is compiled and developed into a comprehensive picture of not only where and when ozone forms, but also how and why ozone forms in a geographic area. Conceptual models are required by the United States (U.S.) Environmental Protection Agency (EPA) to accompany photochemical modeling performed for State Implementation Plan (SIP) revisions (EPA, 2007). This appendix updates the ozone conceptual model for the Dallas-Fort Worth (DFW) nonattainment area.

Conceptual models can be used as tools for selecting representative modeling episodes and for qualitatively evaluating and assessing photochemical modeling results. They are intended to guide modeling efforts conducted in compliance with SIP revision requirements by presenting the state of the science in terms of current understanding of factors that influence ozone formation and transport. This conceptual model begins with a discussion of the fundamentals of ozone formation photochemistry, followed by a more detailed treatment of the characteristics that make the ozone situation in the DFW area unique. This is followed in Chapter 2: *Air Quality Trends in the Dallas-Fort Worth Area* by presentation of results of detailed investigations of trends and patterns in ozone and local precursor concentrations. Chapter 3: *Recent Findings in Local Ozone Dynamics in the Dallas-Fort Worth Area* continues with analyses of local factors contributing to ozone formation, accumulation, transport, and fate in the DFW area. Finally, Chapter 4: *Recent Findings in Transported Ozone and Background Ozone in the Dallas-Fort Worth Area* explores meteorological factors contributing to transport of background ozone into the DFW area. All of these investigations point to the same general conclusion: decreasing trends in measured ozone concentrations are largely a result of real, quantifiable reductions in precursor emissions, and are not due to unusual meteorological conditions.

1.1 Basic Ozone Formation Photochemistry and Meteorology

Tropospheric, or ground level, ozone pollution is a public health concern in many metropolitan areas throughout the U.S. (National Academy of Sciences, 1991; Bell, 2004, EPA, 2006, Currie, 2007). Other studies have linked ozone to damage to vegetation (Heck, 1984; Westenbarger and Frisvold, 1994; EPA 2010) and other materials (EPA, 2006). Large urban areas are prone to

generating elevated levels of ozone in the ambient air because of a confluence of contributing factors: the presence of millions of people and a multitude of sources of ozone precursor emissions that support and serve that population, and meteorological conditions favorable to the formation of ozone from those emissions.

Ozone production is generally associated with relatively clear skies, light winds, abundant sunshine, and temperatures above 80 to 85 degrees Fahrenheit. Typically, these meteorological conditions are associated with high-pressure areas that migrate across the U.S. during the spring and summer (Nobis, 1998). Regional background ozone varies strongly by season, with peaks in spring and late summer, and a local minimum during mid-summer. The mid-summer minimum is probably caused by the dominance of high pressure in the southeast U.S., which results in flow from the Gulf of Mexico over eastern Texas, and hence low background concentrations (Estes, 2010).

Ozone is a molecule of three oxygen atoms, expressed chemically as O3. Ozone is created from oxygen, NO_X and VOC in the presence of sunlight. When discussing atmospheric chemistry, NO_X refers to the sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2). The catalytic cycle of ozone formation and destruction is displayed in Figure 1-1: Chemical Reactions that Form Ozone. This diagram shows that in the presence of ultraviolet energy from sunlight, denoted by the term "hv," NO_2 reacts with oxygen to form ozone and NO. In the absence of sunlight or under high NO_X concentrations, the process reverses and is known as ozone titration, or "scavenging." The first reaction usually operates forward in sunlight and reverses in the dark. However, even in sunlight, it may reverse immediately downwind of a very large NO_X source.

$$\xrightarrow{h\nu} \quad NO_2 + O_2 \Leftrightarrow O_3 + NO$$

$$NO + VOC \rightarrow NO_2$$

This reaction runs forward in sunlight, and reverses in the dark.

Figure 1-1: Chemical Reactions that Form Ozone

The accumulation of ozone slows as the concentration of the NO_X or VOC reactants decreases. If the reactant in short supply is NO_X, the area is said to be "NO_X-limited" because no further ozone is accumulated even though excess VOC might remain. Similarly, when the ozone accumulation slows due to a lack of VOC, the area is termed "VOC-limited." Some areas may be NOx- or VOC-limited at different times of the day, depending on wind direction and the concentrations of NO_X and VOC, in the ambient air and transported from upwind emission sources. Winds from one direction may transport emissions from a NO_X source to the area, while winds from a different direction may transport VOC emissions to the area. Therefore, consideration of changes in wind patterns, along with types and locations of emission sources, is essential in formulating effective policies to control ozone formation and accumulation.

Because the precursor compounds of NO_X and VOC also exist under natural conditions, ozone is created and destroyed on a natural cycle according to atmospheric conditions and chemical concentrations, even in the absence of additional anthropogenic precursor sources. This natural ozone formation is known as "natural background" ozone and is the starting point for measuring the contribution of ozone and precursors attributable to human activity. Within an urban area, not all ozone formation is necessarily caused by emissions produced locally because anthropogenic precursors, along with ozone formed by them, are often transported over long

distances. Background ozone is discussed further below, and in detail in Chapter 4 of this Conceptual Model.

Figure 1-2: Typical Diurnal Ozone Cycle shows that ozone formation occurs in a daily, or diurnal, cycle, starting from low levels before sunrise, increasing during the morning and into the afternoon, then declining to low (background) levels again after nightfall. Each morning, emissions of NO_X and VOC begin to mix with precursors remaining from the previous day. As the sun heats the atmosphere, providing energy in the form of light, this mixture begins to form ozone. As the energy of the sun dissipates in the evening, the process slows and finally halts overnight.

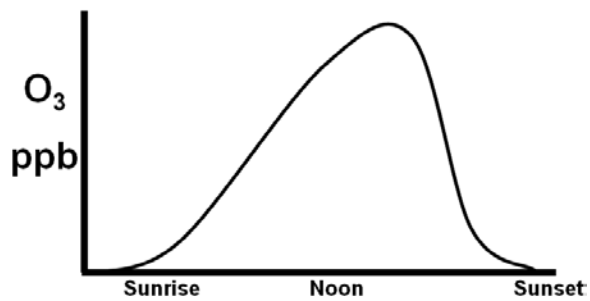


Figure 1-2: Typical Diurnal Ozone Cycle

At locations downwind of a major NO_X source, such as depicted in Figure 1-3: Example of Ozone Scavenging Downwind of a NO_X Source, there may be initial scavenging of ozone due to high levels of NO_X near the source. However, with additional time and sunlight, the NO_X is gradually converted to additional ozone, resulting in even higher ozone concentrations farther downwind from the source (EPA, 2006). In the figure, note the initial spike in NO_X emissions (1 - blue line) near mile zero and the corresponding drop in ozone (2 - dark red line) soon after. Even though NO_X has dropped precipitously by about mile eight, ozone soon rebounds from its nadir and begins accumulating (3).

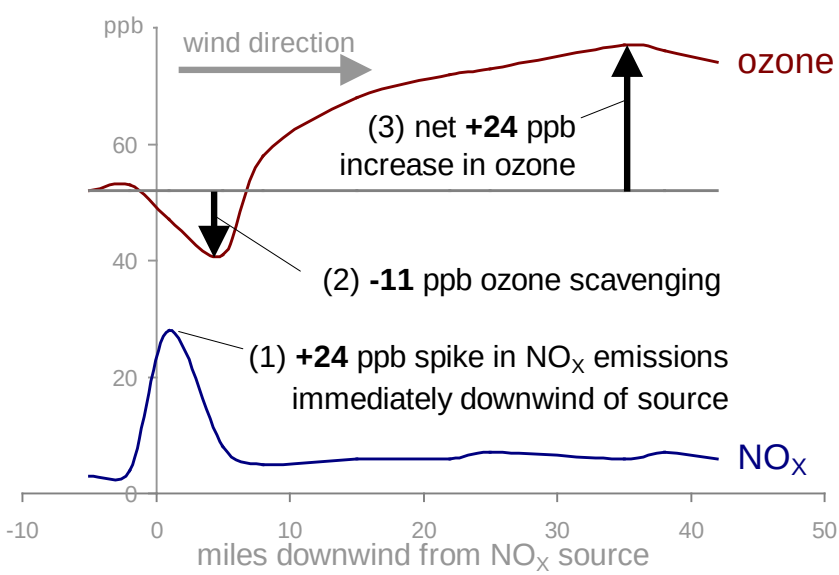


Figure 1-3: Example of Ozone Scavenging Downwind of a NO_X Source

Meteorological conditions, such as wind direction and speed, temperature, mixing height, solar radiation and other factors, affect the rates at which ozone formation and scavenging reactions occur. The types as well as the concentration of precursors present affect net reactivity of precursor compounds found in a plume of emissions. Concentration is determined by the quantity of emissions and volume of well-mixed air, which in turn is determined by the speed of winds and the mixing height. The mixing height, which is determined by temperature and other factors, forms an atmospheric "ceiling" on the available volume of air in which mixing can occur. Figure 1-4: Example of Dynamics of Atmospheric Mixing Height demonstrates this process. During daylight hours, sunlight heats the ground, which in turn heats surface air. Warm surface air rises and cools until it reaches the mixing height, where the relatively cooler air sinks downward. The cycle repeats until sundown.

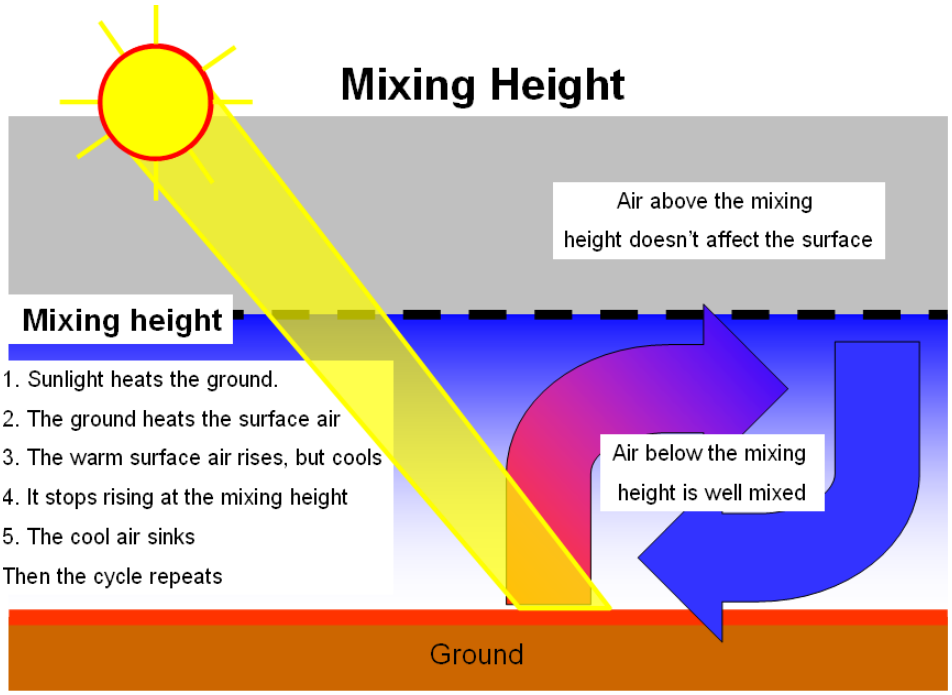


Figure 1-4: Example of Dynamics of Atmospheric Mixing Height

For a fixed mass of precursor emissions, a lower mixing height results in a smaller volume of air than does a higher mixing height (Figure 1-5: Effect of Mixing Height on Parcel Concentration). This gives a more concentrated, and thus more reactive, air parcel. A higher mixing height dilutes the precursors into a larger volume, thus resulting in a less reactive parcel.

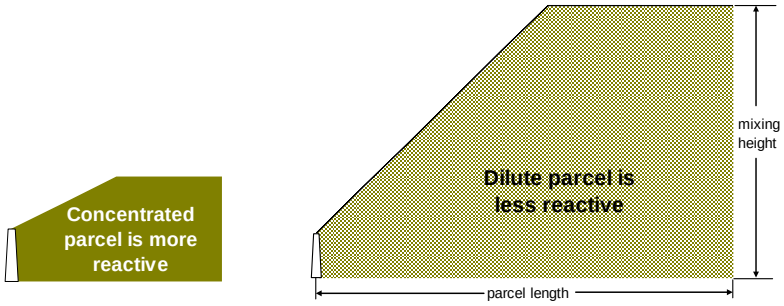


Figure 1-5: Effect of Mixing Height on Parcel Concentration

1.2 Ozone in the Dallas-Fort Worth Area

Ozone formation in the DFW area, as in most areas, depends largely on interaction of three factors: local emissions of ozone precursors, ozone-conducive meteorology, and existing or transported background ozone and precursors. The Dallas-Fort Worth-Arlington area is the fourth largest metropolitan area in the U.S., home to over 6.7 million residents as of 2012 (U.S. Census Bureau, 2013). These residents own and use motor vehicles, recreational vehicles, lawn and garden equipment, and other emission sources in their daily activities. They work, shop, and recreate at a multitude of commercial, industrial, educational, and recreational sites that contribute emissions from all manner of equipment.

Substantial amounts of precursor compounds, chiefly NO_X and VOC, are emitted by three major source categories: mobile sources, point sources and area sources. Mobile sources include cars, trucks, ships, planes, locomotives, and construction equipment. Point sources include most industrial equipment such as cement kilns, boilers, process heaters, gas, diesel, and dual-fuel fired stationary engines, stationary gas turbines, duct burners used in turbine exhaust ducts, lime, brick and ceramic kilns, metallurgical heat treat and reheat furnaces, lead smelting, reverberatory and blast furnaces, incinerators, glass, fiberglass and mineral wool processing facilities, natural gas-fired heaters dryers and ovens, and electricity generation facilities. The DFW area hosts all of the above equipment.

Other stationary sources of emissions that lack an identifiable exhaust aperture are grouped into area sources. These facilities include gas stations, dry cleaners, facilities such as commercial shopping centers or schools with compressors for heating and cooling, fertilizer application, personal care products and many more. Natural or biogenic sources, mainly trees, emit ozone precursors such as isoprene and pinene, which are known to react particularly quickly with NO_X to form ozone (Rapid Science Synthesis Team, 2006). Finally, precursor compounds, along with ozone, are often transported into urban areas from external locations.

Background ozone concentrations in north central Texas average about 50 ppb. However, this estimate is one of many and depends to a great extent on the definition being used, averaging time, time of year, and other factors. Natural background ozone, or the background ozone that would prevail in the absence of anthropogenic influences, tends to be lower than regional background ozone, or ozone transported into the region from elsewhere.

Higher background ozone concentrations in the DFW area are usually observed when winds originate from the south and southeast, while lower concentrations are observed when winds originate from the north and west. Background and transport appear at this time to play a secondary, though not inconsequential, role in DFW ozone photochemistry, at least when compared to local sources. However, these sources may contribute a greater fraction of the total in the future as local emissions reductions are implemented. Background ozone will be explored in detail in Chapter 4.

In the absence of accidental releases or spills, whether high concentrations of pollutants form on a given day is controlled mostly by meteorological processes, which may transport the pollutants and either dilute pollutant emissions or allow them to accumulate. Meteorology also affects other key processes, such as chemical reaction rates (Banta et al., 2005). High ozone concentrations are observed most frequently in the DFW area on days lacking strong synoptic, or large-scale, pressure gradients. When synoptic (large-scale) weather systems move through the region, ozone and precursor emissions tend to be diluted and carried out of the city, rather

than concentrated in still, stagnating air, to be heated, reacted and turned into ozone. Days dominated by strong synoptic weather systems tend to experience low ozone levels (Banta et al., 2005).

Absent dominant synoptic weather systems, smaller-scale local wind patterns govern ozone formation. As precursor emissions are advected across the region, they mix with other local emissions, as well as compounds transported into the region, to generate elevated concentrations of ozone. On days with light winds, precursors generated in the morning, along with those remaining from the previous day, accumulate, and then react during the warmest and sunniest portion of the day. Ozone rich air masses typically begin to form in the center and south of the city. Later in the afternoon, southeasterly breezes can advect, or horizontally transport, the pool of high ozone over the city toward the west and northwest.

During the ozone season, and especially in late summer, the DFW area experiences relatively light winds and persistent hot, humid, and sunny conditions. The DFW area tends to have more frequent high ozone in the late summer compared to most other areas. Days with eight-hour ozone above 75 ppb tend to occur in the DFW area from February through November as shown in Figure 1-6: Days with Eight-Hour Ozone Over 75 ppb in Texas (1991 through 2012). Similar to most areas in Texas, DFW tends to record two peaks in high ozone concentrations, one in late spring, and another in late summer.

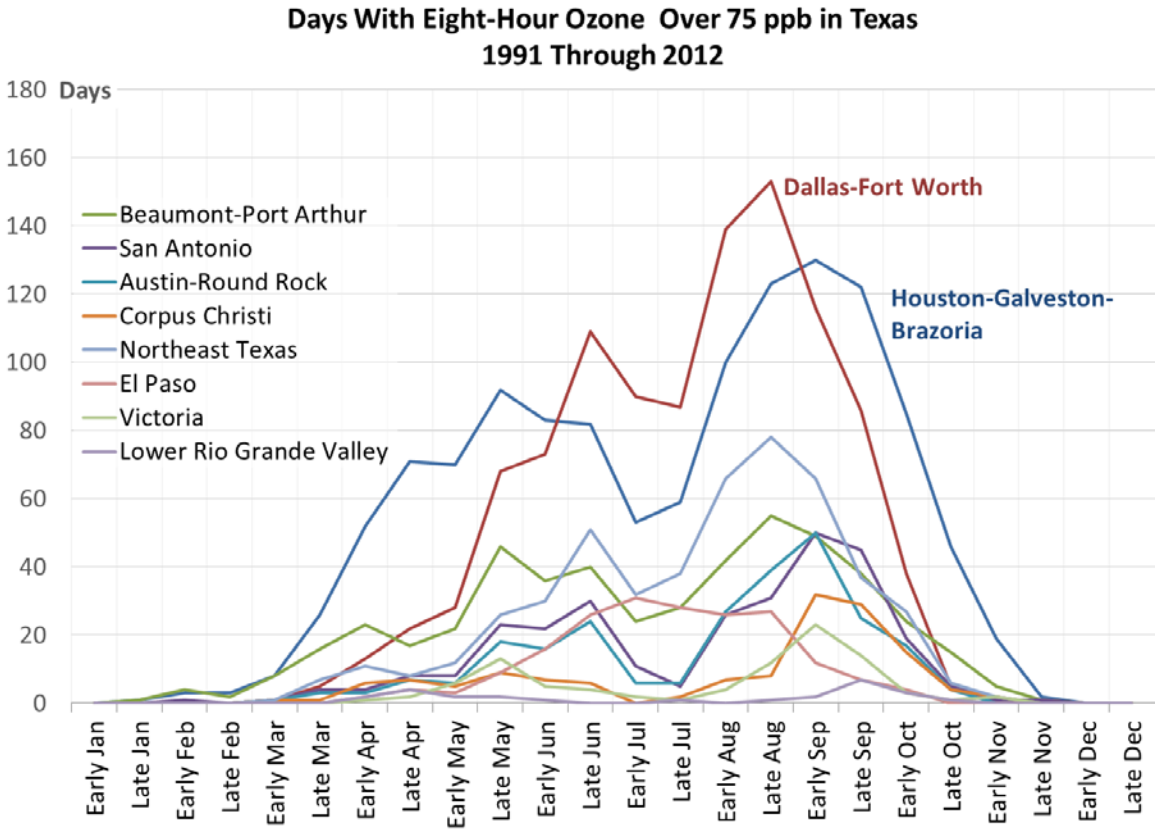


Figure 1-6: Days with Eight-Hour Ozone Over 75 ppb in Texas (1991 through 2012)

While the details of ozone formation, accumulation, transport, and fate are highly technical and require complex algorithms to compute, a conceptual model provides insight into the unique characteristics of ozone processes in a region on a more simplified scale. The insights gained

from a conceptual model provide guidance on modeling distinctive phenomena. This conceptual model draws on established scientific understanding of photochemical, physical, and meteorological processes, as well as recent findings on local ozone and precursor patterns, background ozone, and meteorology specific to the DFW area.

2. AIR QUALITY TRENDS IN THE DALLAS-FORT WORTH AREA

Trends in ozone and its precursors demonstrate not only the substantial progress the Dallas-Fort Worth (DFW) area has made in improving air quality, but also the magnitude of the future challenge in attaining the National Ambient Air Quality Standard (NAAQS) for ozone. Trends are also useful as a first look at how ozone is related to its precursors. Ozone is a secondary pollutant, formed through a photochemical reaction of nitrogen oxides (NO_X), volatile organic compounds (VOC), and sunlight. VOC can amplify ozone production, causing accumulation of ozone in the atmosphere. Decreases in NO_X and VOC demonstrate the effectiveness of policies to reduce emissions; however, due to its dependence on meteorological variables, ozone may not always exhibit trends identical to its precursors. Separating variations in meteorological factors from trends in ozone and its precursors can highlight whether ozone reductions are caused by decreases in precursor emissions or by to year-to-year variability in local meteorology (Sullivan et al., 2009; Camalier et al., 2007). This chapter discusses trends, both temporal and spatial, in ozone and its precursors.

2.1 Ozone Trends

A design value is a statistic used to compare an area's concentrations of a particular pollutant to the pollutant's NAAQS. Design values are commonly used to characterize ambient ozone concentrations because they summarize the severity of a local ozone problem into a single number. The criteria for attainment of the ozone NAAQS have changed over the past 12 years. Until its revocation on April 30, 2004, the ozone NAAQS was based on concentrations of 0.12 parts per million (ppm) averaged over one hour (EPA, 2004). An exceedance occurred when the fourth highest one-hour ozone concentration in a three-year period equaled or exceeded 0.125 ppm. The eight-hour NAAQS for ozone was adopted in 1997, but not implemented until 2004, and was set at 0.08 ppm averaged over 8 hours. In 2008, the EPA adopted a more stringent eight-hour ozone NAAQS set at 0.075 ppm. A monitor exceeds the eight-hour ozone standard when its design value, a three-year average of the fourth highest eight-hour ozone concentration for each year, exceeds 0.075 ppm. The design value of record for an area is the highest design value recorded at any monitor in the area.

This section examines the frequency at which the NAAQS for ozone are exceeded, with the understanding that the eight-hour standard of 0.075 ppm is being used for control strategy development. While the NAAQS is expressed in units of parts per million, this chapter will express concentrations in parts per billion (ppb). Because of EPA rounding conventions, the 1997 eight-hour ozone NAAQS is essentially 84 ppb and the 2008 eight-hour ozone NAAQS is expressed as 75 ppb.

The trend in design values and population in the DFW area is seen in Figure 2-1: Ozone Design Values for the DFW Area. While the DFW area continues to exceed both eight-hour ozone standards, eight-hour ozone design values have decreased over the past nine years. The eight-hour ozone design value in 2013 was 87 ppb, a 16% decrease from the 1997 design value of 104 ppb. The 2013 value is approaching the 1997 ozone NAAQS of 84 ppb, but still must decrease further to reach the 2008 NAAQS of 75 ppb. Work presented in Chapter 3: Recent Findings in Local Ozone Dynamics in the Dallas-Fort Worth Area investigates whether recent ozone reductions are due to anomalous meteorology or may be expected to continue as further emission reductions are achieved.

The DFW area one-hour ozone design value in 2013 was 108 ppb, a 22% decrease from the 1997 design value of 139 ppb. The one-hour design value in the DFW area has met the previous one-hour ozone NAAQS of 124 ppb since 2006. The one-hour standard has been revoked and the design values shown are for trend purposes only.

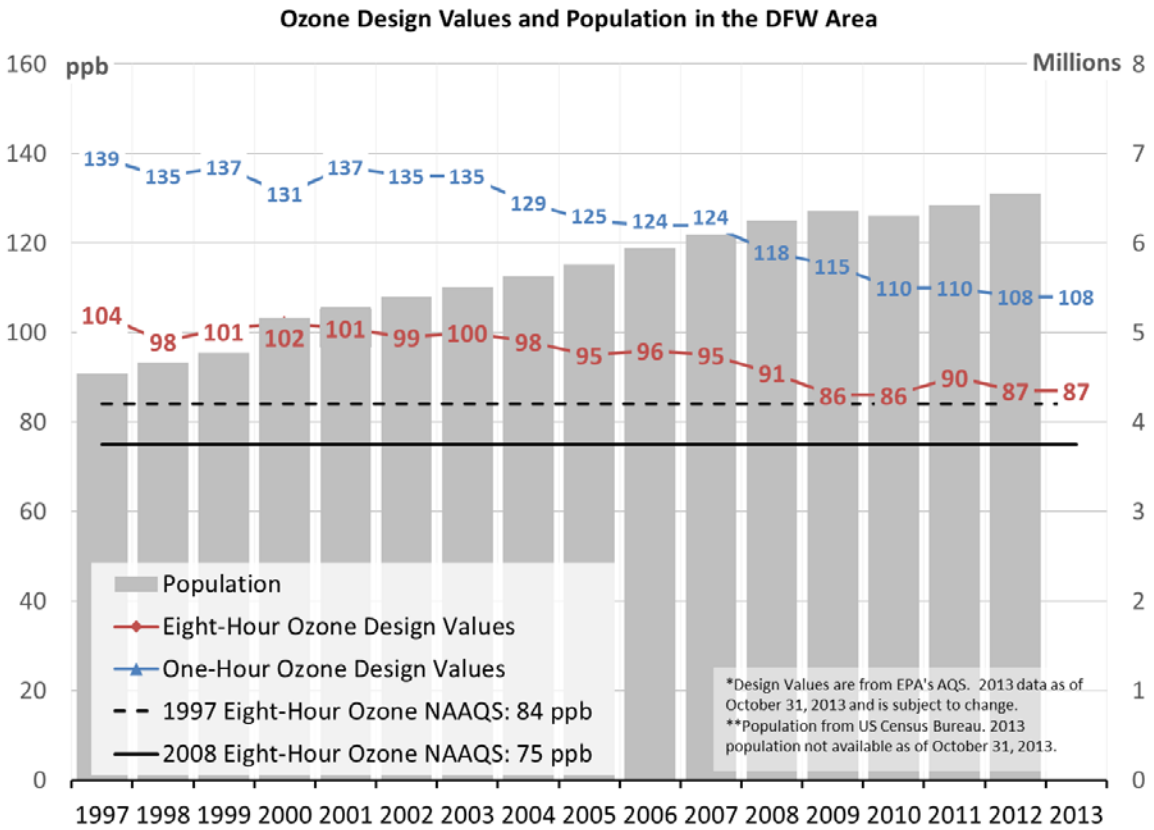


Figure 2-1: Ozone Design Values for the DFW Area

The design value of record in a metropolitan area is the highest design value of all individual design values at monitors in an area. Because ozone varies spatially, it is prudent to investigate trends at all monitors in an area, not just those recording the highest design values. Table 2-1: Eight-Hour Ozone Design Values by Monitor in the DFW Area contains the eight-hour ozone design values at all regulatory monitors in the DFW area from 1997 through 2013. Only four monitors in the DFW area are currently below the eight-hour ozone NAAQS. The highest eight-hour ozone design values are typically observed at Denton Airport South, Grapevine Fairway, Keller, Fort Worth Northwest, and Eagle Mountain Lake; however, in the past two years, the Eagle Mountain Lake and Fort Worth Northwest monitors no longer observe some of the highest eight-hour ozone concentrations.

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

Monitor/CAMS #	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Denton Airport South C56				102	101	99	97	96	93	95	94	91	85	80	83	83	87
Grapevine Fairway C70						95	100	98	93	93	92	87	84	82	86	86	86
Keller C17	97	92	95	97	97	98	100	98	95	94	92	87	86	86	90	87	85
Frisco C31	101	98	101	101	99	93	88	89	91	92	88	83	79	77	81	83	84

Monitor/CAMS #	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Pilot Point C1032												81	77	78	82	82	84
Dallas Hinton Street C401/C60	90	88	91	93	92	91	90	89	90	87	84	74			73	82	84
Dallas North No.2 C63					93	89	86	87	90	89	86	80	81	78	79	81	83
Eagle Mountain Lake C75						95	96	94	95	96	95	89	86	85	83	82	81
Fort Worth Northwest C13	96	97	99	99	97	96	96	94	95	94	91	83	79	79	82	80	81
Dallas Redbird Airport C402	91	91	92	88	84	84	85	87	88	88	85	82	78	78	79	81	80
Arlington Municipal Airport C61								87	87	87	84	79	77	79	79	83	80
Cleburne Airport C77						89	90	90	89	87	85	83	83	80	79	79	79
Parker County C76						86	89	86	87	88	91	84	81	75	79	78	79
Granbury C73						84	84	81	81	84	84	81	77	75	76	77	77
Rockwall Heath C69						83	81	82	81	80	78	75	75	74	77	77	77
Midlothian OFW C52/C137												75	73	72	74	76	77
Kaufman C71						70	73	73	73	75	76	73	70	67	68	70	74
Greenville C1006									79	79	76	70	66	64	69	72	74
Italy C1044														68	69	69	72
Corsicana Airport C1051																70	72

*Values are sorted in descending order of design values in 2009, then 2008, 2007, et cetera.

