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Effects Of Non-Conventional Gas And Oil Production Activities On Local And Regional Fine Particles And Ground-Level Ozone

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EFFECTS OF NON-CONVENTIONAL GAS AND OIL PRODUCTION ACTIVITIES ON LOCAL AND REGIONAL FINE PARTICLES AND GROUND-LEVEL OZONE

By

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This thesis, submitted by Swetha Mallula in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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This thesis is being submitted by the appointed advisory committee as having met all of the requirements of the School of Graduate Studies at the University of North Dakota and is hereby approved.

Dr. Grant McGimpsey
Dean of the School of Graduate Studies

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Department Civil Engineering

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To my grandmother, **LAKSHMI,** for her unconditional love and support.

I would like to extend my gratitude to my advisor and committee chair Dr. Feng "Frank" Xiao for his continuous support and assistance during this thesis as well as my time at the UND. I am also grateful to my committee members Dr. Sukhvarsh Jerath and Dr. Yeo Howe Lim for their advice and help. My appreciation is also extended towards the faculty and the staff of the Civil Engineering Department for their support throughout my study at UND.

ABSTRACT

Unconventional oil and gas production in North Dakota and Texas has been rising significantly since 2007 with the advances in hydraulic fracturing technology. The effects of unconventional oil and gas production on the environmental quality and public health, however, are not well understood. The goal of this study was to investigate the effects of unconventional energy production on two types of air pollutants (fine particles and ground-level ozone). We analyzed the air quality data from publicly accessible sources, focusing on two major oil producing states (North Dakota, Texas) and two control states (Minnesota and Connecticut). The specific objectives of this study were to understand 1) the effects of unconventional oil/gas production on the regional air quality; 2) the annual and seasonal variations of criteria air pollutants in these states; and 3) correlations between different air pollutants in these states.

This thesis focuses on two selected criteria air pollutants (particulate matter (PM2.5, PM10 and ground-level ozone). PM2.5 and PM10 refer to the fine particles that pass through a size-selective inlet with a 50% efficiency cut-off at 2.5 and 10 μm aerodynamic diameters, respectively. The key finding of this research is that unconventional oil/gas production activities appear not be a major contributor to the local PM and ground-level ozone. We have also observed strong seasonal variation of PM and ground-level ozone. In all the studied states, PM2.5 is high in the summer and winter but low in spring and fall season. Ground-level ozone reaches the highest in summer and the lowest in winter season due to the variation of sunlight radiation. In three relatively urbanized states (Connecticut, Texas, Minnesota), the annual mean PM2.5 and ground-level ozone decline

gradually since 1999, especially in the highly-urbanized state (Connecticut), which suggests a decline in emissions from major sources of PM and ground-level ozone. In the rural state (North Dakota), on the other hand, PM2.5 and ground-level ozone remain a relatively low and stable level since 1999. Furthermore, a strong correlation between PM2.5 and PM10 was observed; no significant correlation was found between PM2.5 and ground-level ozone. Finally, in the source identification study, it is found that the annual decline in PM2.5 is strongly associated with the reduction industrial emissions but not with utility and mobile sources. These observations will significantly advance our understanding of annual and seasonal variations of PM2.5 and ground-level ozone in these states, especially the effects of non-conventional gas and oil production, which has implications on public health protection and environmental quality.

CHAPTER I

INTRODUCTION

1.1. Air pollutants

Air pollutants including particulate matter (PM) and ground-level ozone are airborne particles and gasses that occur in concentrations, which endanger the health and well-being of organisms or disrupt the orderly functioning of the environment. There are two categories of air pollutants, as illustrated in Figure 1: primary air pollutants and secondary air pollutants (Masters and Ela, 2008). Primary air pollutants are emitted directly from identifiable source, including PM, sulfur dioxide, nitrogen oxides, volatile organic compounds (VOCs), carbon monoxide, and lead. Approximately 38% of primary air pollutants in the United States are PM2.5 (size smaller than 2.5 μm) and PM10 (size smaller than 10 μm) (Masters and Ela, 2008).