**2013 design values are current as of November 5, 2013 and are subject to change.

Figure 2-2: Eight-Hour Ozone Design Value Statistics in the DFW Area displays three summary statistics for the eight-hour ozone design values: the maximum, median, and minimum values computed across all monitors in the DFW area. The median statistic as used here indicates that half the observed design values are above the median, and half below it. These figures facilitate assessment of the range of design values observed within a year, as well as how these distributions change over time. The eight-hour ozone design values exhibited a general decreasing trend at all of the monitors from 1997 through 2013. There was a slight increase in the maximum and minimum design values after 2010. It appears that 2010 experienced lower ozone than normal while 2011 had higher ozone than normal.

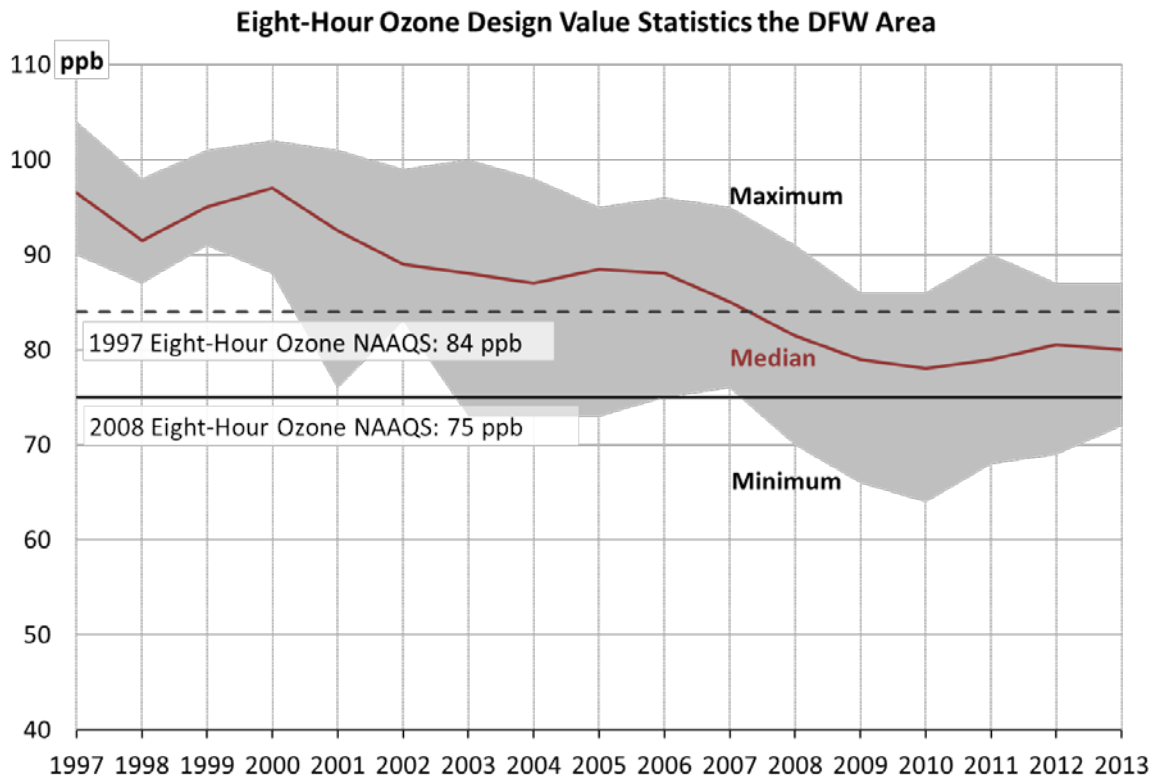


Figure 2-2: Eight-Hour Ozone Design Value Statistics in the DFW Area

The Denton Airport South monitor currently sets the eight-hour design value of record for the DFW area. The 2013 design value, 87 ppb, is calculated (as with all monitors) by averaging the 2011 through 2013 fourth-highest concentrations, and truncating any decimal. At Denton Airport South, these values were 95, 81, and 85 ppb, as shown in Table 2-2: Annual Fourth-Highest Eight-Hour Ozone Values and Design Values. Table 2 shows that the fourth-highest eight-hour ozone values were higher at many monitors in 2011. Because 2011 will be excluded from the 2014 calculation, many monitors could have lower design values in 2014. Denton Airport South, however, would only need to record a fourth-highest eight-hour ozone concentration of 62 ppb or higher in 2014 to violate the 2008 NAAQS.

Table 2-2: Annual Fourth-Highest Eight-Hour Ozone Values and Design Values

Monitor	4th High 2011	4th High 2012	4th High 2013	2013 Eight-Hour Ozone Design Value	2014 Fourth-Highest Needed to Violate the NAAQS
Denton Airport South C56	95	81	85	87	62
Grapevine Fairway C70	91	86	83	86	59
Keller C17	97	79	80	85	69
Pilot Point C10320	91	78	84	84	66
Frisco C31	91	84	78	84	66
Dallas Hinton St. C401	84	87	81	84	60
Dallas North No. 2 C63	88	86	77	83	65
Ft. Worth Northwest C13	82	77	94	81	67

Eagle Mountain Lake C75	80	87	77	81	64
Dallas Redbird Airport C402	82	85	74	80	69
Parker County C76	88	76	74	79	78
Cleburne Airport C77	79	82	77	79	69
Arlington Municipal Airport C61	80	92	68	79	68
Rockwall Heath C69	80	80	73	77	75
Midlothian OFW C52	80	78	75	77	75
Granbury C73	76	80	75	77	73
Kaufman C71	74	73	75	74	80
Greenville C1006	77	75	70	74	83
Italy C1044	75	71	72	72	85
Corsicana Airport C1051	74	70	74	72	84

*Monitors are sorted in descending order by 2013 design value.
**2013 data current as of November 5, 2013

Ozone trends can also be investigated by looking at high ozone days, or the number of days that peak eight-hour ozone was over 75 ppb. Research by the TCEQ (Savanich, 2006) has shown that, the number of high ozone days was positively correlated with the number of monitors in a particular area. That is, as the number of monitors increases, so does the number of high ozone days recorded, at least until either the area has been saturated with monitors, so that no previously unobserved high ozone days are detected, or until ozone concentrations truly decrease. Because of this correlation, when examining high ozone day trends, the number of monitors must always be considered. Thus, it is especially noteworthy that Table 2-3: Number of Days with Eight-Hour Ozone Greater Than 75 ppb shows that, despite an increase in the number of monitors, the number of days with eight-hour ozone over 75 ppb and over 84 ppb has generally decreased. The decrease is especially pronounced after 2007. Since 1997, the number of eight-hour ozone days over 75 ppb occurring in the DFW area has fallen 41% and the number of eight-hour ozone days over 84 ppb has fallen by 86%. Similar to the design value trends, trends in high ozone days appear to be lower than normal in 2010 and higher than normal in 2011.

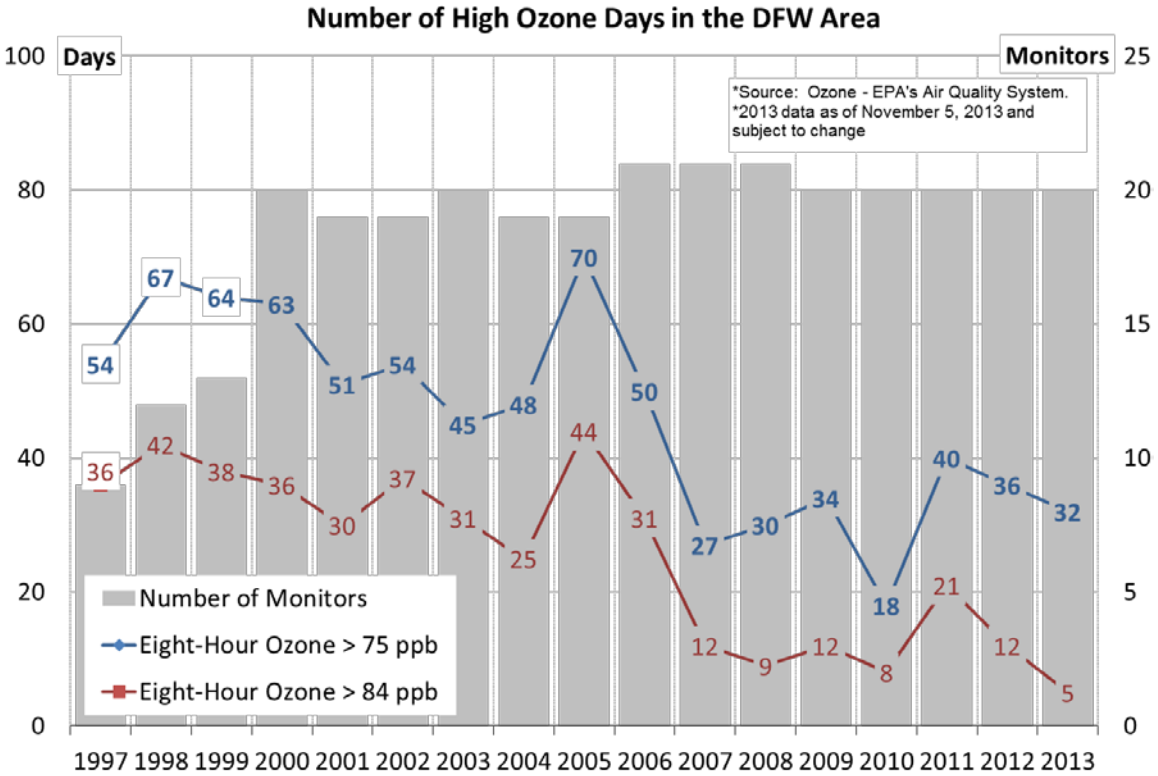


Figure 2-3: Number of Monitors and High Ozone Days in the DFW Area

Results for individual monitors are listed in Table 2-3: Number of Days with Eight-Hour Ozone Greater than 75 ppb. The number of high ozone days at individual monitors also appears to be decreasing. There appears to be a larger number of high ozone days in 2011, but the number of high days has decreased in the past two years.

Table 2-3: Number of Days with Eight-Hour Ozone Greater than 75 ppb

Monitor/CAMS #	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Denton Airport South C56		44	43	29	35	29	23	21	38	32	12	10	12	3	23	10	19
Grapevine Fairway C70				7	36	26	30	21	33	29	8	4	14	10	15	12	12
Keller C17	17	25	29	31	31	37	34	20	41	33	12	18	18	10	26	10	12
Pilot Point C1032										23	3	5	7	6	27	11	11
Fort Worth Northwest C13	21	31	27	35	24	23	28	21	35	26	7	1	9	6	10	6	11
Frisco C31	35	54	33	44	32	17	13	15	33	28	11	5	5	3	23	15	8
Dallas Hinton Street C401/C60	22	27	31	20	11	23	17	12	28	17	4	0	0	3	14	8	8
Dallas North No.2 C63			35	30	16	8	20	15	37	20	5	4	6	2	21	14	6
Cleburne Airport C77				12	15	25	16	20	21	9	8	10	5	5	7	10	5
Eagle Mountain Lake C75				23	30	38	29	15	38	31	12	15	16	7	9	7	4
Parker County C76				6	17	23	16	11	21	17	4	5	9	2	15	4	3
Midlothian OFW C52/C137										6	4	1	2	0	7	6	3
Granbury C73				7	10	12	9	8	14	10	5	1	6	4	4	8	3
Kaufman C71				1	3	4	3	1	6	7	3	3	0	0	2	2	3
Dallas Redbird Airport C402	25	34	22	15	5	16	17	10	25	20	5	4	9	5	8	8	2

Monitor/CAMS #	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Corsicana Airport C1051													0	0	3	1	2
Arlington Municipal Airport C61						18	21	6	25	16	3	4	12	5	11	9	1
Rockwall Heath C69				14	10	10	7	7	10	14	3	1	5	1	10	5	1
Italy C1044											0	2	0	0	3	2	1
Greenville C1006							5	5	13	8	0	0	0	1	6	3	0

*Monitors sorted in descending order by the number of days over 75 ppb in 2013.
**2013 data as of November 5, 2013 and subject to change.

The ozone season spans March through October in the DFW area (EPA, 2008a); however, the period when elevated ozone concentrations are observed varies from year to year. Table 2-4: Days with Eight-Hour Ozone Greater than 75 ppb by Month and Year shows the frequency of, and variation in, the number days with eight-hour ozone greater than 75 ppb in the DFW area by month and year. Months with more high ozone days are shaded in red, while months with fewer high ozone days are shaded in green; blank cells indicate no high days occurred in that month and year. Despite a decrease in the number of high ozone days over time, the months that experience high ozone have largely remained the same. While the ozone season varies slightly from year to year, in general, higher ozone is experienced in the summer months, mainly June, August, and September.

Table 2-4: Days with Eight-Hour Ozone Greater than 75 ppb by Month and Year

Month	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Jan																	
Feb																	
Mar						1				1						2	
Apr	2	1	1	2	3			2	1	2	3	1	1		2		
May	2	14	4	5	2	4	8	1	8	3	1	3	5	4		4	1
Jun	8	3	5	2	14	12	13	5	16	18	2	6	8	3	4	9	2
Jul	13	9	7	17	12	9	8	9	13	9	3	5	7		6	5	8
Aug	14	19	26	21	14	13	10	17	15	8	11	7	8	9	15	11	7
Sep	12	16	14	15	6	15	6	13	16	5	5	8	5	2	11	1	13
Oct	3	5	5	1				1	1	4	2				2		1
Nov			2														
Dec																	

Varieties of analyses have been presented for understanding ozone trends in the DFW area. The results of these analyses generally agree that ozone concentrations have been decreasing; however, the area still faces challenges in attaining the 2008 ozone NAAQS. Because ozone formation depends on a multitude of factors, these factors must be investigated in detail before conclusions as to causes of the observed decreases can be reached.

2.2 Nitrogen Oxides Trends

NO_X, a precursor to ozone formation, is a variable mixture of nitrogen oxide (NO) and nitrogen dioxide (NO_2). NO_X is primarily emitted by fossil fuel combustion, lightning, biomass burning, and soil (Martin et al., 2006). Examples of common NO_X emission sources, which occur in all

urban areas, are automobiles, diesel engines, other small engines, residential water heaters, industrial heaters and flares, and industrial and commercial boilers. Mobile, residential, and commercial NO_X sources are usually numerous smaller sources distributed over a large geographic area, while industrial sources are usually large point sources, or numerous small sources, clustered in a small geographic area. Because of the large number of NO_X sources, high ambient NO_X concentrations can occur throughout the DFW area.

Other sources of NO_X that impact air quality in the DFW area are large electric generating units (EGU) in and around the metropolitan area, as well as other areas upwind of the DFW area. These facilities can produce large concentrated plumes of emissions that can enhance ozone generation. Analyses done by the Rapid Science Synthesis Team of the 2005-2006 Texas Air Quality Study (TexAQS II) indicate that NO_X emissions at several EGUs decreased by factors ranging from two to four between 2000 and 2006. These reductions were seen at EGUs that implemented NO_X control features, such as Selective Catalytic Reduction (SCR), between 2000 and 2006, suggesting these control strategies are working (RSST, 2006).

NO_X trends are presented in Figure 2-4: Ozone Season (March through October) Daily Peak NO_X Trends in the DFW Area. Trends are for the ozone season only (March through October) and represent the 90th percentile, the 50th percentile, and the 10th percentile of daily peak NO_X concentrations in the DFW Area. The largest NO_X concentrations in the DFW area appear to be decreasing over time, while the lower concentrations have remained flat.

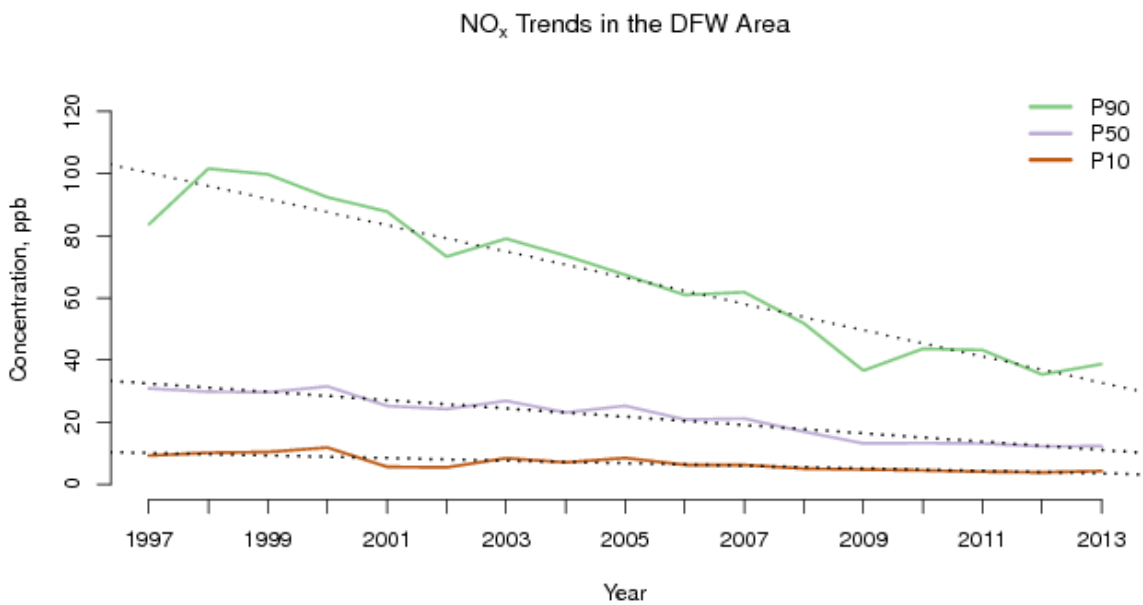


Figure 2-4: Ozone Season (March through October) Daily Peak NO_X Trends in the DFW Area

For a more robust examination of the distribution of NO_X concentrations, Figure 2-5: 90th Percentile Daily Peak NO_X Concentrations in the DFW Area analyzes the 90th percentile of daily peak NO_X at the highest monitors for the ozone season in the DFW area. Most monitors appear to exhibit decreases in 90th percentile daily peak NO_X concentrations. Monitors located near the urban core of the DFW area, Dallas Redbird Airport, Dallas Hinton Street, and Fort Worth Northwest, exhibited the largest decreases. 90th percentile NO_X concentrations at these urban core monitors have steadily decreased and are now within the range of other monitors in the

area. These large decreases may be due to a cleaner automobile fleet and increased regulations on NO_X emissions, though this has not been rigorously tested.

The ozone design value setting monitor, Denton Airport South, also shows a downward trend in 90th percentile NO_X. This monitor is north of the DFW metropolitan area in a small town and often is downwind during ozone season. The Parker County monitor, which has some of the lowest 90th percentile NO_X concentrations, shows a flat trend. This monitor is also a very rural monitor west of the DFW area.

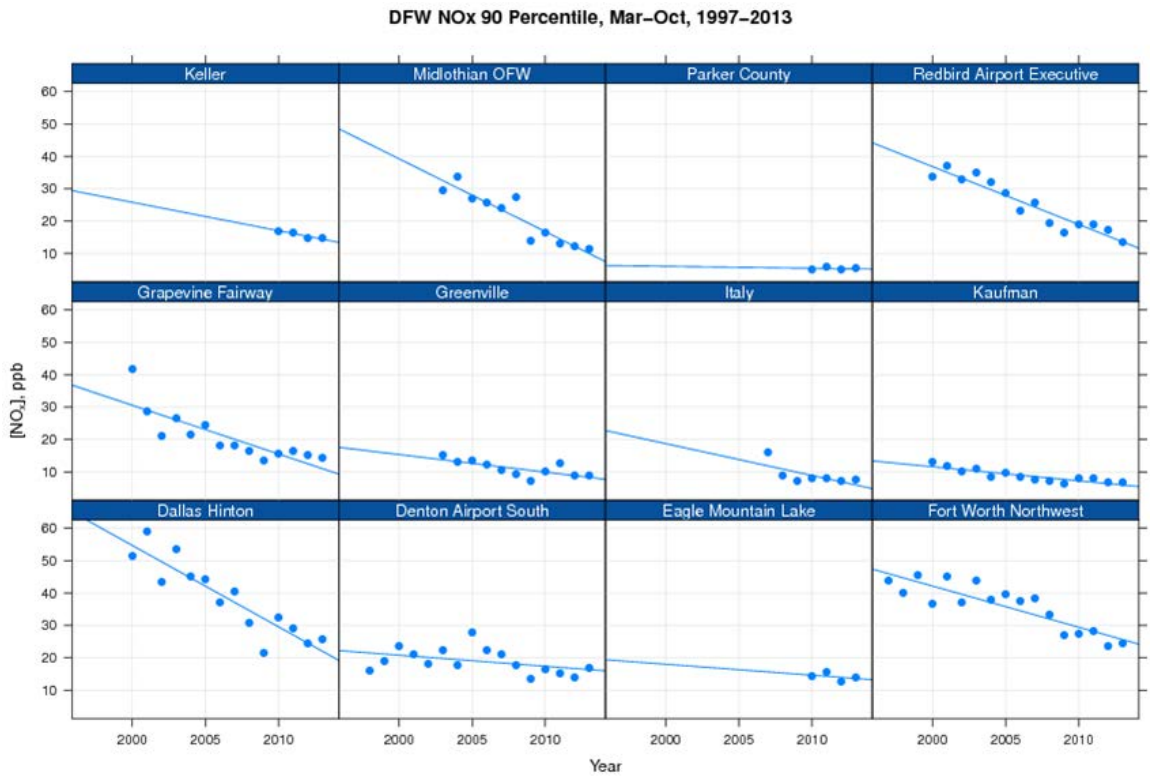


Figure 2-5: 90th Percentile Daily Peak NO_X Concentrations in the DFW Area

Similar to ozone, NO_X concentrations in the DFW area appear to be decreasing over time, in large measure, the result of the comprehensive suite of NO_X-targeted controls implemented since 2000. Stringent point source NO_X standards have been adopted along with numerous state and federal controls affecting mobile source NO_X emissions. Besides normal fleet turnover, as older vehicles are replaced by newer, less polluting ones in the on-road fleet, mobile source NO_X reductions since 2000 could also be due to improvements in the Air Check Texas motor vehicle inspection and maintenance (I/M) program, expansion of the Low Income Vehicle Repair and Replacement Assistance Program, and expansion of the Texas Emission Reduction Program for diesel trucks and heavy equipment.

2.3 Volatile Organic Compounds Trends

VOCs play a central role in ozone production. Since the mid-1990s, the TCEQ has collected 40-minute measurements on an hourly basis of up to 58 VOC compounds using automated gas chromatograph (auto-GC) instruments. These instruments automatically measure and report chemical compounds resident in ambient air. Initially, there was only one auto-GC collecting measurements in the DFW area, Dallas Hinton Street (C401/C60/AH161). In 2003 a second

auto-GC monitor was added, at Fort Worth Northwest (C13/AH32); since 2010, another twelve have been added, as shown in Table 2-5: Auto-GC Monitors in the DFW Area, 2000 through October 2013, due to interest in monitoring ambient air in and near the Barnett Shale area. At five of the sites, monitoring was conducted, then ceased; subsequently, monitoring at the site started anew with a new instrument run by a new operator under a different owner. These cases are seen in the table as two records with a single Aerometric Information Retrieval System (AIRS) code, but with two site names and two sets of monitoring start and end dates.

Table 2-5: Auto-GC Monitors in the DFW Area, 2000 through October 2013

County	AIRS Code	Site Name	Start Date	End Date
Dallas	481130069	Dallas Hinton Street C161 (Site E)	January 2000	Active
Denton	481211007	Flower Mound Shiloh (Site 45)	November 2010	April 2013
Denton	481211007	Flower Mound Shiloh (Site 2F)	May 2013	Active
Denton	481211013	DISH Airfield (Site 43)	April 2010	May 2013
Denton	481211013	DISH Airfield (Site 2D)	May 2013	Active
Johnson	482511063	Mansfield Flying L Lane (Site 63)	October 2012	Active
Johnson	482511501	Godley FM2331 (Site 2G)	July 2013	Active
Tarrant	484390075	Eagle Mountain Lake C75 (Site 42)	April 2010	February 2013
Tarrant	484390075	Eagle Mountain Lake C75 (Site 2E)	April 2013	Active
Tarrant	484391002	Fort Worth Northwest (Site F)	May 2003	Active
Tarrant	484391009	Everman Johnson Park (Site 46)	July 2011	April 2013
Tarrant	484391009	Everman Johnson Park (Site 2J)	May 2013	Active
Tarrant	484391018	Arlington UT Campus (Site 2A)	September 2012	Active
Tarrant	484391062	Kennedale Treepoint Drive (Site 62)	July 2013	Active
Tarrant	484391065	Fort Worth Joe B. Rushing Road (Site 65)	September 2013	Active
Tarrant	484391503	Fort Worth Benbrook Lake (Site 2B)	September 2013	Active
Wise	484970088	Decatur Thompson (Site 44)	October 2010	April 2013
Wise	484970088	Decatur Thompson (Site 2T)	June 2013	Active
Wise	484971064	Rhome Seven Hills Road (Site 64)	November 2013	Active

The TCEQ has also employed two types of canisters in the DFW area, one that samples ambient air over a 24-hour period and another that samples ambient air for a single hour at a time, usually at four different times of day. The one-hour canisters stopped operating in 2006 and were not included in the present analyses. The locations of the auto-GC and 24-hour canister monitors in the DFW area are shown in Figure 2-6: Locations of DFW VOC Monitors Active between 2000 and October 2013. On the map, monitor type is indicated in parenthesis as follows: AGC=auto-GC; C24=24-hour canister; and C1=1-hour canister. Some of the 24-hour canister monitors shown have been deactivated (see Table 2-6: 24-Hour Canister Monitors in the DFW Area, 2000 through September 2013), but were included as they have valid

measurement data somewhere between 2000 and 2013. Four sites in Table 2-6 commenced operation after June 2013; they are listed in the table but not included in the analysis because the analysis only used data through June 2013.

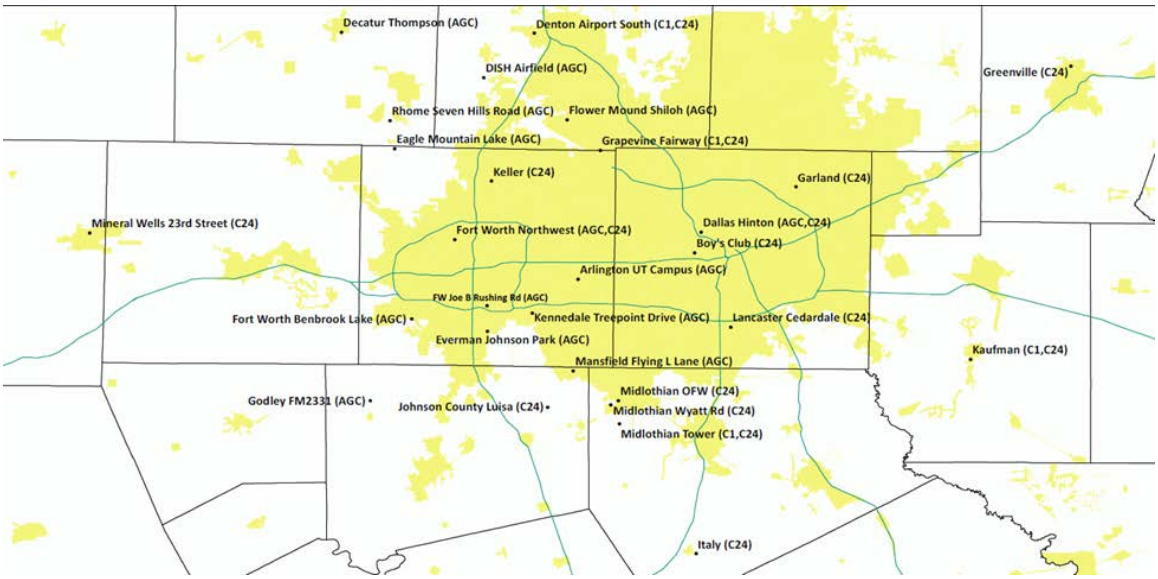


Figure 2-6: Locations of DFW VOC Monitors Active between 2000 and October 2013

Table 2-6: 24-Hour Canister Monitors in the DFW Area, 2000 through September 2013

County	AIRS Code	Site Name	Start Date	End Date
Dallas	481130057	Boy's Club	January 2000	January 2008
Dallas	481130069	Dallas Hinton Street	July 2000	Active
Dallas	481131006	Garland	January 2000	February 2003
Dallas	481131500	Lancaster Cedardale	September 2013	Active
Denton	481210034	Denton Airport South	June 2000	Active
Ellis	481390015	Midlothian Tower	April 2004	August 2007
Ellis	481390016	Midlothian OFW	January 2000	Active
Ellis	481390017	Midlothian Wyatt Road	October 2004	March 2006
Ellis	481391044	Italy	September 2007	Active
Hunt	482311006	Greenville	March 2003	Active
Johnson	482511008	Johnson County Luisa	December 2010	Active
Kaufman	482570005	Kaufman	April 2004	Active
Palo Pinto	483631502	Mineral Wells 23rd Street	August 2013	Active
Tarrant	484391002	Fort Worth Northwest	November 2013	Active
Tarrant	484392003	Keller	July 2013	Active
Tarrant	484393009	Grapevine Fairway	October 2003	Active

2.3.1 VOC Trends at Auto-GC Monitors

Trends in total non-methane hydrocarbons (TNMHC) concentrations, as a proxy for VOC, provide insight into variation in VOC levels in the DFW area over time. For VOC data, the annual geometric mean was used to assess trends. Though this analysis includes data through October 2013, data from the most recent months have not been validated and are subject to change.

VOC measurements exhibit many extremely small values and few extremely high ones. For series with these characteristics, logarithmic transformation often greatly improves analytical capacity. Therefore, for analyses of VOC trends, the geometric mean TNMHC was calculated. The geometric mean is preferred to the median or the arithmetic (ordinary) mean for evaluating the central tendency of data when the data are not symmetrically, or normally, distributed, but clustered around extreme high or low values. For these series, a geometric mean is more robust than an ordinary average, meaning its value is not greatly influenced by one or a few very high or very low values.

In order to calculate the annual geometric mean TNMHC concentration by monitor, the natural log of each hourly concentration was computed. Daily mean log values were calculated for all days with at least 75% valid hours (18 hours). Monthly mean log values were calculated for months with at least 75% valid days, and quarterly mean logs were calculated for quarters with at least two valid months. Finally, annual mean logs were calculated for years with at least three valid quarters; these values were exponentiated to give annual geometric mean concentration by monitor. For 2013, annual geometric means were calculated using the exponentiated average of the first three quarters' average log values at monitors whose first three quarters were valid. This analysis also examines the 90th percentile because it provides information about trends at the upper end of the distributions, but is more robust than the maximum values.

Figure 2-7: Annual Geometric Mean TNMHC at Auto-GCs in the DFW Area shows the trends in the annual geometric mean TNMHC concentrations in the DFW area. Data from auto-GCs with two AIRS codes and site names listed in Table 5 have been combined into a single site name for this analysis. The two monitors with the highest concentrations, DISH Airfield and Decatur Thompson, are located in the Barnett Shale, an area with numerous gas wells and correspondingly high TNMHC emissions. Neither of the two long-term monitors, Dallas Hinton and Fort Worth Northwest, appears to show notable trends. In fact, trend statistics calculated for the five monitors with at least three years of data showed no trends that were significant at even the 10% level. The possible effect of changes in gas production from year to year and corresponding VOC emissions changes on the ambient concentrations seen in this figure was not explored in this analysis.

All five monitors with at least three years of data show a decrease in TNMHC in 2013. Every monitor seen here with 2013 values had only three complete quarters of data as the fourth quarter was incomplete and was not included. 2013 was included in this in order to maximize data presented, but this inclusion potentially introduces bias because there can be large differences in concentrations in cooler versus warmer months. It is possible that when 2013 annual geometric means are calculated using a full year's data, this trend may be reduced or eliminated. This is because concentrations tend to be higher in the cooler months compared to the summer months, and the last quarter in the year can be expected to have average temperatures lower than the annual average; therefore, inclusion of fourth quarter data may raise the annual geometric mean concentrations.

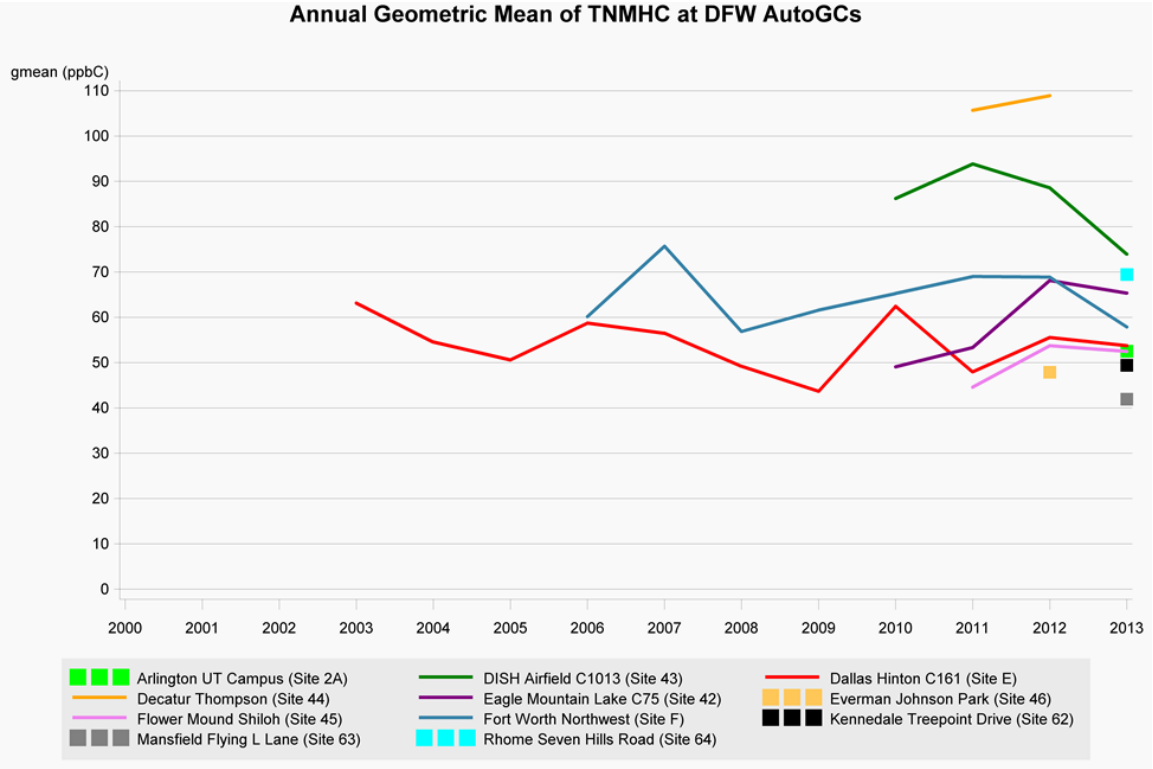


Figure 2-7: Annual Geometric Mean TNMHC at Auto-GCs in the DFW Area

Figure 2-8: Annual 90th Percentile TNMHC at Auto-GCs in the DFW Area shows the annual 90th percentile TNMHC at the same eleven auto-GCs seen in Figure 2-7. As with the geometric means, it is difficult to see any apparent trend overall in such concentrations; however, two things of note can be seen. First, concentrations at four of the five monitors with at least three years of data showed an increase in 2012; it would be worth investigating Barnett Shale gas production across these years, to see if it could help explain these increases. Second, as with the geometric mean trend analysis, 2013 includes only data from the first three quarters, so the pervasive decreases seen may not remain when the entire year's data are analyzed.

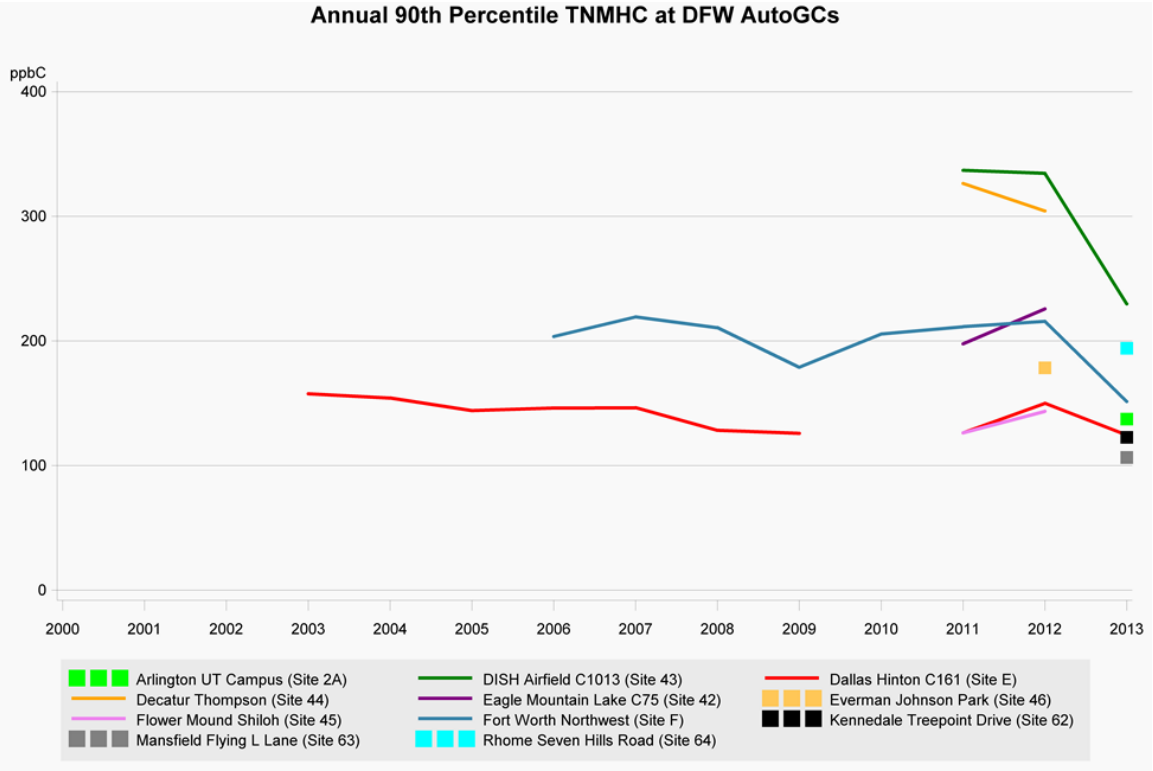


Figure 2-8: Annual 90th Percentile TNMHC at Auto-GCs in the DFW Area

While these results apply to all VOC species, it is the highly reactive species of VOC that are most important to ozone formation. Section 3.3: Ambient Highly Reactive Volatile Organic Compounds (HRVOC) Trends and VOC Characterization will explore HRVOC concentrations and trends in the DFW area in more detail.

2.3.2 VOC trends from Canisters

In addition to continuously operating auto-GC instruments in the DFW area, the TCEQ collects ambient air samples using evacuated canisters at twelve locations throughout the DFW area as of September 2013. Data from these canisters are useful for confirming findings from auto-GCs. The canisters have more long-term data and can therefore provide more robust trend information compared to the auto-GCs.

This analysis investigates 24-hour measurements of TNMOC collected with canister data. Sixteen canisters that collect TNMOC measurements every sixth day were active in the DFW area in the period of 2000 through June 2013 (see Figure 2-6 for map of site locations). Two canister locations coincide with auto-GC instruments: Dallas Hinton Street and Fort Worth Northwest. While comparisons with auto-GC measurements can be instructive for observing trends and other patterns, these instruments have different measurement durations and frequencies, potentially yielding incomparable results.

Similar to the auto-GC measurements, annual geometric mean concentrations were calculated for the seven monitors for which TNMOC measurements were available. Samples that were invalidated and those with warning codes regarding sample accuracy or precision were discarded. Quarters with less than 75% valid measurements (less than 12 samples) were also discarded; annual geometric mean concentrations were calculated for each monitor and year in which 3 or more valid quarters existed. Incomplete data from 2013 were also excluded.

The annual geometric mean TNMOC concentrations are seen in Figure 2-9: Annual Geometric Mean TNMOC at 24-Hour Canisters in the DFW Area. Visual inspection suggests that annual geometric mean TNMOC concentrations in DFW are declining, although there are fewer decreases occurring after 2006.

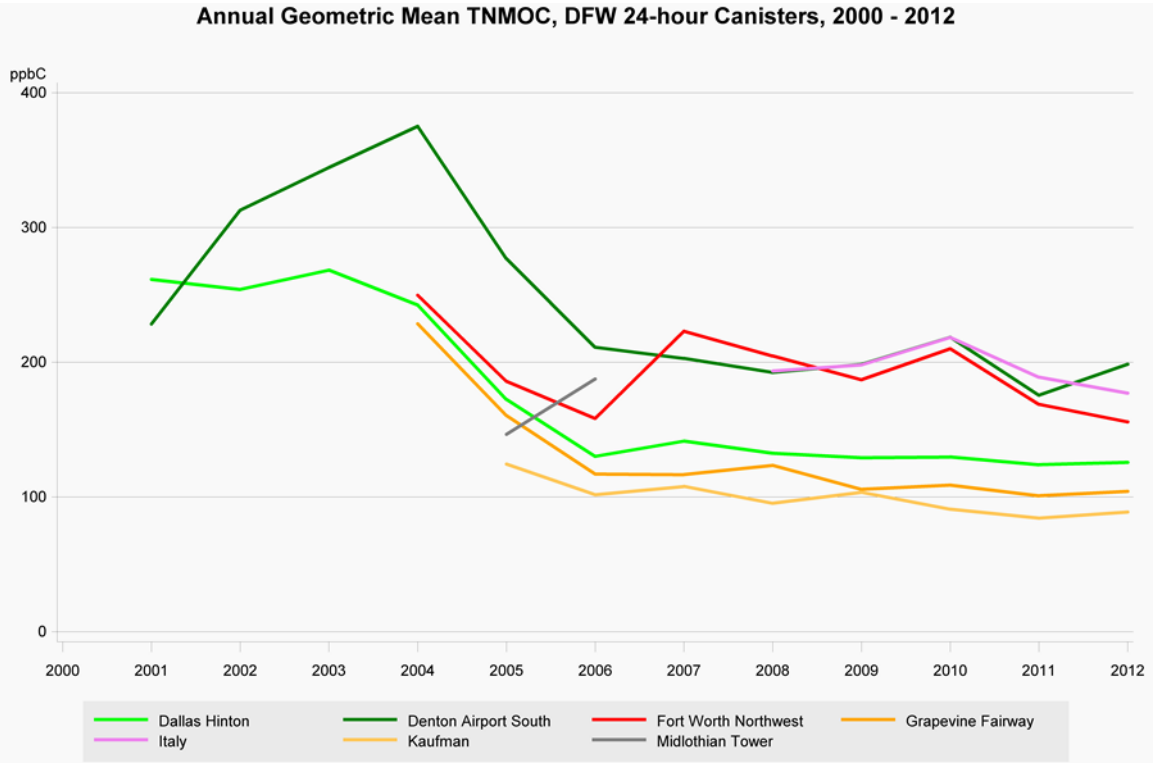


Figure 2-9: Annual Geometric Mean TNMOC at 24-Hour Canisters in the DFW Area

Analysis of VOC data collected with both auto-GCs and canisters revealed slight decreases in total VOC at Dallas Hinton Street. The auto-GC at Dallas Hinton showed less of a decrease in total VOC compared to the 24-hour canister data. Neither the auto-GC nor the 24-hour canister data showed much, if any, of a decrease in total VOC concentrations at Fort Worth Northwest.

2.4 Summary of Trends in Ozone and Ozone Precursors

Identifying and assessing trends in ozone and its precursors provide an initial appraisal of the current ozone situation in the DFW area, the magnitude of progress made to date, and the scale of future challenges. Examination of ozone trends shows that ozone design values, the statistics used to compare observed ambient ozone levels to the NAAQS, have decreased in the DFW area over the past seventeen years. The eight-hour ozone design value of record in 2013 was 87 ppb, a 16% decrease from the 1997 design value of 104 ppb. The one-hour ozone design value in 2013 was 108 ppb, well below the vacated one-hour ozone NAAQS of 124 ppb, and a 22% decrease from the 1997 design value of 139 ppb.

Examination of design values at individual monitors corroborates these decreases; however, 2010 seems to have experienced lower than normal ozone, while 2011 experienced higher than normal ozone. Since 1997, the number of days in the DFW area with eight-hour ozone greater than 75 ppb has fallen 41%. Decreases in high ozone days are apparent despite an increase in the

number of monitors located throughout the DFW area. The ozone season was also determined to be less severe in recent years.

A variety of methods has been presented for understanding ozone trends in the DFW area. These methods generally agree that ozone concentrations have been decreasing; however, the area still faces challenges in achieving attainment of the 2008 ozone NAAQS. Because ozone formation depends on a multitude of factors, these factors must be investigated and understood in detail before conclusions as to the causes of the observed decreases can be reached.

Similar to ozone, NO_X concentrations in the DFW area are decreasing over time. NO_X concentrations have shown larger decreases in the 90th percentile values compared to the median or 10th percentile values. Monitors with larger 90th percentile NO_X concentrations, located near the urban core of the DFW area, tended to show larger decreases compared to monitors with lower 90th percentile NO_X concentrations.

VOC data collected with auto-GCs showed little to no decreases at monitors with more than three years of data. Data from VOC 24-hour canisters showed overall decreases at most of the monitors; however, the majority of these decreases occurred before 2006.

NO_X trends from 1997 through 2013 show that most monitors in the DFW area experienced decreases in both median and 90th percentile concentrations of these pollutants, but VOC trends from 2000 through 2013 show less of a decrease. While NO_X and VOC are precursors to ozone formation, meteorology can play an important, if not more significant, role in ozone concentration and precursor trends. The next chapter will take a closer look at local variables that contribute to ozone formation in the DFW area, including meteorology.

3. RECENT FINDINGS IN LOCAL OZONE DYNAMICS IN THE DALLAS-FORT WORTH AREA

Analyses of ozone trends demonstrate that ozone and its precursors in the Dallas-Fort Worth (DFW) area have steadily decreased over the past several years. The complexity of ozone formation, however, requires a comprehensive examination of contributing factors. Observed ozone is the aggregate of background ozone and locally produced ozone. Background ozone is either formed by naturally occurring processes, or generated elsewhere and transported into a region. This type of ozone is largely outside the purview of state and local air control authorities. Even much of the locally produced ozone is difficult for state and local authorities to control.

This chapter examines patterns of local precursor emissions, local ozone formation and transport, and local meteorology, beginning with a detailed look at spatial and temporal patterns of ozone variability across the region. This is followed by a presentation of recent findings in local patterns of nitrogen oxides (NO_X) and volatile organic compounds (VOC) emissions, including discussion of emission variability by day of the week and detailed consideration of emissions from oil and gas activity in the Barnett Shale region. Finally, local meteorological factors and their contributions to local ozone formation are explored. The findings presented here support the conclusion that reductions in ozone observed in the DFW area over the previous decade are due in large part to real, quantifiable reductions in precursors, rather than anomalous meteorological conditions that are unlikely to recur.

3.1 Local Variation in Ozone

The previous chapter showed that ozone concentrations can vary by monitor and location. Taking this finding one step further, this section employs a spatial interpolation method borrowed from the field of geostatistics, “kriging”, to identify which specific parts of the DFW

area experience higher or lower ozone concentrations (Krige, 1951). These patterns guide a more detailed examination of variability in the factors contributing to ozone formation, both across time and space.

Annual eight-hour ozone design values at each monitor in the DFW area were interpolated onto a two dimensional grid using the kriging procedure, a spatial estimation technique. The kriging procedure uses a variogram to express spatial variation and minimize the error of predicted values. It is most robust where a monitoring network is most dense. Performing this procedure for multiple years provides additional corroboration of the decreasing temporal trends identified previously. The three years of 2003, 2008 and 2013 were selected for analysis.

The eight-hour ozone design values for each monitor in the DFW area for the selected years are displayed in Figure 3-1: Eight-Hour Ozone Design Values for 2003, 2008, and 2013. Pink represents higher ozone design values while green represents lower ozone design values. The outermost monitors in each direction bound the area of interpolation. As monitors are shut down and others are started up, the interpolation domain changes.

The highest eight-hour ozone design values in 2003 were 100 ppb and occurred to the north northwest of the DFW core area at Grapevine and Keller. High design values (greater than 95 ppb) were also observed at the Fort Worth Northwest, Eagle Mountain Lake, and Denton Airport South monitors. The lowest eight-hour ozone design values in 2003 occurred southeast of downtown Dallas at Kaufman.

By 2008, peak eight-hour ozone design values had dropped considerably across the region. The highest concentrations shifted more to the north and northwest of the DFW core area, with a peak of 91 ppb occurring at Denton Airport South and a peak of 89 ppb occurring at Eagle Mountain Lake. Keller and Grapevine still had high ozone with a design value of 87 ppb at both monitors, but it was 13 ppb lower than the 2003 peak of 100 ppb. The minimum eight-hour ozone concentration also shifted to the north with the minimum occurring at Greenville, but low ozone concentrations still occurred at Kaufman as well.

In 2013, eight-hour ozone design values dropped even further. The maximum eight-hour ozone design value is now considerably lower at 87 ppb, and still occurs at Denton Airport South. The highest ozone concentrations have shifted more east with peaks still occurring at Keller and Grapevine, but no longer occurring at Eagle Mountain Lake. The minimum eight-hour ozone in 2013 shifted to the south and west, and is now occurring at the Corsicana Airport and Italy monitors. Changes in the areas of minimum ozone concentrations may be due to the addition of monitors in these areas in recent years. While the area where the minimum peak occurs may have shifted, in general, ozone is typically lower in the southern and eastern parts of the DFW area.

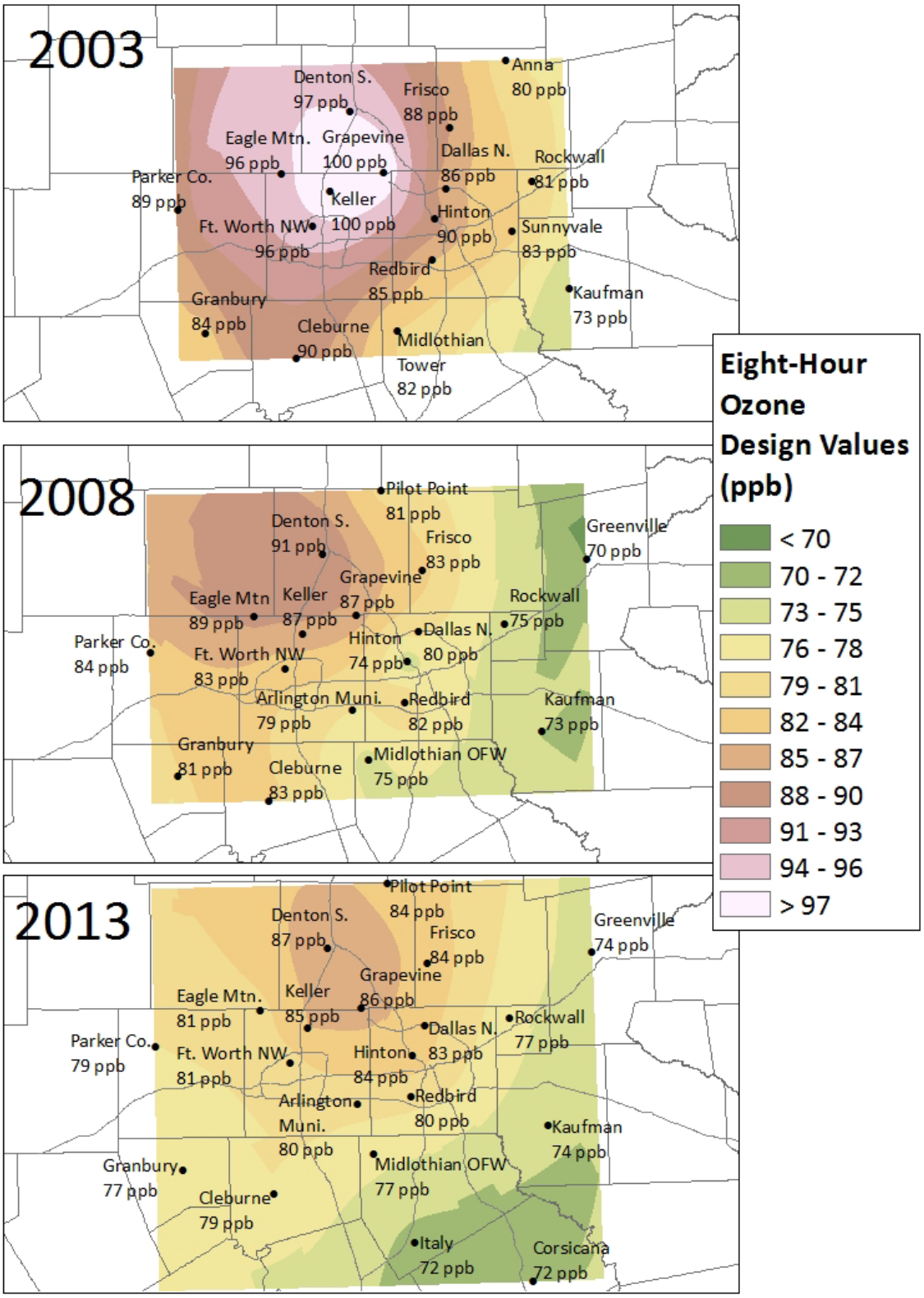


Figure 3-1: Eight-Hour Ozone Design Values for 2003, 2008, and 2013

The kriging method can also be employed to investigate the geographic origins of high ozone concentrations. Comparison of temporal patterns of ozone formation on days with high ozone concentrations to days with low ozone concentrations can identify unique features of high ozone days that may corroborate conclusions about sources of high ozone. Daily maximum ozone concentrations were divided into two groups: days with eight-hour ozone values above 75 ppb, and with eight-hour ozone values less than or equal to 75 ppb. The time of day when peak one-hour ozone was recorded at each monitor was determined for each day, then averaged across the two groupings of days. Only monitors that report data to the EPA were included. Data from 1997 through 2013 was used and days were restricted to March through October to exclude months when few or no exceedance days occur in the DFW area.

Spatial interpolation with kriging was performed on the average time of day of peak ozone at each monitor for both low and high ozone days to identify when and where ozone peaks occur, on average, throughout the DFW area. Maps of the time of peak ozone in the DFW area are found in Figure 3-2: Average Time of Peak Hourly Ozone 1997 through 2013. Shades of pink represent times later in the day, while greens represent times earlier in the day. The top map shows time of day of peak one-hour ozone on days when eight-hour ozone was equal to or below 75 ppb, and the bottom map shows time of day of peak one-hour ozone on days when eight-hour ozone was greater than 75 ppb.

The top map shows that on days with low eight-hour ozone values, ozone first peaks in northern Dallas County, in the center of the DFW area, around 13:45 Local Standard Time (LST). Peak ozone occurs in the rest of the DFW area within one hour of the initial peak, with areas at the southern and western edge of the DFW area observing the peaks last. The bottom map shows that on high eight-hour ozone days ozone first peaks in the same spot (northern Dallas County) and almost the same time (between 13:45 and 14:00) on low eight-hour ozone days. Ozone in the rest of the area, however, peaks much later on high eight-hour ozone days. The latest ozone peaks at the Parker County monitor after 16:00 LST. This pattern appears to suggest more stagnant wind conditions on high ozone days, leading to high ozone later in the day occurring at monitors farther away from the urban core of the DFW area.

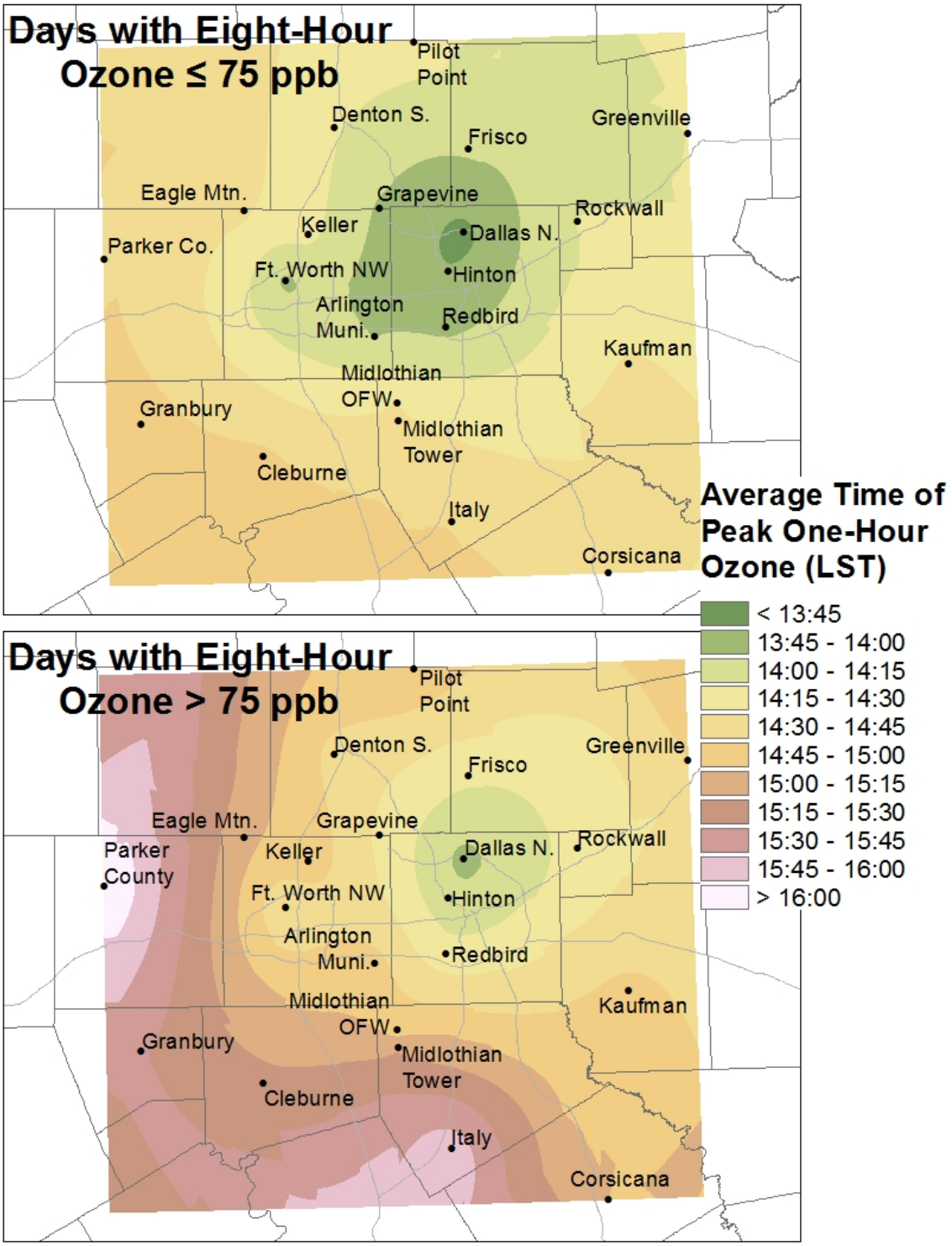


Figure 3-2: Average Time of Peak Hourly Ozone 1997 through 2013

The time of day of maximum ozone on high eight-hour ozone days represents a composite pattern: high ozone formed in the urban core of the DFW area is slowly carried to the surrounding areas. Combined with the earlier spatial design value analysis, it appears that ozone concentrations are first formed in the urban areas of the DFW area, then those concentrations

accumulate as they are slowly transported to the northwest and west, where the highest ozone concentrations are routinely observed. To corroborate these findings, an analysis of NO_X and VOC ozone precursors, along with meteorological patterns, follows.

3.2 Spatial Variation in Nitrogen Oxides

Like ozone, NO_X was shown in Chapter 2: Air Quality Trends in the Dallas-Fort Worth Area to vary both temporally and spatially. The trend in spatial NO_X patterns is clear when displayed on a map. All monitors with available data in each year were used in this analysis, even though some monitors were shut down and others were started up during that time. Similar to the ozone plots, ordinary kriging interpolation was used to determine the spatial variation of mean NO_X in 2003, 2008, and 2013 in the DFW area.

Figure 3-3: Median Daily Peak NO_X Concentrations for the Ozone Season in the DFW Area for 2003, 2008, and 2013 illustrates the spatial variation of median ozone season NO_X in the DFW area. NO_X concentrations appear to be decreasing over time; however, the location of the highest and the lowest NO_X concentrations appears to remain the same. The urban core of Dallas and Fort Worth, which is dominated by mobile source emissions, has the largest median NO_X concentrations. The highest concentrations of mean NO_X occur at Dallas Hinton Street, the same monitor that first observes peak one-hour ozone concentration on eight-hour ozone exceedance days. It appears that ozone may be formed in the area near Dallas Hinton Street and then transported throughout the DFW area. Monitors that observed the lowest NO_X levels are located to the south and southeast of Dallas County, in areas that are more rural.

The largest NO_X decreases occur within the more urban areas of Dallas and Fort Worth. Dallas North, Dallas Redbird Airport, and Midlothian OFW all saw median NO_X decreases of 64% from 2003 through 2013. NO_X concentrations at the Dallas Hinton Street monitor, the monitor with the largest median NO_X, have dropped from 16.7 ppb to 8.4 ppb over the 2003 through 2013 period, a 50% decrease. Areas on the periphery of the DFW area appear to show some decreases from 2003 through 2013, but those decreases are not as large as those observed at monitors in the more urban areas, which happen to be located near many major roadways. This suggests that the measured decreases may be a result of decreases in NO_X emissions from mobile sources.

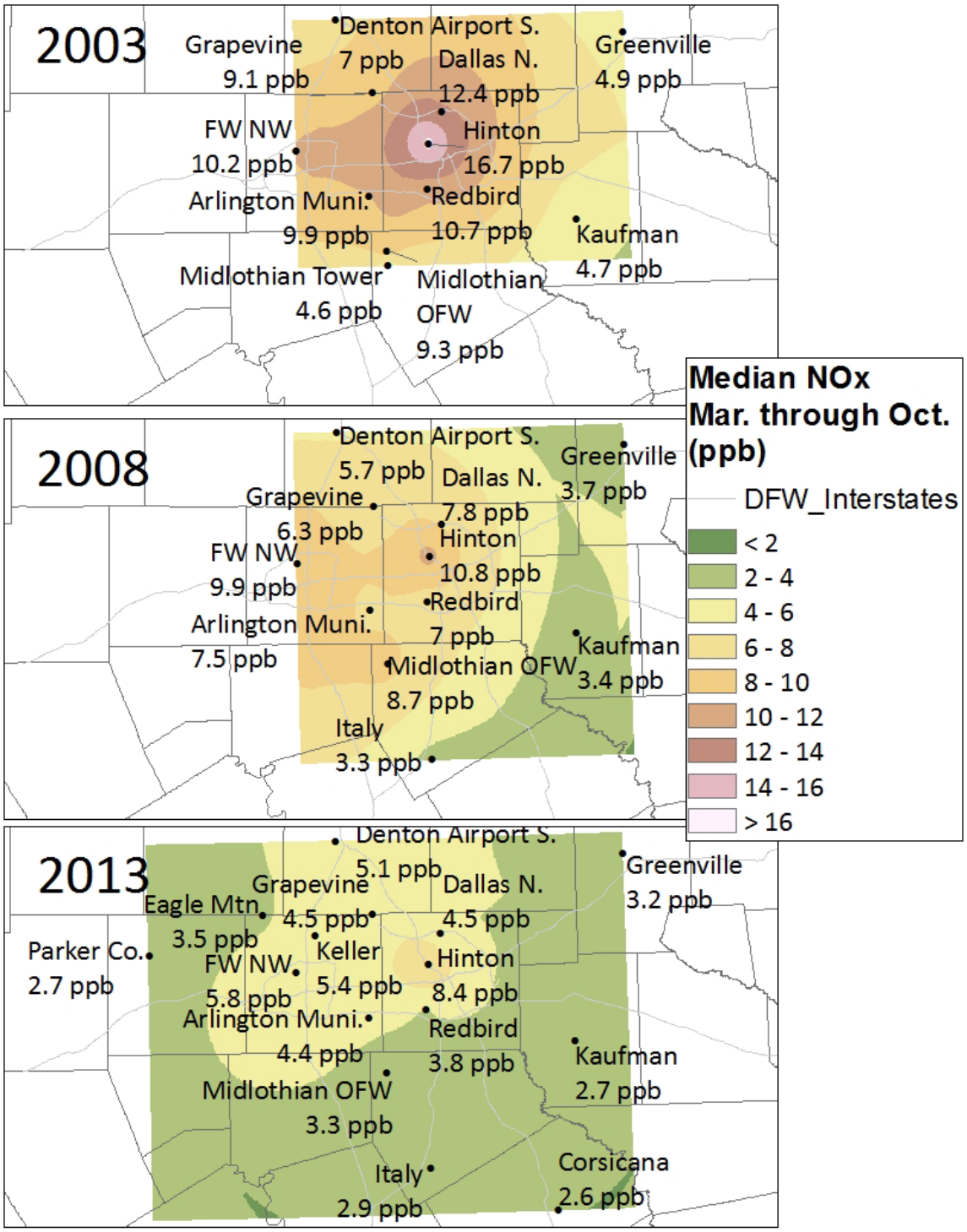


Figure 3-3: Median Daily Peak NO_X Concentrations for the Ozone Season in the DFW Area for 2003, 2008, and 2013

Because of the variety of NO_X sources, there can be a variety of reasons why NO_X concentrations in DFW have been decreasing. One potential cause for the decrease in NO_X over the entire DFW area is on-road vehicle fleet turnover, although this hypothesis has not yet been rigorously tested. Transport of industrial NO_X can obscure the patterns of mobile source emissions. An

investigation of other variables in ozone formation, such as VOC and meteorology, may help to explain not only patterns in ozone, but also observed patterns in NO_X concentrations.

3.3 Ambient Highly Reactive Volatile Organic Compounds (HRVOC) Trends and VOC Characterization

Six VOC species monitored by the TCEQ are classified as highly reactive VOC (HRVOC): ethene (ethylene), propene (propylene), 1,3-butadiene, 1-butene, cis-2-butene, trans-2-butene (TCEQ, 2006). An additional five species monitored by TCEQ auto-GCs and canisters are highly reactive but are not included in the TCEQ's classification: 1-pentene, t-2-pentene, c-2-pentene, isoprene, and 1,2,3-trimethylbenzene. HRVOCs react more rapidly than other VOC species to form ozone; therefore, trends in these species may be important in understanding changes in ozone formation dynamics in the area. In addition to HRVOC trends, a complete characterization of VOC composition will help to show what types of VOC are present in the DFW area, and how likely they are to react to form ozone.

3.3.1 HRVOC Trends at Auto-GC Monitors

As with TNMOC, geometric means were used to measure trends in HRVOC concentrations. Annual geometric means of ethylene and propylene were calculated for all complete years from 2000 through 2013 for the eleven AutoGC monitors with at least one year of complete data. The same method used to calculate annual geometric means for TNMOC was also used here. Only days with at least 75% valid hours (18 hours) were used in the calculation. Monthly mean log values were calculated for months with at least 75% valid days, and quarterly mean logs were calculated for quarters with at least 2 valid months. Finally, annual mean logs were calculated for years with at least 3 valid quarters; these values were exponentiated to give annual geometric mean concentration by HRVOC compound by monitor. For 2013, annual geometric means were calculated using the exponentiated average of the first three quarters' average log values for those monitors whose first three quarters were valid.

Figure 3-4: Annual Geometric Mean Ethylene at DFW AutoGCs and Figure 3-5: Annual Geometric Mean Propylene at DFW AutoGCs show the trends in annual geometric mean ethylene and propylene. Gaps in data series indicate years with incomplete data. Dallas Hinton Street and Fort Worth Northwest nearly always have the highest geometric mean ethylene and propylene concentrations. As noted earlier in this document, both monitors are exposed to considerable emissions from on-road mobile sources, of which ethylene and propylene are components. Ethylene and propylene both appear to show decreasing trends at Dallas Hinton Street and Fort Worth Northwest. There appear to be flat trends at the other monitors; however, these other monitors do not have data prior to 2010, which is not enough data to discern a strong trend. If reductions in these compounds in the DFW area occurred mostly or entirely before 2010, the limited duration of operation of AutoGC monitors will not reflect these earlier downward trends.

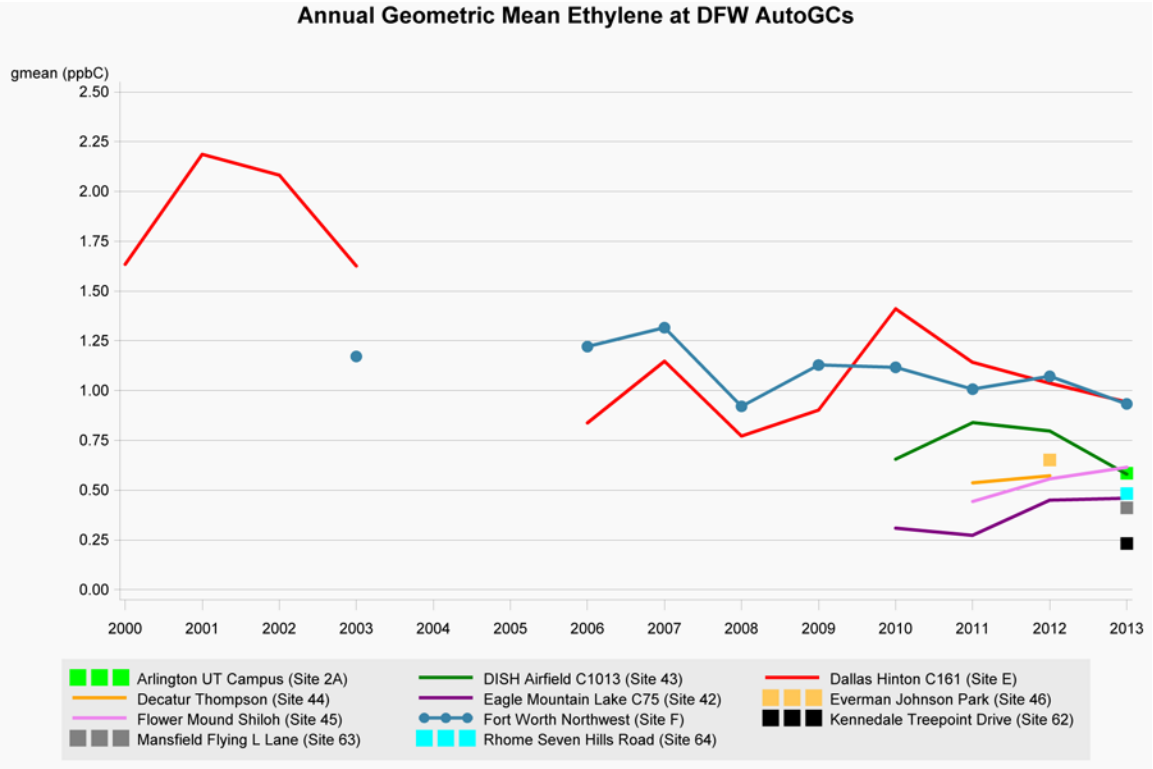


Figure 3-4: Annual Geometric Mean Ethylene at DFW AutoGCs

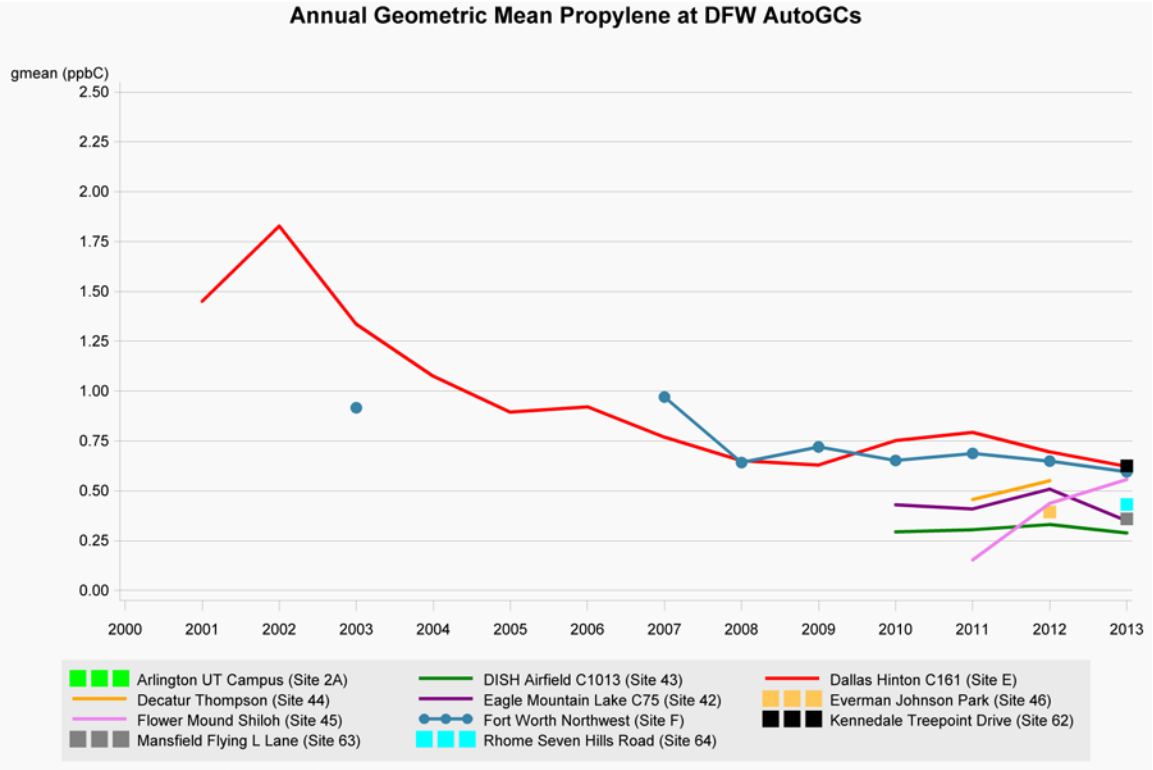


Figure 3-5: Annual Geometric Mean Propylene at DFW AutoGCs

3.3.2 HRVOC Trends from Canisters

Means of each of the eleven HRVOCs were calculated from the dataset comprising all canister measurements (all monitors aggregated) in the entire thirteen-year study period (2000 through 2012). It was found that ethylene (mean: 1.84 ppbC) and propylene (mean: 1.00 ppbC) had the two highest concentrations, and 1-butene (mean: 0.78 ppbC) was relatively high compared to the other eight species; therefore, only those three species were analyzed here. Annual geometric means of these were calculated for the 12 DFW canister monitors with at least two consecutive complete years of data from 2000 through 2012. The one monitor with just one year of data, Midlothian Wyatt, was dropped because its data were older, with its only valid year occurring in 2005. Annual geometric means were calculated as described in Section 2.3: Volatile Organic Compounds Trends. Only quarters with at least 75% valid samples and years with at least three valid quarters were used in these trends.

Figure 3-6: Annual Geometric Mean Ethylene from Canisters in the DFW Area, Figure 3-7: Annual Geometric Mean Propylene from Canisters in the DFW Area, and Figure 23: Figure 3-8: Annual Geometric Mean 1-Butene from Canisters in the DFW Area show the trends for ethylene, propylene, and 1-butene annual geometric mean concentrations. For all three compounds, the Boys Club monitor showed the highest concentrations from 2000 through 2006, the only years for which it has data. Boys Club was located just 0.8 miles from Interstate 30 and typically measured air dominated by mobile emissions, of which these three HRVOC are components.

Ethylene and propylene show patterns similar to one another. Both ethylene and propylene concentrations at Dallas Hinton Street and Fort Worth Northwest are higher than all monitors, with the exception of Boys Club. All monitors show general decreases up until about 2009, when concentrations appear to stabilize. Overall, most monitors show a significant decrease in ethylene and propylene concentrations, with the exception of Fort Worth Northwest and Italy for ethylene, and Garland and Italy for propylene. Dallas Hinton Street and Fort Worth Northwest typically capture emissions dominated by mobile sources. Given the number of monitors analyzed and their broad geographic coverage of the DFW area, the number of significant decreases suggests that the DFW area as a whole has experienced decreased ethylene and propylene concentrations from 2000 through 2012.

Different patterns are exhibited by 1-butene. Concentrations of 1-butene do not appear to be decreasing across any part of the study period, and Fort Worth Northwest has markedly higher concentrations compared to Dallas Hinton Street. Only three monitors exhibited significant decreases in 1-butene: Dallas Hinton Street, Italy, and Midlothian OFW.

To summarize, because of the large number of canister monitors with multiple years of data, and the broad geographic area covered by the monitors, the analysis of HRVOC trends using canister data provided a much better look at the evolution of concentrations of three HRVOC in the DFW area. The pervasive downward trends in ethylene and propylene seen in canister data were seen at the AutoGCs at Dallas Hinton and Fort Worth Northwest, but no other monitors in the network. Most of the AutoGC monitors are too new to be able to capture much useful trend information.

Patterns apparent in the trends suggest that area wide, ethylene and propylene have decreased from 2000 to 2012, with most of this decrease occurring from 2000 to 2009. Three monitors whose ambient air is dominated by vehicle emissions, Boys Club C134, Dallas Hinton, and Fort Worth Northwest, had the highest concentrations of these two compounds, and all three showed the same pattern of decrease seen in the other monitors. This suggests that vehicle emissions are

the most important source of these two HRVOCs, and that reductions in vehicle emissions are the likely reason for the decrease.

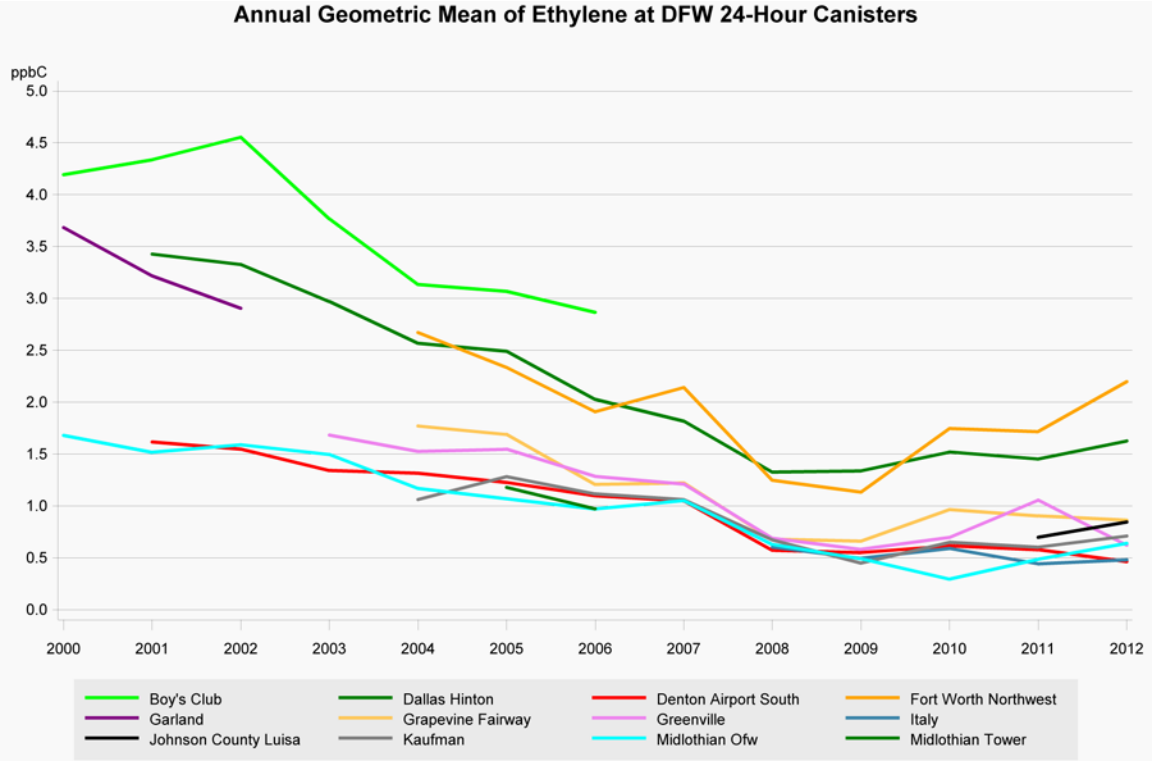


Figure 3-6: Annual Geometric Mean Ethylene from Canisters in the DFW Area

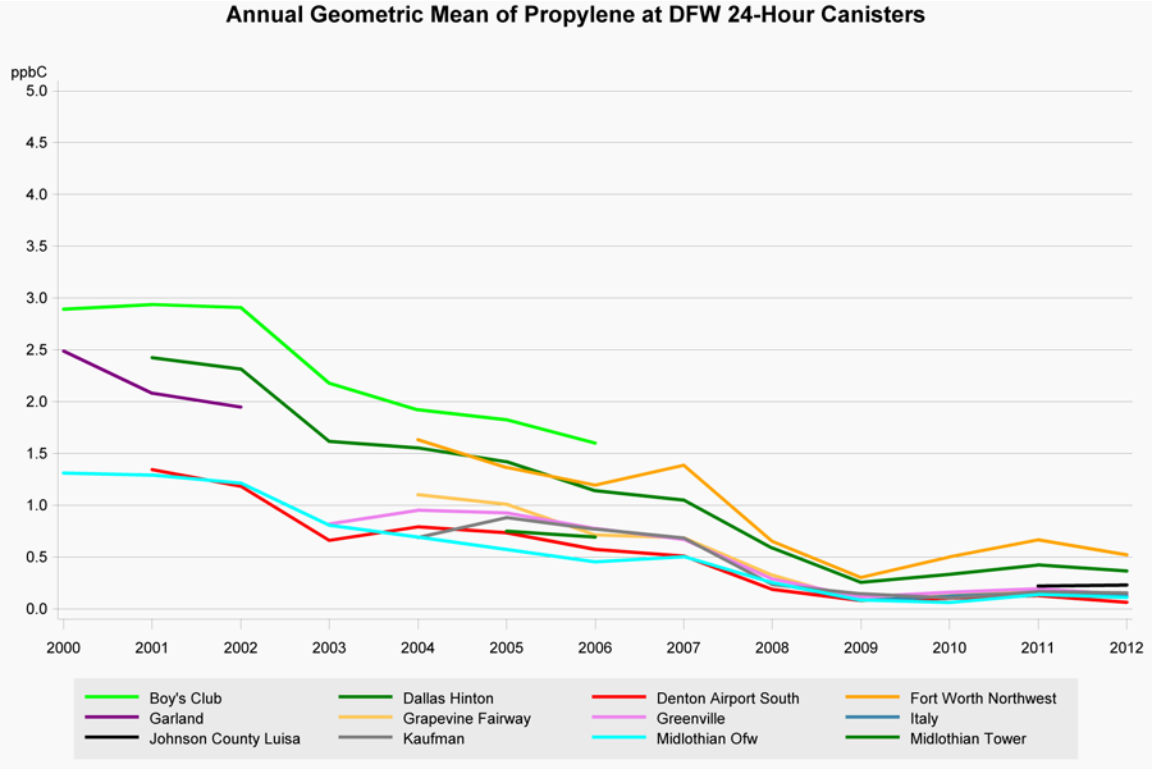


Figure 3-7: Annual Geometric Mean Propylene from Canisters in the DFW Area

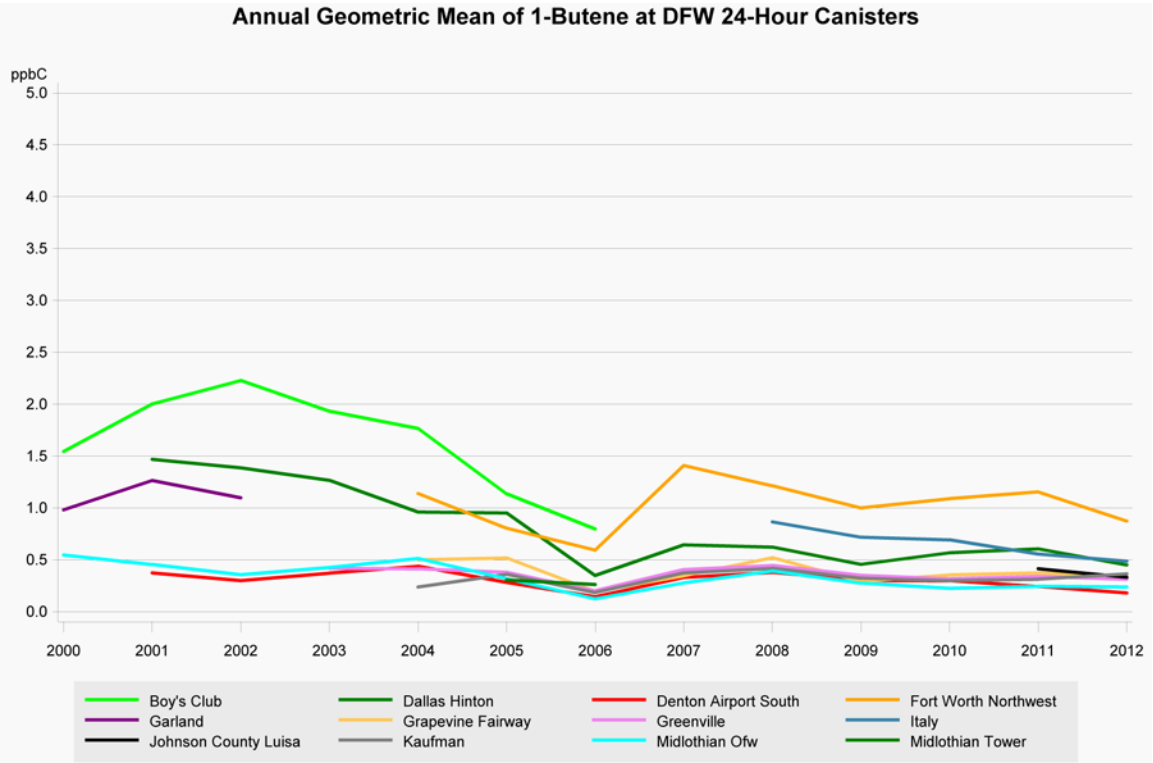


Figure 3-8: Annual Geometric Mean 1-Butene from Canisters in the DFW Area

3.3.3 Characterization of VOCs Using AutoGC Monitors

In addition to looking at HRVOC trends, the composition of total VOC, including HRVOC, at each AutoGC monitor was examined. The composition of total VOC measured in the DFW area can provide insight into how much reactive VOCs are present and how efficient these VOCs are at forming ozone.

Geometric mean total VOC, the sum of all VOC species measured, was calculated for each AutoGC monitor in the DFW area for the period July 2012 through June 2013. The total VOC was split into six classifications: HRVOC, aromatics, ethane, propane, total butanes, and other alkanes. Each monitor's composition is presented in Figure 3-9: Geometric Mean VOC Composition at Eleven AutoGCs in the DFW area, July 2012 through June 2013. The monitors in the figure are geographically aligned left to right such that the leftmost monitor (Decatur Thompson) is located the farthest northwest, and the rightmost (Dallas Hinton Street) is located the farthest southeast. The leftmost four monitors are located in the Barnett Shale area. The influence of emissions from gas production in that area are most obviously reflected in their geometric mean ethane and propane concentrations, which drive the total VOC concentrations higher than the other seven monitors. Both propane and ethane are abundant constituents of natural gas, whereas their contributions to vehicle emissions are relatively much smaller. Decatur Thompson has the greatest propane, butanes, and other alkanes concentrations. The greater amounts of heavier alkanes (the butanes and other alkanes) at this monitor may be due to its location, which is closer to wells producing petroleum liquids such as condensate and oil,

than are the other monitors. Emissions from petroleum liquids are likely to have heavier constituents, on average, than are emissions from natural gas.

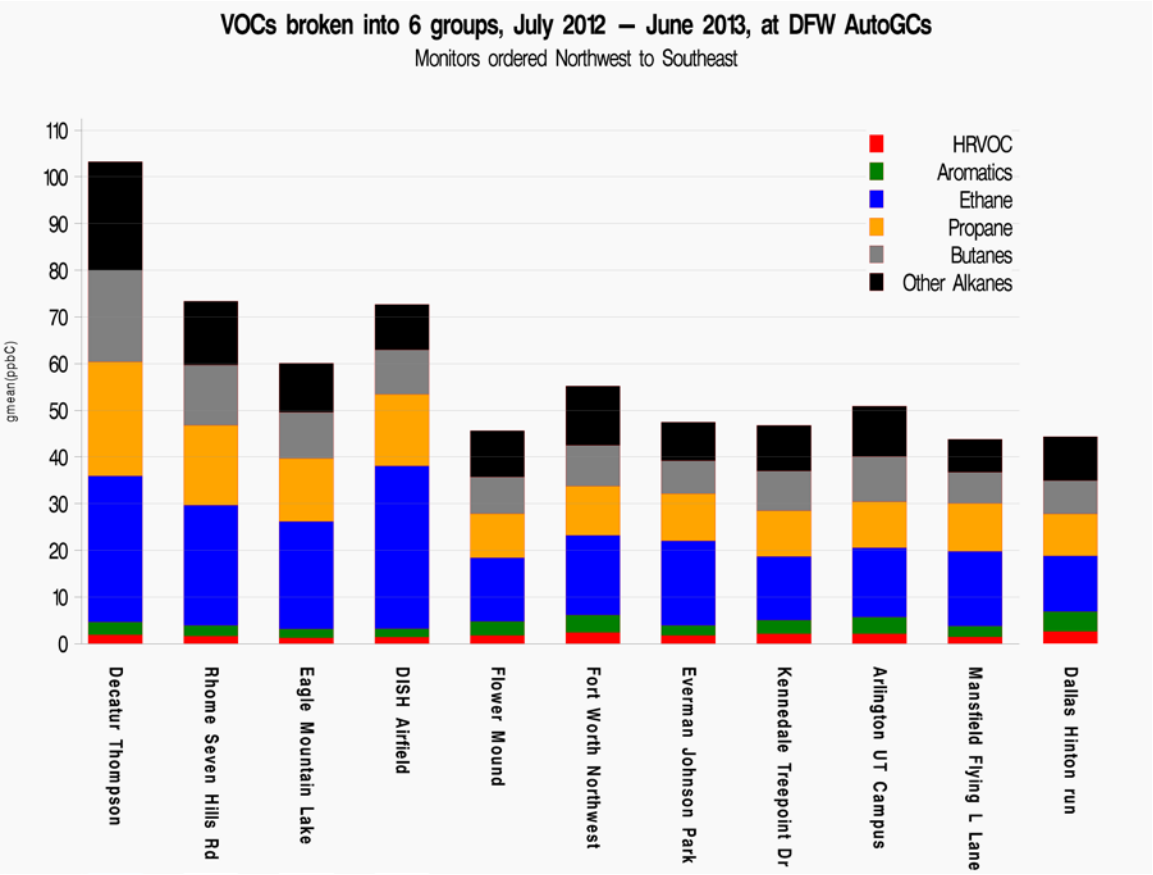


Figure 3-9: Geometric Mean VOC Composition at Eleven AutoGCs in the DFW area, July 2012 through June 2013

The mean concentrations seen in Figure 3-9 were multiplied by the Maximum Incremental Reactivity (MIR)-based conversion factors to get estimates of a reactivity-based concentration. Multiplying VOC concentrations by the MIR factor weights VOCs based on their ozone formation potential (Carter, 2000; Carter, 2010). VOCs that are more reactive can form more ozone at lower concentrations. Investigating VOC composition based on reactivity will help identify which compounds are most important in relation to ozone formation.

The geometric means of the reactivity-weighted VOC composition at the AutoGC monitors in the DFW area are shown in Figure 3-10: Geometric Mean of Reactivity Weighted VOC Composition in the DFW Area, July 2012 through June 2013. When VOC concentration is adjusted for reactivity, total VOC concentration remains highest at Decatur Thompson; however, the next highest monitors are two urban ones, Fort Worth Northwest and Dallas Hinton Street, as well as Rhome Seven Hills Road, located in the Barnett Shale. Total reactivity-weighted VOC concentrations at the urban monitors, Fort Worth Northwest and Dallas Hinton Street, is driven by HRVOC and aromatic species. The total reactivity-weighted VOC concentration at Decatur Thompson appears to be driven by the less reactive species of butanes and other alkanes. The concentrations of butanes and other alkanes at Decatur Thompson are large enough to make an impact on VOC concentrations even when weighted by reactivity.

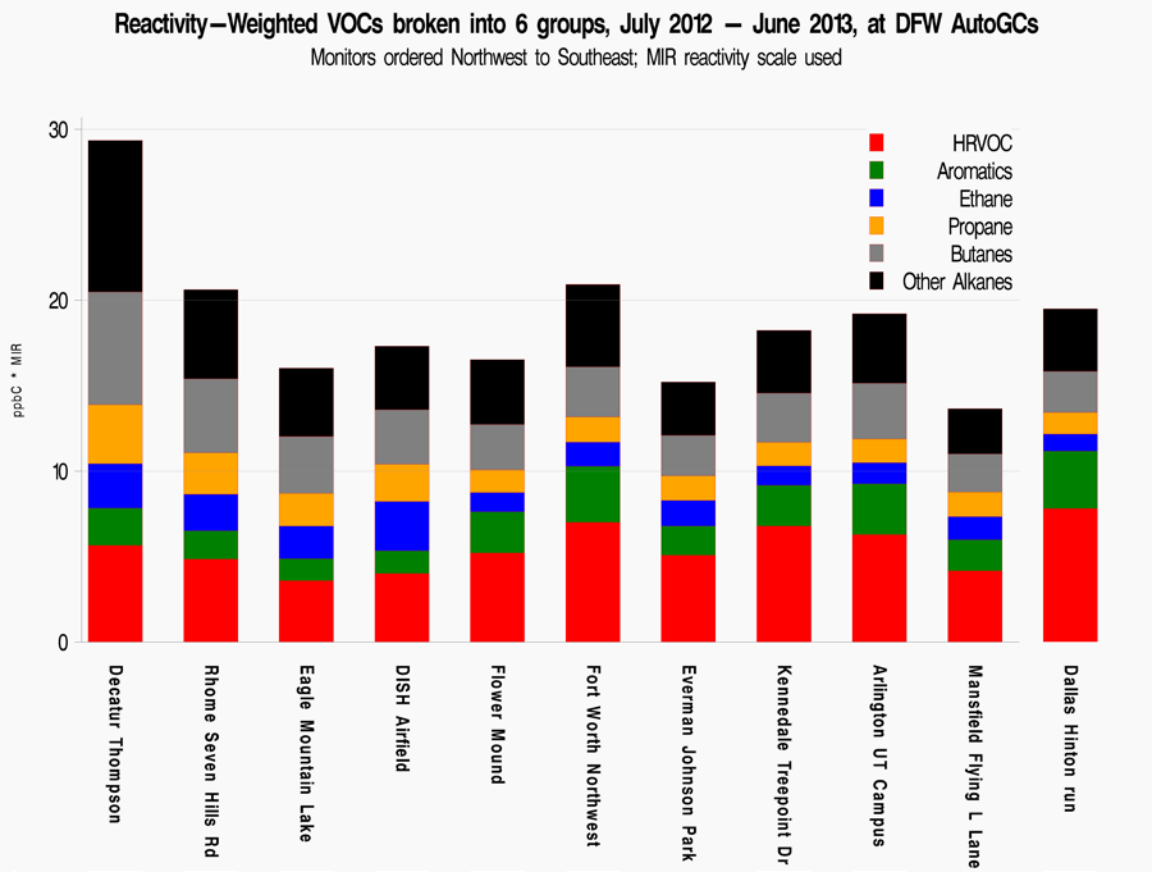


Figure 3-10: Geometric Mean of Reactivity Weighted VOC Composition in the DFW Area, July 2012 through June 2013

3.4 Relationship of Barnett Shale to Ozone in the DFW Area

Barnett Shale is a geological formation of sedimentary rock in north-central Texas that contains oil and gas. In the past several years, the quantity of gas produced from wells operating in the play has grown from a daily average of 216 million cubic feet (MMcf) per day to a peak of 5,748 MMcf per day in 2012, and has since dropped to 4,751 MMcf per day in 2014 (Railroad Commission of Texas, 2014). The geological area containing oil and gas is estimated to extend from the city of Dallas in the east, west to Shackleford County, south to Coryell County, and north to the Red River, encompassing roughly 5,000 square miles and 18 counties in Texas.

Because of the proximity of the Barnett Shale formation to the DFW area, it has been hypothesized that emissions from oil and gas drilling, extraction, and transport activity in this region could be influencing air quality in the DFW area. Analysis of VOC composition in Section 3.3 showed that monitors in the Barnett Shale area had the largest total concentration of VOC; however, much of those VOC are not very reactive in regards to ozone formation. Another analysis (Sullivan, 2013) shows larger amounts of total VOC present in the Barnett Shale area compared to the area around Eagle Mountain Lake. Although larger amounts of VOC are present in the Barnett Shale area, extensive analysis performed in the previous conceptual model (TCEQ, 2011) failed to confirm an influence from the Barnett Shale on ozone. Positive Matrix Factorization (PMF) of total VOC identified source profiles from automobiles and drilling; however, analysis of upper level and surface wind trajectories indicated that emissions from drilling activity are rarely encountered east of the Barnett Shale region.

3.5 Recent Findings on VOC- and NO_x-Limitations

This section examines NO_X- and VOC-limitation in the DFW area using several methods. Determining if an area is VOC- or NO_X-limited may inform photochemical modeling and provide a basis for developing control strategies for an area; however, there are many other components of ozone formation potential that must be considered in developing effective control strategies for the DFW area.

A NO_X-limited region occurs where radicals from VOC oxidation are abundant, and therefore ozone formation is more sensitive to the amount of NO_X present in the atmosphere. In these regions, controlling NO_X would reduce ozone concentrations. In VOC-limited regions, NO_X is abundant, and therefore ozone formation is more sensitive to the amount of radicals from VOC oxidation present in the atmosphere. In VOC-limited regions, controlling VOC would reduce ozone concentrations. Areas where ozone formation is not strongly limited by either VOC or NO_X are considered transitional, and controlling either VOC or NO_X emissions in these regions would reduce ozone concentrations.

Different methods can be used to determine if an area is VOC- or NO_X-limited, but it is often difficult to compare these different methods because they use different ratios, VOC species, and data sources to determine limitations. This chapter will investigate two methods used to determine VOC- and NO_X-limitations: a VOC:NO_X ratio analysis and a weekend effect analysis using high ozone days and daily peak NO_X.

3.5.1 VOC:NO_X Ratios

The VOC:NO_X ratio expresses the efficiency of ozone formation in air mixtures containing both VOC and NO_X. The VOC:NO_X ratio, q, is computed as:

$$q = \frac{VOC(ppbC)}{NO_X(ppbV)}$$

If q is less than 5, the area is considered VOC-limited, if q is greater than 15, the area is considered NO_X-limited, and if q is greater than or equal to 5, but less than or equal to 15, the area is considered transitional (Chinkin, Main, and Roberts, 2005).

Ratios were calculated for two different types of VOC data: auto-GC data, and 24-hour canister data. Although the TCEQ also collects VOC data in one-hour canisters in the multi-can (MCAN) network, sampling does not occur each day. MCAN canisters are triggered manually depending on the ozone forecast and the monitor site; therefore, there are not enough data available to do a complete study using MCAN data. Three sites in the DFW area have both auto-GC data, which contains 40-minute samples taken every hour, and NO_X data: Dallas Hinton Street (C401), Fort Worth Northwest (C13), and Eagle Mountain Lake (C75). Auto-GC and NO_X data are available at Dallas Hinton Street from 1999 through 2013, at Fort Worth Northwest from 2003 to 2013, and at Eagle Mountain Lake from 2010 through 2013. The 24-hour canisters, part of the Community Air Toxics Monitoring Network (CATMN), collect samples every sixth day. CATMN data from 1999 through 2013 were used in this study. Although there are several VOC data sources available, varying sample times limit comparisons between the data.

Total non-methane organic carbon (TNMOC) was used as a proxy for VOC concentrations in the VOC:NO_X ratios for both CATMN and auto-GC data. Both types of data directly measure TNMOC concentrations. VOC:NO_X ratios were calculated for every available day for each type of data, then daily ratios were averaged together to determine limitations in the area.

Figure 3-11: Annual Median VOC:NO_X Ratio Using Auto-GC Data shows the annual median of daily VOC:NO_X ratios for auto-GC data at Dallas Hinton Street, Eagle Mountain Lake, and Fort Worth Northwest. VOC:NO_X ratios at all three monitors appear to be increasing from VOC-limited and transitional to transitional and NO_X-limited. The increases could be due to the changes observed in NO_X and VOC concentrations.

Ratios at Dallas Hinton Street show that monitor to be more VOC-limited compared to Fort Worth Northwest, which is more transitional, and Eagle Mountain Lake, which is NO_X-limited. The difference in VOC:NO_X ratios at the three monitors may be due to the location of the monitors. Dallas Hinton Street is located near Interstate 35E, a large source of mobile source NO_X emissions. The spatial NO_X analysis above showed that Dallas Hinton Street exhibits higher NO_X concentrations than Fort Worth Northwest, which is located farther west, or Eagle Mountain Lake, which is located to the northwest of the DFW urban core. Automobile emissions are a large source of ozone precursors in Dallas, with mobile emissions contributing about 86% of total NO_X emissions and 66% of total anthropogenic VOC emissions (Qin et al., 2007). In addition, Fort Worth Northwest and Eagle Mountain Lake are closer to oil and gas activity in the Barnett Shale, and exhibit larger VOC concentrations compared to Dallas Hinton Street.

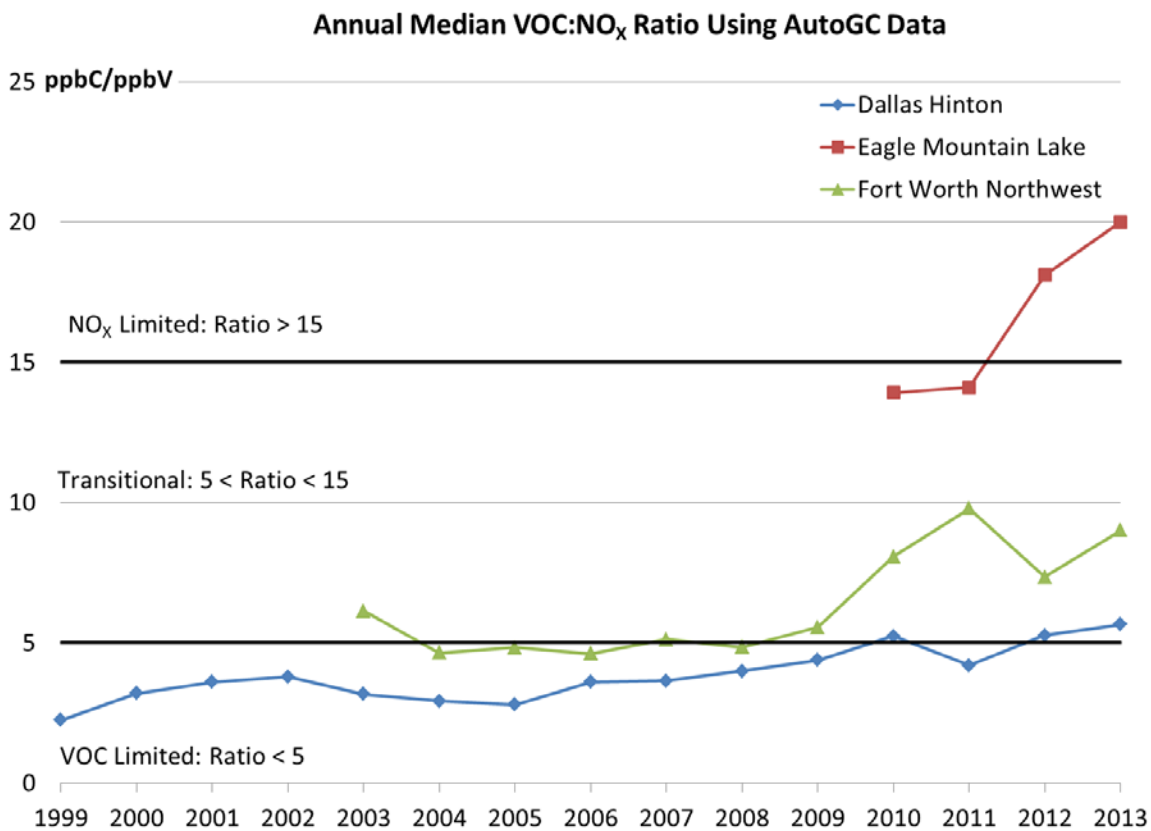


Figure 3-11: Annual Median VOC:NO_X Ratio Using Auto-GC Data

Because VOC and NO_X emissions vary throughout the day, the VOC:NO_X ratio will also vary during different times of the day. Figure 3-12: Hourly Median of Auto-GC VOC:NO_X Ratios shows how VOC:NO_X ratios change from hour to hour. For all monitors, the ratio increases during the early morning, from about 0:00 LST (midnight) to 3:00 LST, decreases until about 7:00 LST, begins to increase again until about 12:00 LST (noon), and then decreases throughout the afternoon. In addition to the diurnal variation of the mixing layer height, the morning and

afternoon decrease in VOC:NO_X ratios may be related to changes in work commuters' driving patterns, which is a source of NO_X emissions (Qin et al., 2007). Dallas Hinton Street may show less change from hour to hour because it is situated in the midst of many roadways, which may be filled with drivers during all hours of the day. Similar to annual mean ratios, hourly median ratios suggest the Fort Worth Northwest monitor mostly exhibits a transitional regime, the Eagle Mountain Lake monitor mostly exhibits a NO_X-limited regime, and the Dallas Hinton Street monitor exhibits a VOC-limited regime.

The Eagle Mountain Lake monitor does show a large decrease in the VOC:NO_X ratio during nighttime hours and this could be due to several reasons. One reason could be that VOC concentrations at Eagle Mountain Lake remain constant throughout the day and night due to gas production activity in the nearby Barnett Shale, but NO_X concentrations increase during nighttime hours (due to no sunlight and decrease in the mixing layer), thus causing a decrease in the VOC:NO_X ratio. Another reason could be that by the nighttime hours, the air mass from the core of the DFW area moves into the Eagle Mountain Lake area, causing the ratios to decrease to levels that are observed in the urban core. More analysis is needed to determine the exact cause for the decrease in VOC:NO_X ratios during nighttime hours at Eagle Mountain Lake.

Figure 3-12 illustrates the fact that VOC:NO_X ratios calculated from 24-hour canister data may not reflect the diurnal variability of the ratio at a monitor. While 24-hour canister data may not reflect the true VOC:NO_X sensitivity of the DFW area, it can be useful for corroborating findings from auto-GC data, and it is more widely available throughout the DFW area.

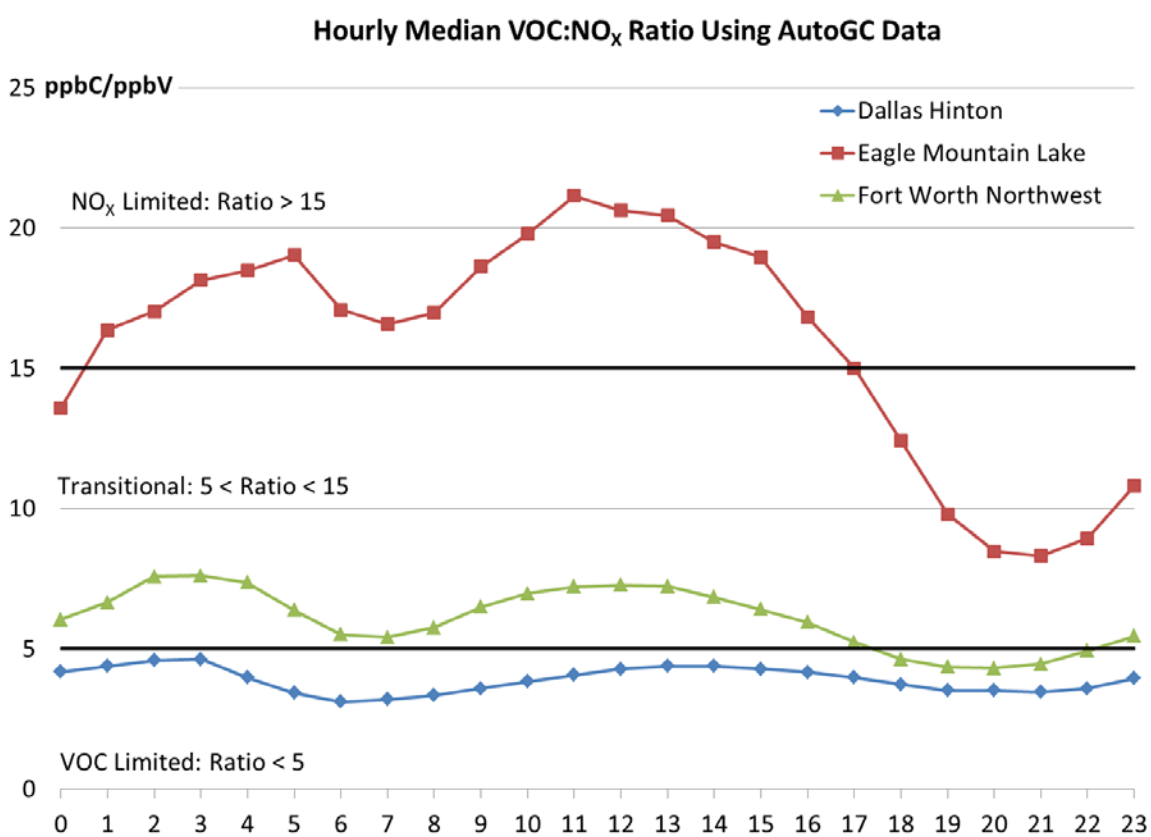


Figure 3-12: Hourly Median of Auto-GC VOC:NO_X Ratios

VOC:NO_X ratios calculated using seven CATMN monitors are displayed in Figure 3-13: Annual Median VOC:NO_X Ratio Using Canister Data. All monitors exhibit ratios in the transitional to NO_X-limited range, with Fort Worth Northwest, Dallas Hinton Street, and Grapevine Fairway in the transitional regime, and with Denton Airport South, Midlothian Tower, Kaufman, and Italy in the VOC-limited regime. The Fort Worth Northwest and Grapevine Fairway CATMN data shows the area has fluctuated between NO_X-limited and transitional since 2003, while the AutoGC data for Fort Worth Northwest has been increasing from VOC-limited to transitional. The Dallas Hinton Street ratio is still lower than Fort Worth Northwest, similar to what was shown from AutoGC data, but instead of being VOC-limited with a slight increase in recent years, CATMN data shows the area always to be transitional.

Although the AutoGC data shows increases in the VOC:NO_X ratio at both Dallas Hinton Street and Fort Worth Northwest, there is no apparent trend in the ratios from the CATMN data. Denton Airport South, Grapevine Fairway, and Kaufman seem to have fluctuations in the VOC:NO_X ratio, but no overall trend. For the Midlothian Tower monitor, the rapid increase in VOC from 2004 to 2007 is likely due to expanding quarrying operations near the monitor. The monitor has since moved to a location slightly farther north in Midlothian, and is now called the Midlothian OFW monitor. However, the new monitor no longer measures TNMHC so it is not included in this analysis. The Italy monitor shows a substantial drop in the past year, but is still NO_X-limited. The Italy monitor appears to be showing a decreasing trend since 2010; however, the area has remained NO_X-limited. Italy and Denton Airport South showed large decreases from 2012 to 2013, and Kaufman showed a large increase from 2012 to 2013; however, since 2013 does not contain a complete year of data, and this pattern may change when all data are considered.

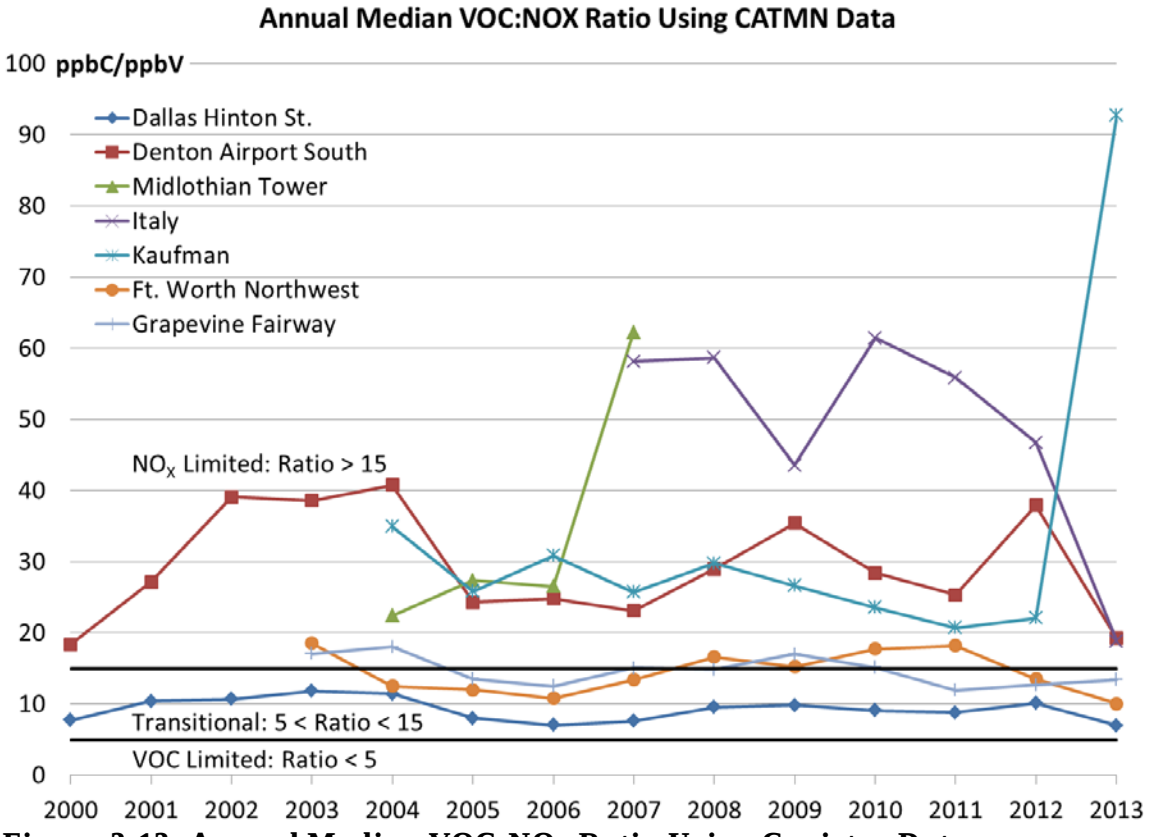


Figure 3-13: Annual Median VOC:NO_X Ratio Using Canister Data

VOC:NO_X ratios from 2012, the last year with complete VOC and NO_X data, for each source and monitor are represented spatially in Figure 3-14: 2012 VOC:NO_X Ratios in the DFW Area. Because no monitor measured VOC-limited conditions in 2012, only NO_X-limited and transitional regimes are represented on the map. Midlothian Tower has no data because it was deactivated in 2007. Only Dallas Hinton and Fort Worth Northwest have both AutoGC and CATMN data. Both AutoGC results and canister results show transitional and NO_X-limited regimes. The map shows that monitors in the urban core, near the center of the DFW area, record air masses that are transitional (blue), whereas monitors on the periphery measure air masses that are NO_X-limited (red). This indicates that monitors located near large NO_X sources, which are the major roadways, interstate highways, and airports in the DFW area, tend to measure transitional to VOC-limited conditions. Monitors located in more rural areas tend to measure more NO_X-limited conditions.

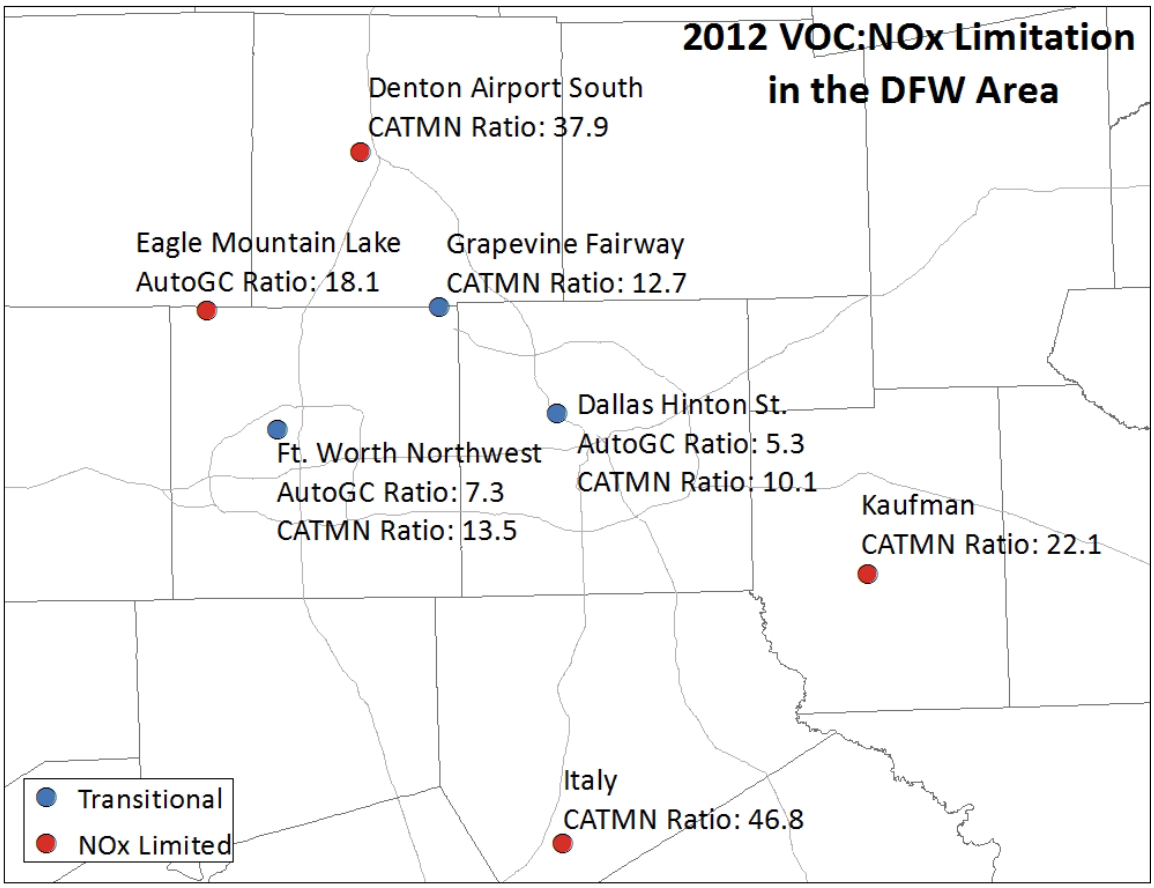


Figure 3-14: 2012 VOC:NO_X Ratios in the DFW Area

3.5.2 Comparison of Ozone and Precursors on Weekdays and Weekends

Studies (Croes et al., 2003; Fujita et al., 2003a; Fujita et al., 2003b; Heuss et al., 2003) have shown that ozone concentrations can exhibit not only annual and diurnal, but weekly patterns of variation. These studies have found that some cities exhibit substantially greater ozone concentrations on weekends, while others do not. Identification of a weekend effect can be valuable for guiding ozone photochemical modeling and control strategy development. Because a weekend effect is hypothesized to result from emissions from specific types of emitters, that is, mobile rather than point sources, its presence, if confirmed, could be used to tailor policies to

target specific sources. Even more importantly, a weekend effect can provide inferences as to whether an area is VOC-limited or NO_X-limited, hence providing clues to the efficacy of various candidate control strategies. A decrease in monitored ozone on weekends (compared to weekday levels) indicates NO_X-limitation, since weekend NO_X concentrations are generally lower compared to their weekday counterparts. Conversely, a weekend increase in ozone concentrations can indicate VOC-limitation. Finally, a weekend effect provides a natural laboratory for evaluating photochemical model response. If the model can reproduce observed weekend effects, then there is greater confidence in its ability to correctly predict the effects of future emission changes.

Causes of weekly patterns in ozone concentrations have been related to changes in emissions during weekends compared to weekdays, and the sensitivity of ozone formation to those changes. Several hypotheses have been proposed to explain increased ozone concentrations on weekends (Croes et al., 2003; Lawson, 2003; Heuss et al., 2003). Generally, these tend to focus on variation in motor vehicle driving patterns and use of recreational and lawn and garden equipment: lower mobile source NO_X emissions are hypothesized to result in less ozone titration by NO, or fewer radical termination reactions, resulting in an increase in radical concentrations; weekend postponement of mobile source NO_X emissions until later in the day enhances ozone formation in aged, NO_X-depleted air; and increased weekend emissions from recreational and lawn and garden equipment enhance weekend ozone formation.

Following extensive investigation by the California Air Resources Board (CARB) and a host of researchers, several of the above hypotheses were discarded (Croes et al., 2003; Fujita et al., 2003a, 2003b; Blanchard et al., 2008; Blanchard and Tanenbaum, 2005; Heuss et al., 2003; Pun et al., 2003; Yarwood et al., 2003). Instead, the most likely explanations were attributed to lower mobile source NO_X emissions on weekends. Specifically, studies suggest the primary cause of increased ozone on weekends is a decrease in NO + O3 titration reactions occurring on weekends due to lower NO_X emissions from heavy duty diesel vehicles. Furthermore, there is some indication that areas that see a pronounced weekend effect, with increasing ozone and decreasing NO_X, exhibit ozone formation in a VOC-limited regime. Areas for which a decrease in NO_X results in a decrease in ozone, however, are more likely to have NO_X-limited ozone formation (Murphy et al., 2007; Gao et al., 2005; Marr and Harley, 2002; Fujita et al., 2003b; Yarwood et al., 2003; Yarwood et al., 2008).

VOC- and NO_X-limitations in the DFW area may impact temporal and spatial patterns of the frequency of ozone exceedance days. A recent study found that the average ozone concentration significantly increased on weekends compared to weekdays in the DFW area (Blanchard and Tanenbaum, 2005). This increase is likely due to the VOC:NO_X ratios found in the DFW area. To determine the effects these limitations might have on the frequency of ozone events in the area, eight-hour ozone high-day counts and peak NO_X by day of the week were examined from 1997 to 2013. Only the ozone season months of March through October were used when looking at the peak NO_X data, because these are the months where NO_X is most likely to impact ozone.

The number of days with peak eight-hour ozone greater than 75 ppb was found for each day of the week at all available monitoring sites in the DFW area from 1997 through 2013. Figure 3-15: Eight-Hour Ozone Days > 75 ppb by Day of the Week (1997 through 2013) shows the total number of days with eight-hour ozone concentrations greater than 75 ppb for each day of the week from 1997 through 2013. Fewer high eight-hour ozone days occur on Sundays (85 days) compared to other days of the week. Sunday had almost 20 fewer high eight-hour ozone days than Mondays, which had the second lowest amount of high eight-hour ozone days (103 days). High eight-hour ozone days occur most often on Fridays, with 137 days. It appears that typically

lower ozone occurs on Sundays, and by the end of the week, the area begins to experience higher ozone.

To determine if these day of the week differences are recent, or still occurring in the DFW area, the number of high eight-hour ozone days by year and day of week was investigated. Table 3-1: Eight-Hour Ozone Days > 75 ppb by Year and Day of the Week shows the number of high eight-hour ozone days by year and day of week since 1997. The table is color coded so that cells colored in red represent days that had more high eight-hour ozone days, and cells colored in green represent days that had fewer high eight-hour ozone days. High eight-hour ozone days occur less frequently on Sundays and Mondays, although there were more high eight-hour ozone days on Mondays in 2011 and 2012. While the number of high eight-hour ozone days has decreased throughout the past 17 years, overall, high days appear to occur most frequently towards the end of the week, and occur less frequently earlier in the week.

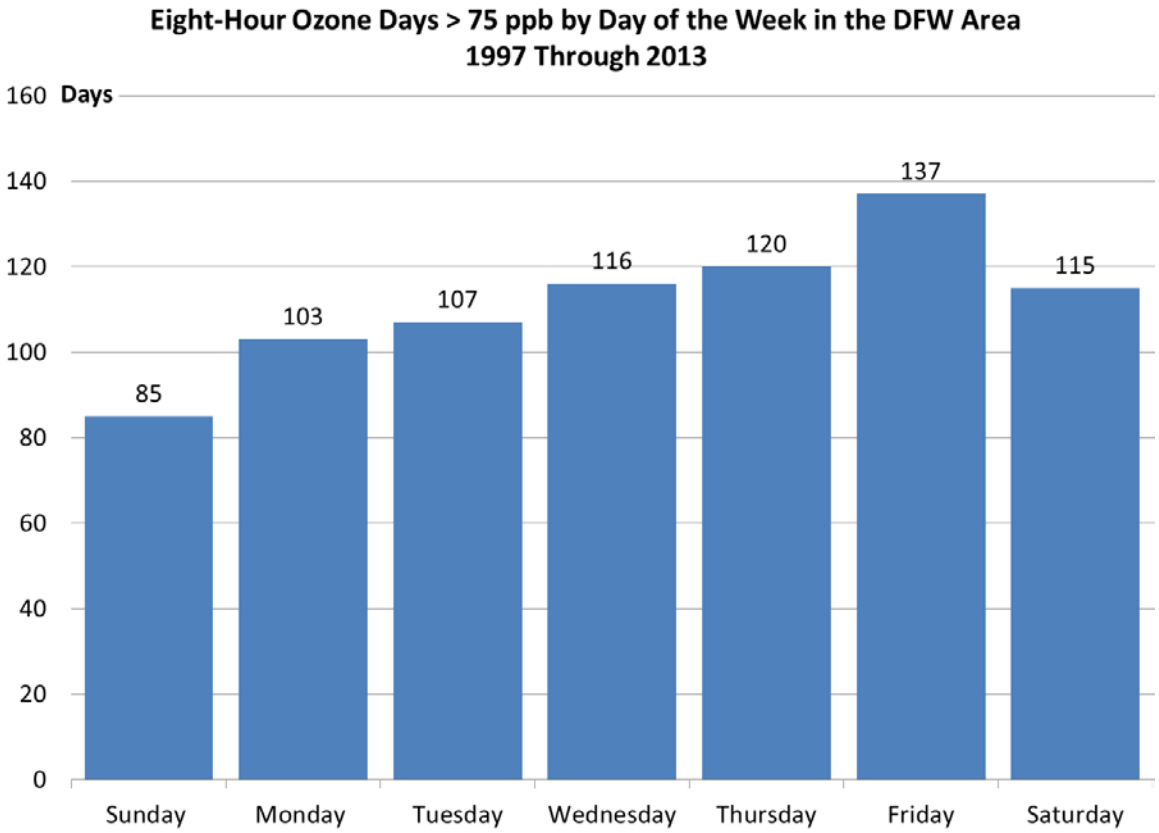


Figure 3-15: Eight-Hour Ozone Days > 75 ppb by Day of the Week (1997 through 2013)

Table 3-1: Eight-Hour Ozone Days > 75 ppb by Year and Day of the Week

	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Sunday	6	9	8	10	7	6	6	4	9	4	3	3	3	0	3	2	2
Monday	8	7	6	7	7	7	8	7	10	8	3	4	1	1	8	8	3
Tuesday	7	10	9	6	9	7	3	7	9	6	4	5	6	1	9	6	1
Wednesday	9	10	10	8	9	8	5	6	11	6	2	4	7	4	8	4	5

	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Thursday	7	8	9	11	4	8	6	8	10	10	3	6	7	5	6	5	7
Friday	8	10	11	10	9	10	9	10	11	9	7	6	5	4	4	7	7
Saturday	9	13	11	11	6	8	8	6	10	7	5	2	5	3	2	4	5

In the absence of a day-of-week or weekend effect, each day would be expected to have an equal likelihood of observing a high eight-hour ozone day. Over the five year period of 5,995 ozone season days with valid data, there were 752 days with eight-hour ozone greater than 75 ppb, for a frequency of about 12.5%. Thus, there is about a 12.5% chance that any particular day will observe eight-hour ozone greater than 75 ppb over the period; however, as shown in Table 3-2: High Eight-Hour Ozone Days and Chi-Square by Day of the Week, 1997 through 2013, Sundays observed high eight-hour ozone at less than the expected rate, only 9.7% of the time. Fridays, on the other hand, observed high eight-hour ozone days more frequently than expected, at 15.2%.

A chi-squared goodness of fit test was performed to test whether exceedance days were independent of day of the week. The test compares the observed distribution to a hypothetical pattern of equal likelihood of exceedance on any particular day. The test does not determine whether a particular group, in this case a particular day, is out of the ordinary, but it assesses whether the overall distribution is what would be expected based on random assignment of observations to days (groups). The chi-square test ($X^2 = 12.88$, p-value = 0.045) determined that the observed distribution was statistically different from what would be expected if high eight-hour ozone days were observed randomly, suggesting there is a day of the week effect. The contribution to the total chi square value of exceedance on each day is also presented in Table 3-2. The chi-square value for high ozone days on Sundays and Fridays was much larger than any of the other days. The chi-square values for non-exceedance days are not presented.

Table 3-2: High Eight-Hour Ozone Days and Chi-Square by Day of the Week, 1997 through 2013

	Sun.	Mon.	Tue.	Wed.	Thur.	Fri.	Sat.	All Days
Low Ozone Days (≤ 75 ppb)	773	756	751	746	744	727	746	5243
High Ozone Days (> 75 ppb)	83	100	105	111	113	130	110	752
Percent (%)	9.7	11.7	12.3	13.0	13.2	15.2	12.9	12.5
High Ozone Day χ^2	5.53	0.51	0.05	0.11	0.28	4.71	0.06	

Another way to investigate the weekend effect on ozone is to look at how high eight-hour ozone days vary spatially. Previous conceptual models (TCEQ, 2007) have shown that, on weekdays, high ozone is most often observed outside the urban core of the DFW area, while, on weekends, more high ozone days were observed at monitors within the urban core. Figure 3-16: Frequency of High Eight-Hour Ozone Days by Day of the Week shows a contour plot of the frequency of high eight-hour ozone days for each day of the week in the DFW area from 1997 through 2013. The plot shows that for all days of the week, the largest number of high eight-hour ozone days occur in the same area as the peak eight-hour ozone design values, northwest of the DFW urban core. This peak does not seem to change location by day of the week, instead the number of high eight-hour ozone days increases throughout the week, and then decreases significantly on Sundays.

High ozone may no longer be observed in the DFW urban core on the weekends because of changes in the VOC:NO_X ratio. As discussed in section 3.5.1, the urban area of DFW has become

more transitional in recent years. When the urban core was more VOC-limited, weekend NO_X decreases could have increased the ozone concentrations. Now that the area is more transitional, weekend decreases in NO_X could in turn result in less ozone formed.

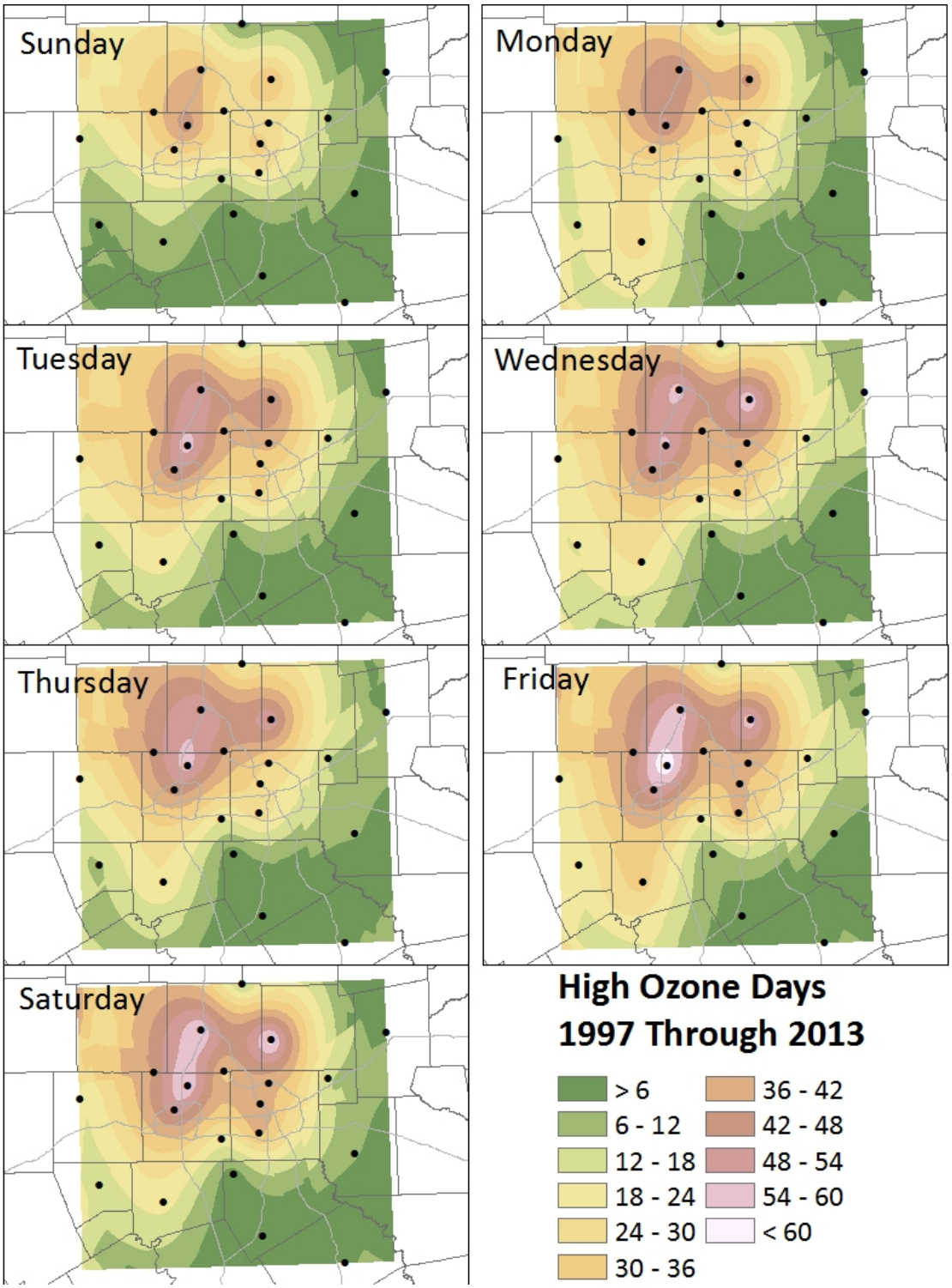
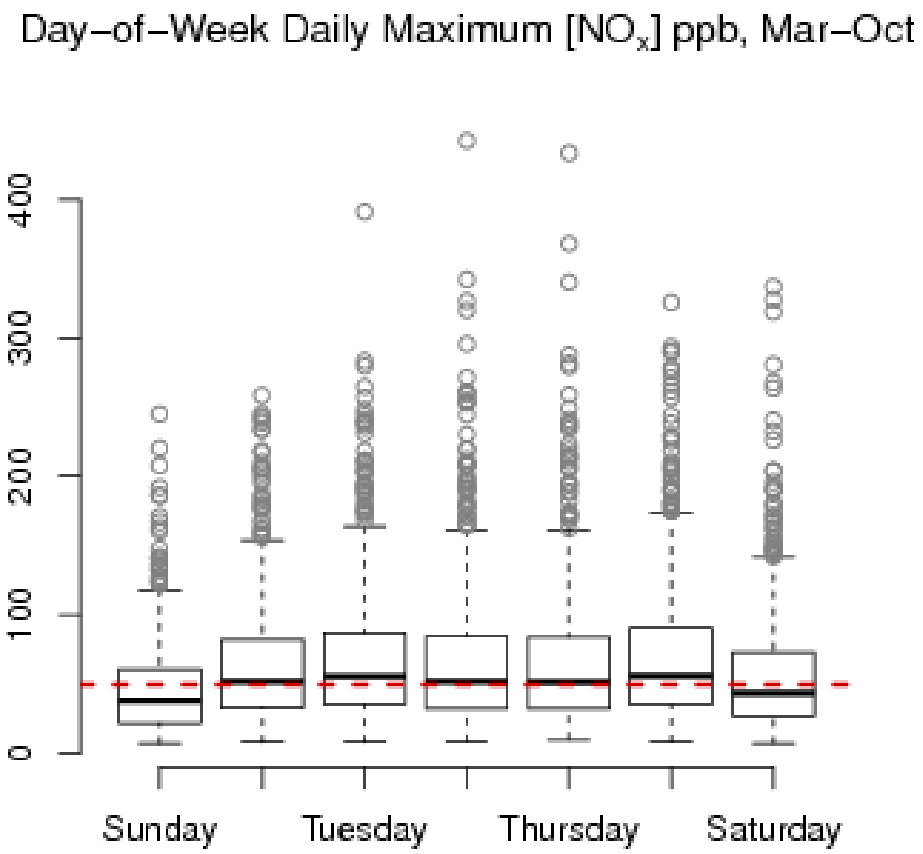


Figure 3-16: Frequency of High Eight-Hour Ozone Days by Day of the Week

Investigating changes in NO_X concentrations by day of the week will help in identifying a possible weekend effect on ozone concentrations. A day of week effect in NO_X concentrations would suggest that a large amount of the NO_X emissions originate from mobile sources. NO_X emissions from mobile sources would be expected to decrease on weekends when there are fewer people commuting to and from work.

To examine NO_X concentrations by day of the week, a daily maximum NO_X concentration was calculated and plotted as a boxplot by day-of-week. Boxplots help to infer the distribution, the quantiles, and the data spread. All data from all monitors in the DFW area for the ozone season from 1997 through 2013 were used in this analysis.

The boxplots shown in Figure 3-17: Daily Maximum Ozone Season NO_X in the DFW Area by Day of the Week, 1997 through 2013 display a possible day of the week effect in the DFW area. Sunday and Saturday contain the two lowest median daily peak NO_X concentrations, which are both below the median NO_X from all available days. Tuesday and Friday have the highest median daily peak NO_X concentrations, which are also both higher than the median NO_X. This pattern is not only visible in the median daily peak NO_X, but also in the higher and lower percentiles of data. As mentioned previously, high ozone days occurred most frequently on Fridays, the day with the largest daily peak NO_X concentrations, and high ozone days occurred least frequently on Sundays, the day with the lowest daily peak NO_X concentrations.



Note: Red ref line denotes median [NOx] for all days

Figure 3-17: Daily Maximum Ozone Season NO_X in the DFW Area by Day of the Week, 1997 through 2013

Investigating daily peak NO_X by monitor site yields a similar day of the week effect as seen in Figure 3-18: Daily Peak NO_X by Site and Day on the Week for the Ozone Season in the DFW Area, 1997 through 2013. Even the more rural monitors, which were not expected to experience a weekend effect due to less mobile emissions, experienced less NO_X on the weekends compared to the weekdays. The Parker County monitor, for example, shows evidence of a weekend effect, with lower daily peak NO_X concentrations measured on Saturday and Sunday. Parker County is located 34 miles west of the DFW metro area, and the surrounding area is farmland and very lightly populated; however, this monitor is located in a heavy diesel trailer truck dispatch, which could potentially be the source for the day of the week effect. Another reason rural monitors may also see a weekend effect is that they may be close enough to the DFW metropolitan area to measure transported NO_X emissions. Also, the communities in which these monitors are placed may be growing in population, therefore creating a day-of-the-week effect as the increase in population in turn increases the commuting traffic.

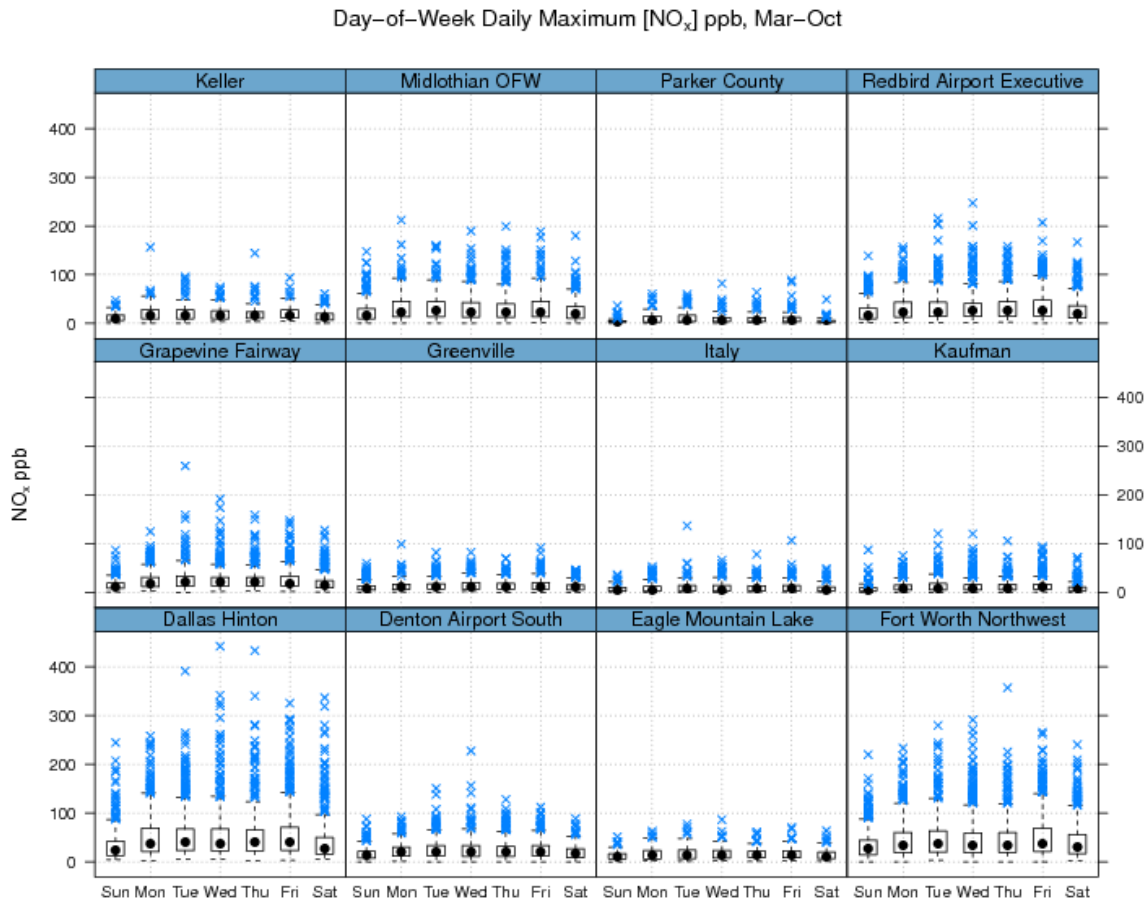


Figure 3-18: Daily Peak NO_X by Site and Day on the Week for the Ozone Season in the DFW Area, 1997 through 2013

The weekend effect analysis showed significant changes in high eight-hour ozone days from weekdays to weekends, especially on Sundays compared to Fridays. Spatial analysis showed that both weekday and weekend high ozone days occur most frequently to the northwest outside of the urban core of the DFW area, but the number of those days decreases on the weekends and increases on the weekdays, occurring most frequently on Fridays. Daily peak NO_X concentrations also exhibited a weekend effect with the highest concentrations occurring on Fridays and the lowest concentrations occurring on Sundays. These trends corroborate what was seen with the VOC:NO_X ratio. The DFW urban core appears to be transitional and the rural areas appear to be more NO_X-limited, meaning that changes in NO_X concentrations are more likely to produce changes in ozone concentrations.

3.6 Meteorological Characterization and Trends

Ozone formation and transport are greatly influenced by atmospheric conditions such as wind patterns in the lower and upper atmosphere that determine the vertical and horizontal mixing and dispersion of ozone and precursors, altitude of the mixing layer, humidity, and temperature. This section examines the relationship between ozone and temperature, and ozone and wind fields, including surface wind speed and direction.

Temperatures above 90 degrees Fahrenheit are favorable for increased ozone formation and are common on high ozone days. Figure 3-19: Climatological Temperature Profile at the Dallas Love

Field Weather Station (SRCC, 2013) shows the climatological temperature profile at the Dallas Love Field weather station, which is located in the center of the DFW urban core. This site was chosen based on its duration of operation while still being located in the urban portion of the area. The figure plots the 2013 daily maxima, minima, and mean, as well as the mean, average maxima, and average minima from all available data from 1939 through 2013. Average high temperatures typically exceed 90 degrees from mid-June through early September, which includes August when the area typically experiences its highest number of exceedance days (see Chapter 2). 2013 temperatures seem to fall within the norm.

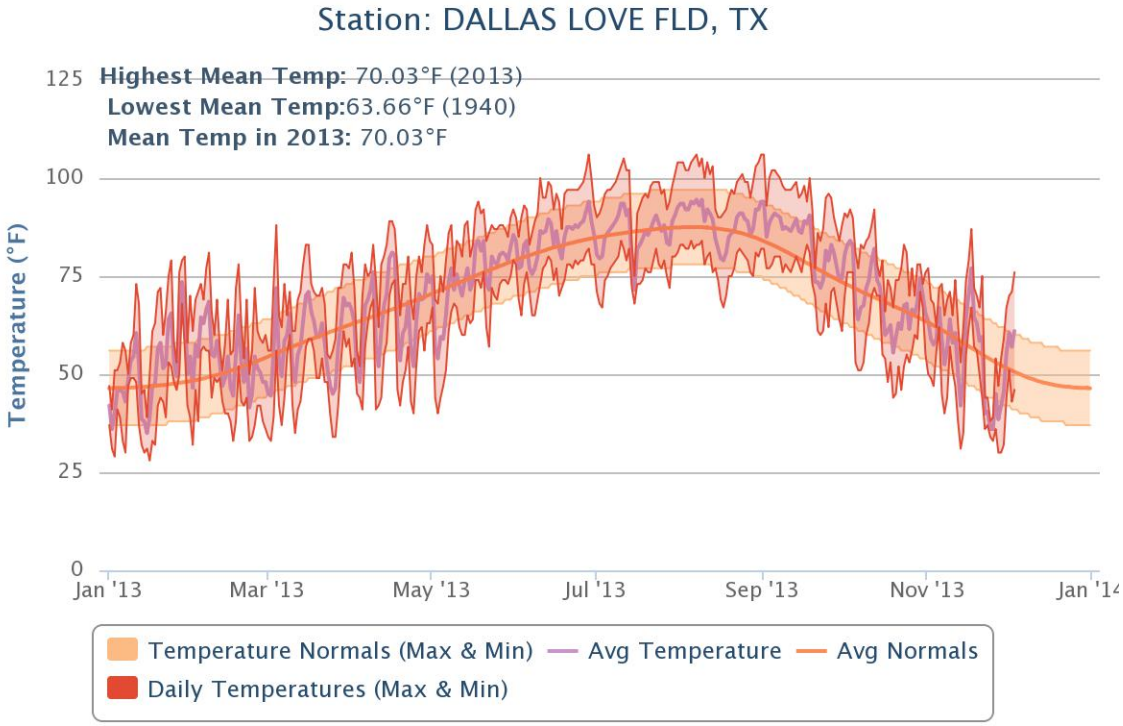


Figure 3-19: Climatological Temperature Profile at the Dallas Love Field Weather Station (SRCC, 2013)

While temperature is a familiar measure, and increases in temperature indicate the potential for ozone formation, high temperatures do not automatically mean that high ozone will form. Wind speed and wind direction are meteorological variables that are more directly associated with ozone concentrations. Wind speed and direction play an important role in ozone formation by affecting mixing and dilution of ozone and ozone precursors. Higher wind speeds tend to dilute precursors and move ozone out of an area. Slower winds can result in stagnation, allowing ozone concentrations to increase in an area as precursors are converted into ozone. Figure 3-20: Wind Climatology in the DFW Area from 1997 through 2013 shows the frequency distribution of daytime winds for May through October from 1997 through 2013. Directions on the x-axis range from 0, which is due north, to 90 (east), 180 (south), 270 (west), and 360, which is back to north again. The colors of the bar segments indicate the frequency with which winds of various speeds were observed from a particular direction.

Figure 3-20 illustrates that wind speed and direction vary as the season transitions from spring into summer. During May and June, prevailing winds in the DFW area tend to come out of the south and south-southeast with few observations below 5 miles per hour (mph). During July,

there is a notable decrease in winds above 15 mph with an increase in winds both in the 5 to 10 mph range and in the calm range (0-5 mph). In August, there is a decrease in wind out of the south with an increase in wind below 10 mph out of the east and southeast. A further decrease in the frequency of wind out of the south is seen in September. The majority of the wind observations in this month are either calm or between 5 and 10 mph, with directions ranging from northerly to southerly. Winds out of the north through east generally indicate continental air masses moving into the area, while winds out of the south and southeast have a larger maritime (i.e., Gulf of Mexico) component to the air mass. In October, wind speed begins to increase again and there are fewer observations of wind out of the northeast.

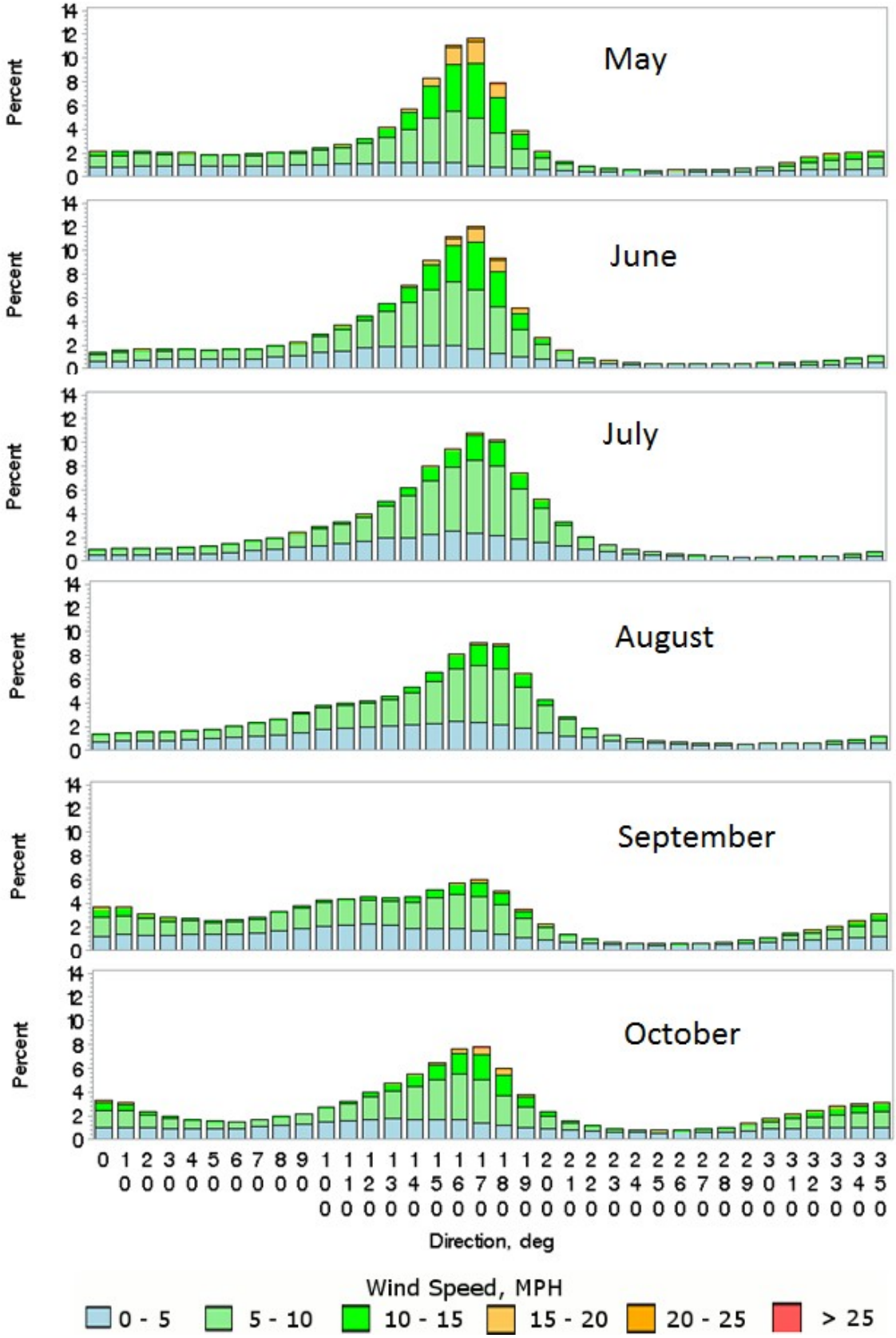


Figure 3-20: Wind Climatology in the DFW Area from 1997 through 2013

Another way to evaluate how winds affect ozone is to look at the wind direction and wind speed on high ozone days versus low ozone days. For this analysis, days with an eight-hour ozone concentration greater than 75 ppb were considered high ozone days and days with an eight-hour ozone concentration lower than or equal to 75 ppb were considered low ozone days. The wind speed and wind direction were grouped according to high ozone days and low ozone days for each monitor. These winds were then plotted onto a map of the DFW area. Only data for daytime hours (0700 through 1900 LST), from March to October from 1997 through 2013, were used for the surface level winds analysis. Only monitors in operation in 2013 were included.

Figure 3-21: Wind Speeds by Wind Direction on High Ozone Days and Figure 3-22: Wind Speeds by Wind Direction on Low Ozone Days show that, for monitors that record the highest eight-hour ozone design values, surface winds were predominately from the southeast and south-southeast on high ozone days, but mainly from the south on low ozone days. High ozone days were calculated for each monitor and not for the entire DFW area. All other days were considered low ozone days. Wind speeds were notably higher on low ozone days, as expected. On high ozone days, very few winds reach the 10 to 15 mph category while on low ozone days winds can be in the 20 to 25 mph category. Slower wind speeds tend to be more conducive to ozone formation; however, the extent of this relationship is unknown.

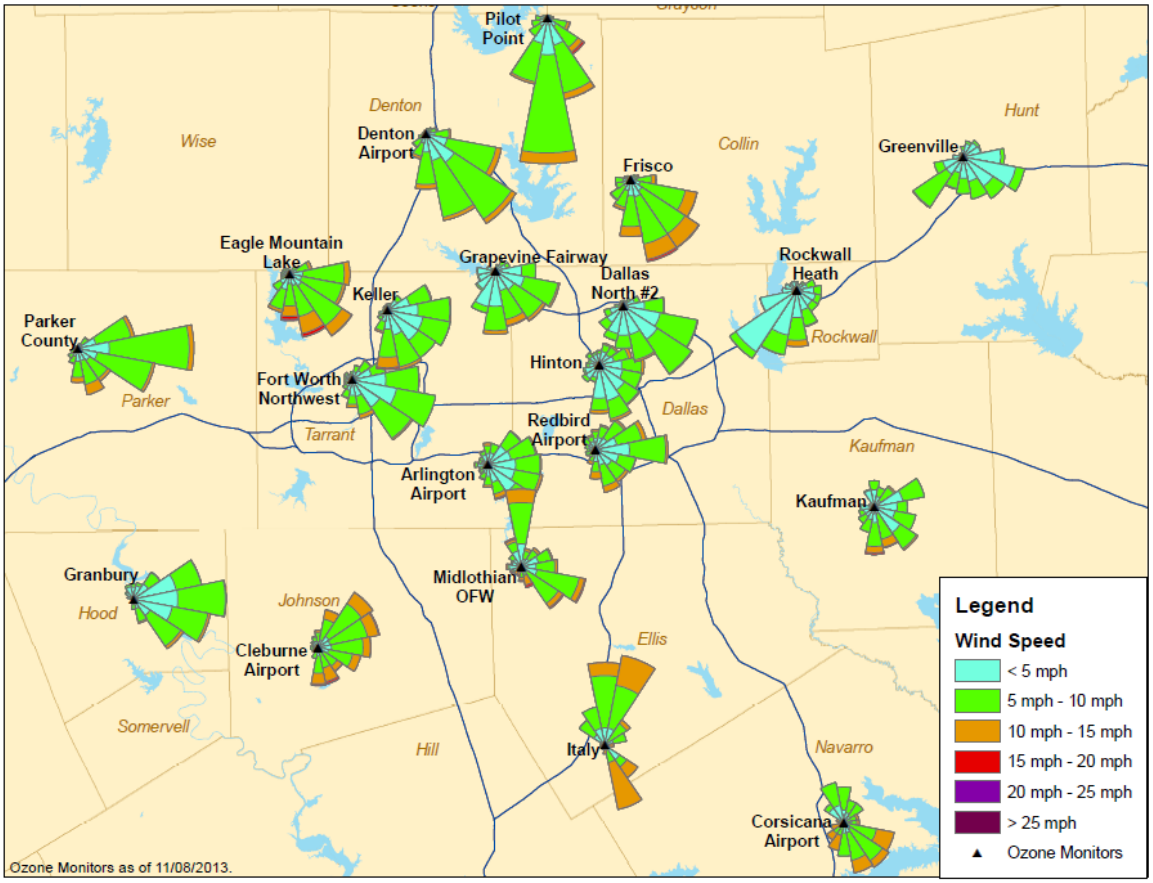


Figure 3-21: Wind Speeds by Wind Direction on High Ozone Days

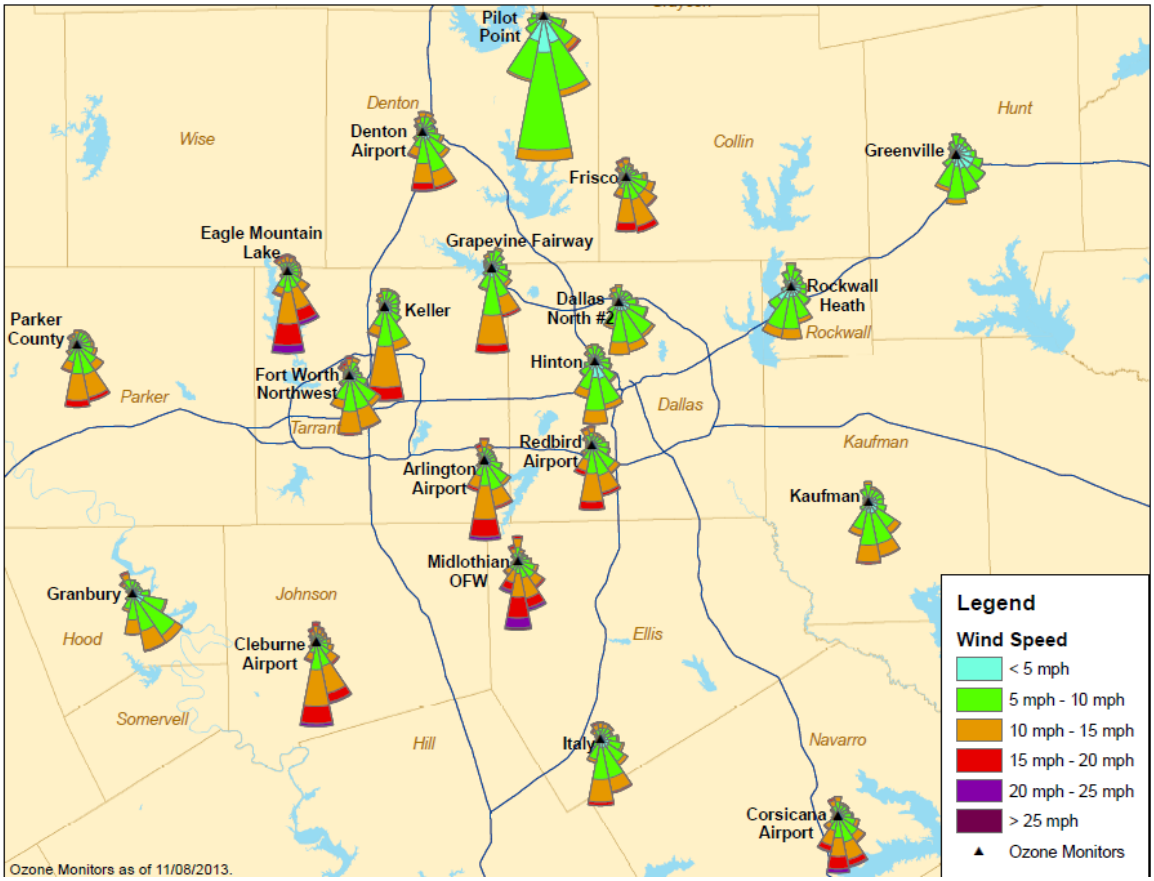


Figure 3-22: Wind Speeds by Wind Direction on Low Ozone Days

Figure 3-21 and Figure 3-22 also suggest that surface winds on high ozone days tend to arrive from a south to southeast direction. On low ozone days, surface winds have a more southerly component. The wind analysis shows that both upper level and surface level winds are generally uniform over the area. High ozone days tend to have slower winds that come from a southeasterly direction while low ozone days tend to have faster winds that come from a more southern direction.

3.7 Summary of Recent Findings in Local Ozone Dynamics

An investigation of geographic patterns in ozone shows that, while ozone concentrations in the DFW area have been decreasing, the same geographic areas tend to experience the highest ozone concentrations year after year. The highest levels of ozone typically occur in the northwestern part of the region. This is largely due to the southeasterly direction of prevailing winds on high ozone days, which slowly advect ozone and precursors over populated areas, where they mix and accumulate before reaching the northwest.

Kriging showed that both peak eight-hour ozone concentrations and peak NO_X concentrations have been declining across the region since 2002, with peak NO_X concentrations showing larger decreases in the more urban areas. Despite the reductions in magnitude, regions that observe the highest and lowest concentrations remain roughly the same. The location of ozone peaks were shown to occur in the same location on high and low ozone days; however, the peak occurs much later on high ozone days, indicating slower winds speeds on high ozone days, which lead to larger accumulation and formation of ozone.

HRVOC trends indicate that ethylene and propylene have decreased from 2000 to 2012, with most of this decrease occurring from 2000 to 2009. Three monitors whose ambient air is dominated by vehicle emissions had the highest concentrations of these two compounds and all three showed the same pattern of decrease seen in the other monitors. This suggests that vehicle emissions are the most important source of these two HRVOCs, and that reductions in vehicle emissions are the likely reason for the decrease. 1-butene data from canisters was also examined, but its concentrations did not show similar decreases.

Analysis of VOC composition at AutoGC monitors determined that geometric mean total VOC concentration was higher at the four Barnett Shale AutoGC monitors than at the other six AutoGC monitors, with the difference due to much higher concentrations of ethane, and to a lesser extent propane, at the four monitors in the Barnett Shale. When this geometric mean concentration was multiplied by a conversion factor based on MIR, the two monitors located in urban core of the DFW area had total concentrations equal to or greater than three of the four Barnett Shale monitors. This increase in total concentration was due to the greater concentrations of aromatics and especially HRVOC at the two urban core monitors. Although high VOC concentrations were observed in the Barnett Shale region, those concentrations have not been shown to affect ozone concentrations in the DFW area.

Investigation of the ratio between VOC and NO_X revealed a variable pattern across the DFW area. Although the more urban monitors traditionally measured VOC-limited conditions, recent trends show these monitors to measure more transitional conditions. The more rural and northwestern monitors located on the periphery of the DFW area have continued to measure NO_X-limited conditions. These findings suggest that different photochemical processes likely dominate in different regions of the modeling domain.

An analysis of ozone exceedances and daily peak NO_X concentrations by day of the week was performed to identify patterns in emission sources and to corroborate VOC:NO_X limitations observed from VOC:NO_X ratios. Analysis showed lower ozone and NO_X concentrations observed on Sundays and higher ozone and NO_X concentrations observed on Fridays. This effect indicates that day of the week changes in NO_X, primarily due to changes in automobile emissions, in turn cause decreases in ozone concentrations. This indicates a NO_X-limited regime and indicates that decreases in NO_X would be an effective measure to control ozone in the DFW area.

The local geography, topography, and meteorology of the DFW area all contribute to ozone dynamics. The physical environment is described by a relatively flat topography, lack of nearby marine influences, and lack of mountains that might constrain air masses. Winds are predominately from the south and southeast, with the majority from the southeast on high ozone days at the monitors that observe the highest eight-hour ozone design values. Wind speeds tend to be slower in the summer months when ozone is observed to increase.

4. RECENT FINDINGS IN TRANSPORTED OZONE AND BACKGROUND OZONE IN THE DALLAS-FORT WORTH AREA

This chapter discusses background ozone and ozone precursor concentrations that are transported into the DFW area from sources outside the region and the state. A better understanding of background and transport phenomena will guide selection of appropriate approaches to state and local control strategy development. Background ozone, defined as ozone that is not produced locally, has been found to vary considerably by geographic region, by season of the year, across years, and by direction of transport (Nielsen-Gammon et al., 2005a). Further, background ozone is a substantial contributor to overall ozone levels in the DFW area. When high concentrations of background ozone are transported into the DFW area, local ozone

production exacerbates an already high baseline concentration, resulting in greater likelihood of violating the ozone National Ambient Air Quality Standards (NAAQS).

In this chapter, background ozone concentrations are examined at selected monitoring sites under specific meteorological restrictions, to determine whether a trend across time is apparent. This approach builds on work by Nielsen-Gammon (2005a) and others (Camalier, 2007; Draxler, 2000) and determines that there is no discernible trend in background ozone. An apparent trend in background ozone, either increasing or decreasing, would have ramifications for local ozone control strategies adopted in the DFW area. Rising background ozone concentrations could overwhelm improvements made through local emission reductions, while falling background ozone concentrations could moderate the amount of local control needed to attain the NAAQS. Further, temporal changes in background ozone complicate modeling by introducing additional complexity in identifying appropriate model input values.

4.1 Transport Wind Trajectories

A thorough assessment of background ozone must include an evaluation of upper altitude winds to supplement the understanding of surface level patterns. Winds at high altitude can transport ozone from sources far upwind of the region. Mixing and subsidence can bring this ozone from the upper atmosphere into the surface layer. Assessing the contribution of these high-level transport winds enhances our understanding of the meteorological factors determining ozone generation, transport, and fate in an area.

While surface level winds can be analyzed using data from ground level monitors, transport trajectories require techniques that are more advanced. Transport winds are modeled in this analysis with Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model 48-hour back-trajectories at 800 meters altitude for May through October from 2000 through 2012. HYSPLIT performs forward and backward trajectory modeling, and is available on the web site of the National Oceanic and Atmospheric Administration (NOAA), at http://ready.arl.noaa.gov/HYSPLIT.php. HYSPLIT reports coordinates of the hourly end points of trajectory segments. Distances between each trajectory hour endpoint were summed to calculate a total length and the deviation of the actual path taken from the shortest possible path (sinuosity) was calculated.

Ozone season months were used in this analysis because they are not often influenced by synoptic cold fronts. Start times were set at the time of peak ozone for each day. The Denton Airport South monitor was chosen as the arrival location for the estimated trajectories because it currently has the highest eight-hour ozone design value in the DFW area.

Figure 4-1: High Ozone Versus Low Ozone Back Trajectory Density shows density plots of the frequencies of end points of the hourly segments of the backward trajectories, separated into high ozone days (days when any monitor in the DFW area recorded eight-hour ozone concentration above 75 ppb) and low ozone days (days when no monitors recorded an eight-hour ozone concentration above 75 ppb). On high ozone days, trajectory lengths tend to have a more easterly and southeasterly direction. Trajectory lengths on those days also tend to be shorter, signifying that wind speeds are slower. Trajectories for low ozone days tend to be longer, signifying higher wind speeds. Wind directions on low ozone days tend to have a more northeasterly or southerly direction, with a slight westerly component. These trajectories appear to corroborate results from the analysis of surface winds: on high ozone days, wind speeds in the DFW area are slower and from the southeast.

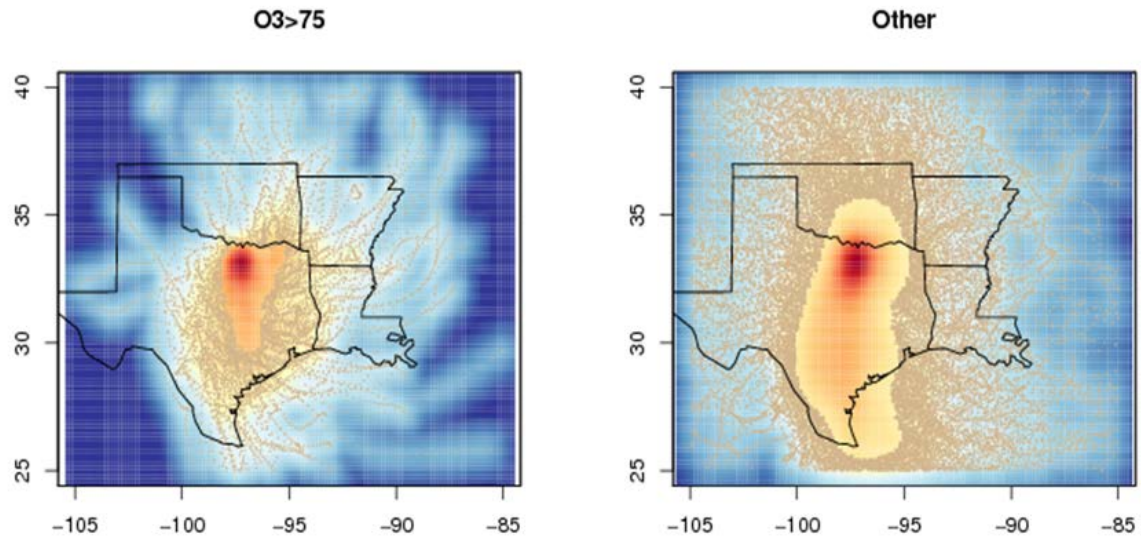


Figure 4-1: High Ozone Versus Low Ozone Back Trajectory Density

Measures of sinuosity, or "curviness," of the trajectory of an air parcel can be used to determine its original source (Nielsen-Gammon et al, 2005a). When winds are straighter, or less sinuous, source identification is enhanced because there is less variability, and thus less uncertainty, in computations of originating directions. This section investigates the sinuosity of winds, specifically transport winds, traveling into the DFW area to determine whether these winds varied from year to year. Variability in transport winds across years could complicate determination of regions contributing background ozone to the DFW area, and, thus obscure selection of appropriate model input values for background ozone.

For this analysis, transport winds are defined as high elevation winds capable of moving air masses over long distances. These winds can carry pollutants from one area to another and affect local ozone concentrations (Cooper et al., 2006). A measure of sinuosity used by Xie and Berkowitz (2005) can be computed for a trajectory using wind speeds and directions. Sinuosity of transport winds (S) is calculated as the tip-to-tip (start point and end point) length (D_{t2t}) of a 48-hour trajectory – i.e., the distance from one tip to the other, "as the crow flies" – divided by the sum of intra-distances between adjacent hourly endpoints for the same trajectory (sum of D_i, for i hours):

$$S = \frac{D_{t2t}}{\sum D_i}$$

When D_{t2t} equals D_i, the trajectory is straight and the sinuosity equals one, the highest possible value. As a trajectory becomes less straight, that is, as ΣD_i increases with respect to D_{t2t}, the sinuosity increases and S becomes smaller. This is depicted in Figure 4-2: Comparison of Two Trajectories, One More and One Less Sinuous, which compares a trajectory with sinuosity equal to 1.0 (the straight trajectory) with one with a sinuosity equal to 0.8 (the curved trajectory). For the straight trajectory, the numerator and denominator of the above equation are the same. For the curved trajectory, the numerator is the total distance of the straight trajectory, while the denominator is the total distance of the curved trajectory, summing the lengths of all intermediate segments. Higher sinuosity values, therefore, correspond to straighter winds.

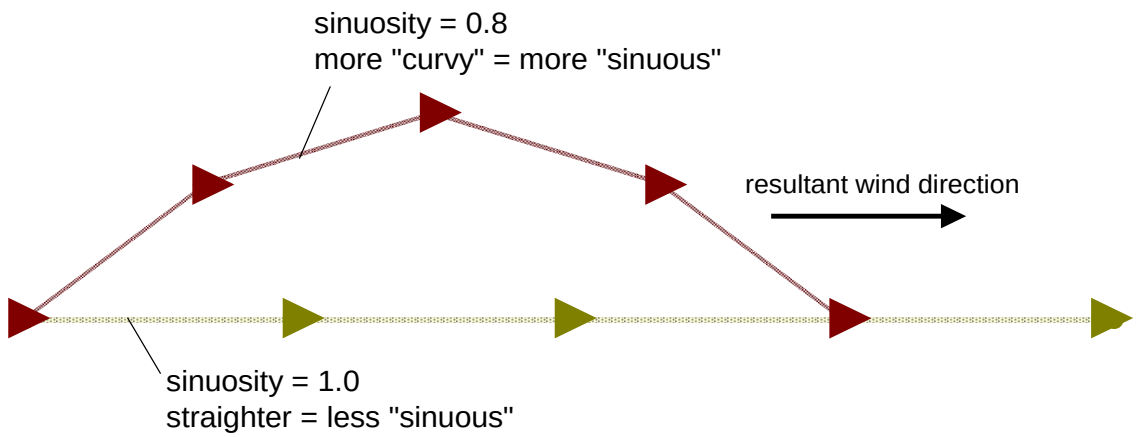


Figure 4-2: Comparison of Two Trajectories, One More and One Less Sinuous

Comparing the sinuosity of trajectories on high ozone days versus low ozone days results in a statistical difference at the medians as shown in Figure 4-3: Sinuosity Comparison on High versus Low Eight-Hour Ozone Days. The notches in the boxplots represent the 95% confidence interval. Sinuosity median for days with ozone above 75 ppb is approximately 0.69 and sinuosity median for other days is 0.80. This suggests that different meteorological patterns prevail for high altitude transport winds on high ozone days compared to low ozone days in the DFW area.

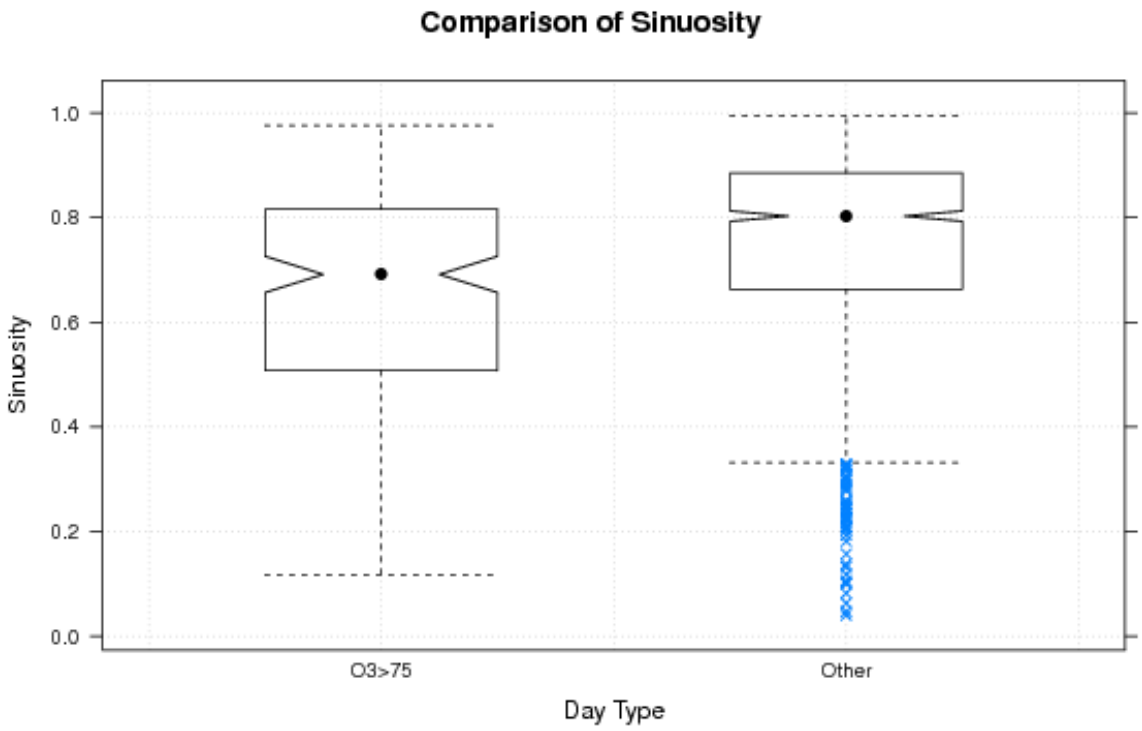


Figure 4-3: Sinuosity Comparison on High versus Low Eight-Hour Ozone Days

Figure 4-4: Sinuosity by Year on High Ozone Days versus Low Ozone Days compares sinuosity medians over time for high ozone days versus low ozone days. The figure shows that from 2007 through 2012, sinuosity tends to be lower on high ozone days, similar to the results from above.

The sinuosity trend from 2007 through 2012 is flat for low ozone days, but is more variable on high ozone days.

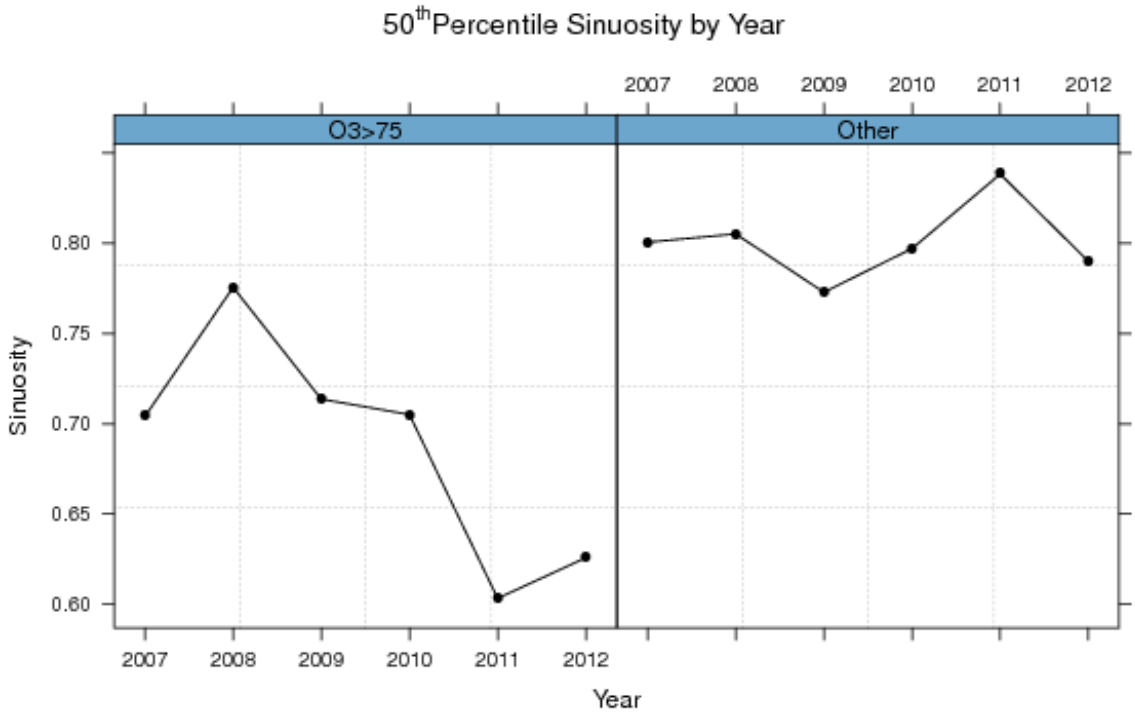


Figure 4-4: Sinuosity by Year on High Ozone Days versus Low Ozone Days

Further work is necessary to link these results to observed ozone concentrations. Regarding local ozone production, it is not clear from the available research that straighter winds correspond to higher ozone concentrations due to the absence of dilution from sources of ozone precursors, or whether the reverse is true where winds that are more sinuous cause greater mixing of ozone precursors and thus dilution. This analysis focuses on large-scale sinuosities, which would not necessarily apply to ozone production on a local level. This analysis does corroborate results from Chapter 3: Recent Findings in Local Ozone Dynamics in the Dallas-Fort Worth Area, which show that on high ozone days, winds appear to be slower and from the southeast, while on high ozone days, winds are faster and from the south.

4.2 Background Ozone

Though definitions vary, background ozone usually refers to regional or transported ozone that has not been influenced, or has been influenced only minimally, by emissions from the area of interest within a day or two of the measurement period. In practice, it is difficult to determine whether the area of interest has influenced regional background, especially when air is stagnant or when recirculation occurs, as is often the case during ozone season in Texas. Techniques that account for locally produced ozone and precursors can reduce or minimize their impacts on estimations of background ozone, Tthe EPA estimates one-hour background ozone to be approximately 40 ppb.

The following bullets are useful for understanding background ozone and transport:

- Natural background is defined as the ozone concentration that would be present in a location if there were no influences from any anthropogenic emissions. Many researchers

use this definition of background ozone, though it is very difficult to sample an air mass anywhere on the globe that truly has no anthropogenic influence.

- Regional background ozone is the amount of ozone entering a locality from outside. Background ozone, as measured in Texas, usually means regional background ozone that has (probably) not been influenced by emissions from the city of interest within a day or two of the measurement period. In practice, it is difficult to determine whether the city of interest has influenced the regional background, especially when air is stagnant or recirculating, as is often the case during ozone season in Texas. Usually, this is the definition used when describing background ozone that can actually be measured.
- EPA defines policy-relevant background as the level of a specific pollutant that would exist in the absence of anthropogenic North American emissions of that pollutant and its precursors. EPA's policy-relevant background cannot be measured with certainty in Texas; it can only be estimated by modeling.
- The rule of thumb is that natural background is lower than EPA policy-relevant background, which is lower than regional background.
- Background ozone must be defined carefully. Lacking standardization, studies often use incomparable definitions. Among the definitional differences are such factors as length of the averaging period (e.g., one-hour or eight-hour); months examined (e.g., all year, May through September, April through October); monitoring sites chosen as background sites; and use of surface-based, aircraft-based, or balloon-based measurements. All of these are important factors affecting calculations for background ozone. Sometimes subtle differences in definition can lead to different conclusions (Estes, 2010).

Previous conceptual models (TCEQ, 2010) estimated the one-hour background ozone coming into Texas at the Texas-Louisiana border to be at concentrations of 60 ppb or higher. The studies also showed that the level of background ozone varied greatly during the ozone season and that, in DFW, regional background ozone appeared to comprise a greater percentage of the observed maximum concentrations than in the HGB area. The previous conceptual model also showed median background eight-hour ozone from monitors in the DFW area (Kaufman, Eagle Mountain Lake, and Pilot Point) ranging from about 35 ppb up to 70 ppb. Background was found to be higher on high eight-hour ozone days versus low eight-hour ozone days.

Differentiating background ozone concentrations on high ozone days from concentrations on low ozone days yields important insight into the characteristics of ozone arriving from upwind sources. For this analysis, wind restricted background ozone concentrations for high ozone days (eight-hour ozone > 75 ppb) during the ozone season (March through October) were examined. HYSPLIT back trajectories were used to estimate the background ozone in the DFW area from 2009 through 2012. These trajectories help identify transport paths of elevated ozone, and were categorized by their direction of origin. In Section 4.1, two trajectory paths were identified as elevated ozone transport paths in the DFW area: an east path and a south path. This analysis will focus on estimating the background ozone from these two paths. All trajectories for this analysis end at the Denton Airport South monitor, since this monitor has the highest eight-hour ozone design value in 2013. The trajectory height was set at 800 meters and was run at hourly intervals for 48 hours. The goal of this analysis is to record the ozone concentrations at monitors upwind of Denton Airport South and the DFW area when ozone is greater than 75 ppb and winds are consistent in direction.

Figure 4-5: Trajectories and Concentrations for Easterly Wind Flow at Background Monitor Greenville and Figure 4-6: Trajectories and Concentrations for Southerly Wind Flow at Background Monitor Italy display the trajectory wind flow (left graphic) as it arrives at the

Denton Airport South monitor. The graphic on the right panel shows a boxplot of the associated ozone concentrations measured at the upwind monitor as well as at Denton Airport South.

Trajectories for easterly wind flows are shown in Figure 4-5. When wind flows from the east, the monitors upwind of Denton Airport South are Rockwall Heath and Greenville. On days when winds are from the east and eight-hour ozone is high at Denton Airport South, median one-hour ozone at the upwind monitors Greenville and Rockwall Heath is 58 ppb and 61 ppb, respectively. The increase in one-hour ozone from the Greenville monitor to the Denton Airport South monitor is, on average, about 7 ppb.

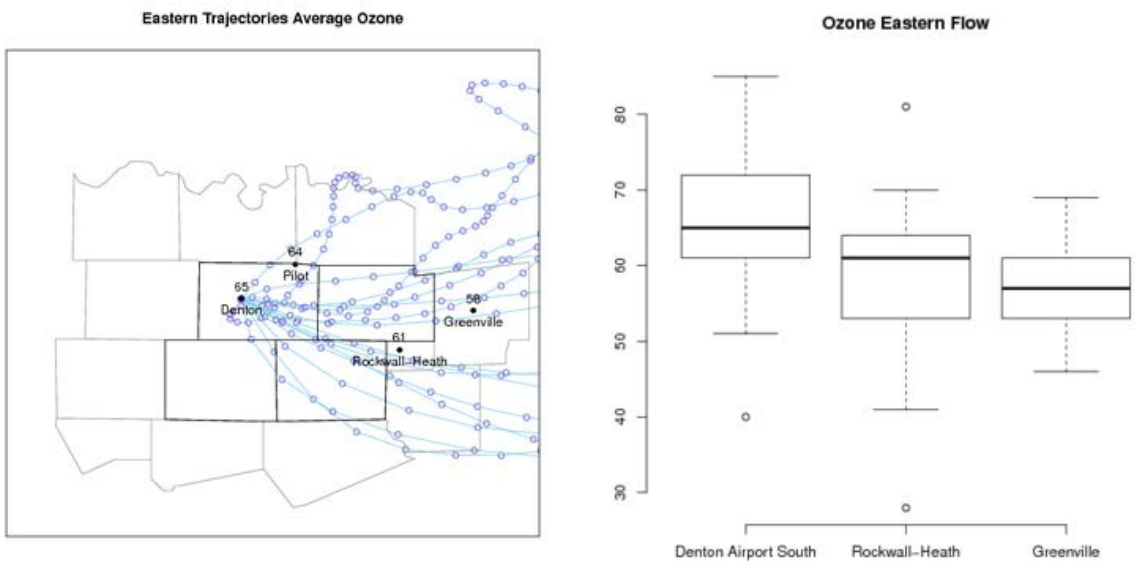


Figure 4-5: Trajectories and Concentrations for Easterly Wind Flow at Background Monitor Greenville

Trajectories for southerly wind flows are shown in Figure 4-6. When winds are out of the south, the monitor upwind of Denton Airport South is Italy. On days when winds are from the south and eight-hour ozone is high at Denton Airport South, Italy records a median one-hour ozone concentration of 59 ppb. The one-hour ozone, on average, increases about 8 ppb from the Italy monitor to the Denton Airport South monitor.

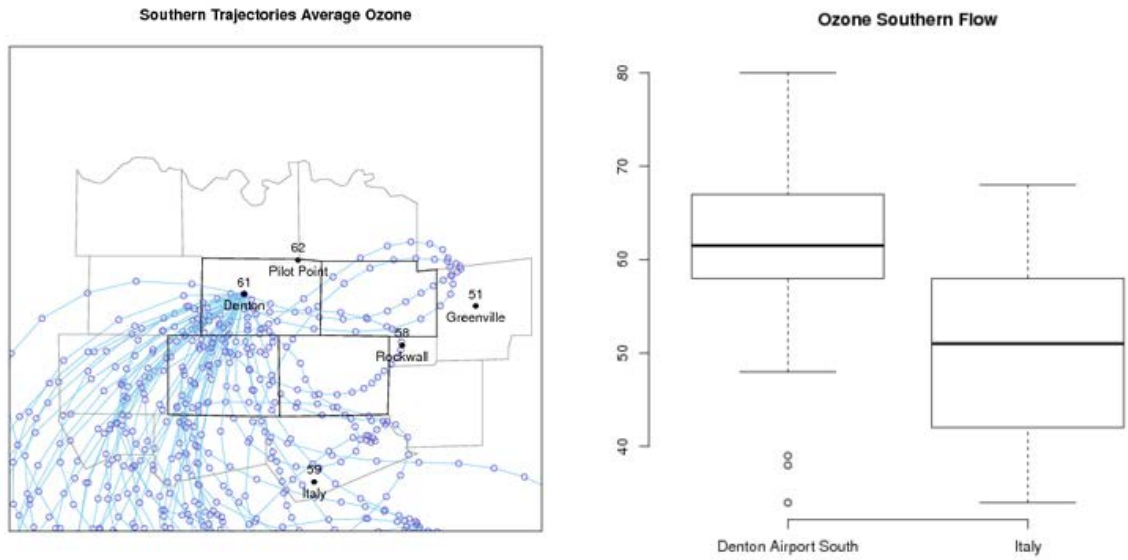


Figure 4-6: Trajectories and Concentrations for Southerly Wind Flow at Background Monitor Italy

The differences in one-hour ozone from the Denton Airport South monitor and the upwind monitors vary widely. The largest differences in eight-hour ozone can be as high as 31 ppb for easterly wind flow and as high as 21 ppb for southerly wind flow. These high values are very dependent on wind flow trajectory path and illustrate the important role that meteorology plays in the DFW area.

Using this technique, background ozone in the DFW area on high eight-hour ozone days is estimated at 58 ppb or 59 ppb on average. These concentrations are at rural monitors, which have no local sources of considerable size to impact the ozone concentrations. As a rule of thumb, EPA has considered 40 ppb as a reasonable background ozone estimate, which implies that background ozone on high eight-hour ozone days is about 1.4 times greater. Moreover, this incoming ozone cannot be easily controlled by stakeholders in the DFW area. There were not enough days in this analysis to be able to create a trend for background ozone.

4.3 Summary of Recent Findings in Background Ozone and Ozone Transport

The need to quantify background ozone, or ozone transported from outside the DFW area, in addition to quantifying local ozone production is essential given that a large metropolitan area, such as DFW, regularly generates enough local ozone to exceed the standard when starting from a high background. Procedures developed by the TCEQ and Nielsen-Gammon et al. (2005a) have demonstrated that background eight-hour ozone levels traveling into Texas are regularly as high as 60 ppb, and often higher.

Investigation of HYSPLIT back trajectories identified likely transport of ozone into north Texas on days following elevated ozone episodes in the eastern U.S. Back trajectories also showed that on high ozone days slower winds from the east and southeast are most frequent, while on low ozone days winds were much faster and mostly from the south.

Studies of regional background eight-hour ozone in the DFW area show that regional background eight-hour ozone is high on days with high ozone. On high eight-hour ozone days, background ozone was found to range from 58 ppb to 61 ppb to the east, and 59 ppb from the south. This analysis shows that regional background eight-hour ozone often exceeds 50 ppb and

is especially pronounced on high ozone days in the DFW area. On high ozone days, background is about 1.4 times higher than the EPA estimated 40 ppb. These background and transport analyses show that efforts focused solely on controlling local emissions may be insufficient to bring the DFW area into ozone attainment given that, on many days, background estimates are well over half the eight-hour ozone NAAQS of 75 ppb.

5. REFERENCES

Banta, R.M., C.J. Senff, J. Nielsen-Gammon, L.S. Darby, T.B. Ryerson, R.J. Alvarez, S.P. Sandberg, E.J. Williams, and M. Trainer. 2005. A Bad Air Day in Houston. Bulletin of the American Meteorological Society, 86(5): 657-669.

Bell, M. L., A. McDermott, S. L. Zeger, J. M. Samet, and F. Domenici. 2004: Ozone and short-term mortality in 95 US urban communities. J. Amer. Med. Assoc., 292, 2372-2378.

Blanchard, C., S. Tanenbaum, and D. Lawson. 2008. Differences between weekday and weekend air pollutant levels in Atlanta; Baltimore; Chicago; Dallas-Fort Worth; Denver; Houston; New York; Phoenix; Washington, DC; and surrounding areas. J. Air & Waste Manage. Assoc., 58: 1598-1615.

Blanchard, C. and S. Tanenbaum. 2005. Weekday/weekend differences in ambient concentrations of primary and secondary air pollutants in Atlanta, Baltimore, Chicago, Dallas-Fort Worth, Denver, Houston, New York, Phoenix, Washington, and surrounding areas, Final Report, NREL Project ES04-1, May 16, 2005.

Camalier, L., W. Cox, and P. Dolwick. 2007. The effects of meteorology on ozone in urban areas and their use in assessing ozone trends. Atmos. Environ., 41, 7127–7137.

Carter, W.P.L., 2000. Documentation of the SAPRC-99 chemical mechanism for VOC reactivity assessment, Report to the California Air Resources Board, Contracts 92-329 and 95-308. (http://www.cert.ucr.edu/~carter/absts.htm#saprc99)

Carter, W.P.L., 2010. Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales; Final Report to the California Air Resources Board, Contract No. 03-318, 06-408, and 07-730, Revised January 27, 2010. (http://www.cert.ucr.edu/~carter/SAPRC/)

Chinkin, L., H. Main, and P. Roberts. 2005. PAMS Data Analysis Workshops, Illustrating the use of PAMS Data to Support Ozone Control Programs. (Accessed November 21, 2005, Last updated on Friday, June 12, 2009).
http://www.epa.gov/oar/oaqps/pams/analysis/index.html#preface

Cooper, O. R., et al. 2006. Large upper tropospheric ozone enhancements above midlatitude North America during summer: In situ evidence from the IONS and MOZAIC ozone measurement network, J. Geophys. Research, 111: D24S05, doi:10.1029/2006JD007306.

Croes, B. et al. (2003), The O3 “weekend effect” and NO_X control strategies: Scientific and public health findings and their regulatory implications. EM, pp. 27-35, July 2003.

Currie, J., E. Hanushek, E.M. Kahn, M. Neidell, S. Rivkin, 2007. Does Pollution Increase School Absences? National Bureau of Economic Research, Working Paper 13252.
http://www.nber.org/papers/w13252.

Draxler, R. 2000. Meteorological Factors of Ozone Predictability at Houston, Texas. J. Air. and Waste Manage. Assoc., 50, 259-271.

Estes, M. 2010. Background ozone for Texas cities: Findings from recent studies of background ozone. White paper on background ozone, April 2, 2010, Mark Estes.

Fujita, E., et al. 2003a. Evolution of the magnitude and spatial extent of the weekend ozone effect in California's South Coast Air Basin, 1981-2000. J. Air & Waste Manage. Assoc., 53, 802-815.

Fujita, E., et al. 2003b. Diurnal and weekly variations in the source contributions of ozone precursors in California's South Coast Air Basin. J. Air & Waste Manage. Assoc., 53, 844-863.

Gao, O. H., B. A. Holmen, D. A. Niemeier. 2005. Nonparametric factorial analysis of daily weigh-in-motion traffic: implications for the ozone 'weekend effect' in Southern California, Atmos. Environ., 39, 1669-1682.

Heck, W.W., W.W. Cure, J.O. Rawlings, L.J. Zaragosa, A.S. Heagle, H.E. Heggestad, R.J. Kohut, L.W. Kress, and P.J. Temple. 1984. Assessing impacts of ozone on agricultural crops: crop yield functions and alternative exposure statistics. J. Air Pollut. Control Ass., 34, 810-817.

Heuss et al. 2003. Weekday/weekend ozone differences: What can we learn from them? J. Air & Waste Manage. Assoc., 53, 772-788.

Krige, Danie G. (1951). "A statistical approach to some basic mine valuation problems on the Witwatersrand". J. of the Chem., Metal. and Mining Soc. of South Africa 52 (6): 119–139.

Lawson, D. R. 2003. The weekend ozone effect—The weekly ambient emissions control experiment, EM, pp. 17-25, July 2003.

Main, H., et al. 1996. PAMS Data Analysis Workshop: Illustrating the Use of PAMS Data to Support Ozone Control Programs.

Marr, L., and R. Harley. 2002. Modeling the effect of weekday-weekend differences in motor vehicle emissions on photochemical air pollution in central California, Environ. Sci. Technol., 36:4099.

Martin, R.V, C. E. Sioris, K. Chance, T. B. Ryerson, T. H. Bertram, P. J. Woodridge, R. C. Cohen, J. A. Neuman, A. Swanson, F. M. Flocke. 2006. Evaluation of space-based constraints on global nitrogen oxide emissions with regional aircraft measurements over and downwind of eastern North America, J. Geophys. Res., 111, D15308, doi:10.1029/2005JD006680.

Murphy et al. 2007. The weekend effect within and downwind of Sacramento—Part 1: Observations of ozone, nitrogen oxides, and VOC reactivity. Atmos. Chem. Phys., 7, 5327-5339.

National Academy of Sciences. 1991. Rethinking the Ozone Problem in Urban and Regional Air Pollution. National Academies Press, 524 pp.

Nobis, T.F., G.R. North, R.C. Harris, N.W. Tindale, D.W. Sullivan, H.J. Newton, August 1998. Texas A&M University Master of Science Thesis: An Ozone Climatology of the Dallas-Fort Worth Area and Its Relationship to Meteorology. http://www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA356380&Location=U2&doc=GetTRDoc.pdf

Pun, B. K., et al. 2003. Day-of-week behavior of atmospheric ozone in three U.S. cities, J. Air & Waste Manage. Assoc., 53, 789-801.

Qin, Y, T. Walk, R. Gary, X. Yao, S. Elles. 2007. C2–C10 nonmethane hydrocarbons measured in Dallas, Atmos. Environ. 41:6018.

Rapid Science Synthesis Team. 2006. Final Rapid Science Synthesis Report: Findings from the Second Texas Air Quality Study (TexAQS II), A Report to the Texas Commission on Environmental Quality, 2006 Texas Air Quality Study.

Savanich, K. 2006. Ozone Exceedance Days as a Function of the Number of Monitors, TCEQ, February, 2006.

Southern Regional Climate Center, 2013. Website on Southern Climate as updated December 31, 2013. http://www.srcc.lsu.edu/station_search.html

Sullivan, D., 2013. Ozone Precursors and Toxic Chemical Compound Monitoring Continuation. Final Report to TCEQ. Grant Activities No. 582-8-86245-FY11-10. Prepared by Dave Sullivan, University of Texas at Austin, Center for Energy and Environmental Resources. May 31, 2013

Sullivan, D., 2009. Effects of Meteorology on Pollutant Trends. Final Report to TCEQ. Grant Activities No. 582-5-86245-FY08-01. Prepared by Dave Sullivan, University of Texas at Austin Center for Energy and Environmental Resources, Prepared for Kasey Savanich, for the Texas Commission on Environmental Quality, March 16, 2009. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/da/5820586245FY0801-20090316-ut-met_effects_on_pollutant_trends.pdf

Texas Commission on Environmental Quality. 2011. Dallas-Fort Worth Attainment Demonstration State Implementation Plan Revision for the 1997 Eight-Hour Ozone Standard. Appendix D: Conceptual Modeling for the DFW Attainment Demonstration SIP Revision for the 1997 Eight-Hour Ozone Standard.

Texas Commission on Environmental Quality. 2010. Houston-Galveston-Brazoria Attainment Demonstration State Implementation Plan for the 1997 Eight-Hour Ozone Standard. Chapter 5: Weight of Evidence, pp. 5-74–5-81.

Texas Commission on Environmental Quality. 2007. Dallas-Fort Worth Eight-Hour Ozone Nonattainment Area Attainment Demonstrations. Appendix G: DFW Nonattainment Area Ozone Conceptual Model.

Texas Commission on Environmental Quality. 2006. Subchapter A: Definitions, 30 TAC § 115.10, adopted December 7, 2006.

Texas Railroad Commission. 2010. Website on the Barnett Shale as updated March 1, 2010: http://www.rrc.state.tx.us/barnettshale/index.php

U.S. Census Bureau, Population Division. 2013. Table 5. Estimates of Population Change for Metropolitan Statistical Areas and Rankings: July 1, 2011 to July 1, 2012 (CBSA-EST2012-05). Release Date: March 2013

U.S. Environmental Protection Agency. Tuesday, January 19, 2010. Proposed Rules, National Ambient Air Quality Standards for Ozone. Vol. 75, No. 11, Proposed Rules, Title 40, Code of Federal Regulations, Parts 50, and 58. http://www.epa.gov/air/ozonepollution/fr/20100119.pdf

U.S. Environmental Protection Agency. April 2007. Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5, and Regional Haze, EPA -454/B-07-002. http://www.epa.gov/ttn/scram/guidance/guide/final-03-pm-rh-guidance.pdf

U.S. Environmental Protection Agency. February 28, 2006. Air Quality Criteria for Ozone and Related Photochemical Oxidants, Volumes I, II, and III, EPA 600/R-05/004aF-cF. http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=149923

U.S. Environmental Protection Agency. Friday, April 30, 2004. Ozone National Ambient Air Quality Standards for Ozone, Vol. 69, No. 84, Rules and Regulations, Title 40, Code of Federal Regulations, Parts 50, 51 and 81. http://edocket.access.gpo.gov/2004/pdf/04-9152.pdf

Westenbarger, D.A., and G. B. Frisvold. 1994. Agricultural exposure to ozone and acid precipitation. Atmos. Environ., 28, 2895-2908.

Xie, Y., and C. M. Berkowitz. 2005. Source attribution and emission adjustment study: Task 1. Back trajectory climatology and identification of key source regions. 10 January 2005. http://www.tceq.state.tx.us/assets/public/implementation/air/am/contracts/reports/ei/Source_Attribution_and_Emission_Adjustment_Study_Task1.pdf

Yarwood, G., J. Grant, B. Koo, A. M. Dunker. 2008. Modeling weekday to weekend changes in emissions and ozone in the Los Angeles basin for 1997 and 2010, Atmos. Environ., 42, 3765-3779.

Yarwood, G., et al. 2003. Modeling weekday/weekend ozone differences in the Los Angeles region for 1997, J. Air & Waste Manage. Assoc., 53, 864-875.