PM in air generally refers to all airborne solid and low vapor pressure liquid particles (Vallero, 2014). Suspended particulate matter in ambient air is a complex, multi-phase system consisting of a spectrum of aerodynamic particle sizes ranging from below 0.01 μm to 100 μm and larger. Historically, PM measurement has concentrated on total suspended particulates, with no preference to size selection. In 1987, the primary standard for total suspended particulates was replaced with a PM10 standard, which included only particles with an aerodynamic diameter of 10 μm or less. In 1997, the primary standard for PM10 was then replaced with a PM2.5 standard.

This standard was promulgated because the EPA now has interest on "respirable" particles (< 2.5 μm), those particles small enough to be drawn into and deposited in the respiratory system. Particles in this size range can have direct health effects (Vallero, 2014).

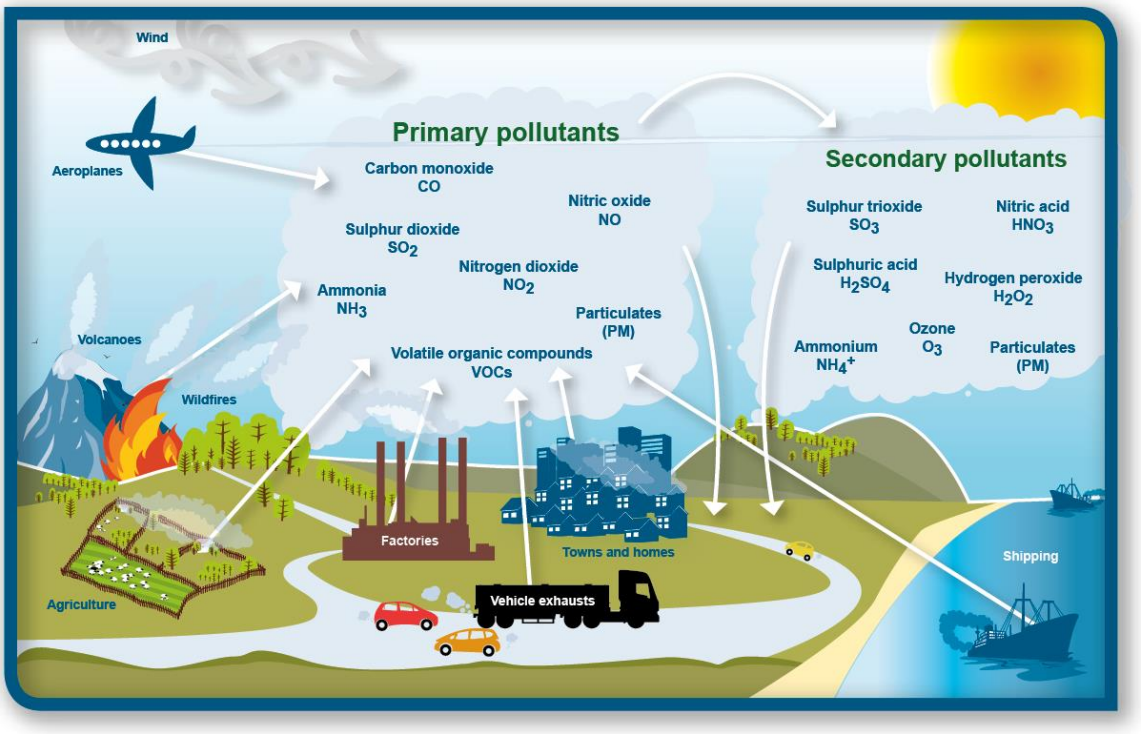

Figure 1. Primary and secondary air pollutants

(source of the figure: https://iasmania.com/wp-content/uploads/2015/12/Sources-of-air-pollution_310314.png).

Other terms have also been used to categorize particulates, depending on their size and phase (liquid or solid) (Masters and Ela, 2008). The most general term is aerosol, which applies to any micron-size particles, liquid or solids. Solid particles are called dusts if they are caused by grinding or crushing operations. Fumes are solid particles that are formed when vapors condense. Liquid particles are also called mist, fog, or smog. It should be noted that PM can be emitted

directly as solid particles from incomplete combustion or formed in the atmosphere. If PM is formed in the air, it is also commonly called secondary organic aerosols. PM2.5 and PM10 are small enough to reach the lung and large enough to be deposited there by sedimentation. The major health effects include the aggravation of existing respiratory and cardiovascular disease and lung disease or lung cancer. Because of the health effects of PM2.5, the EPA lowering the daily PM2.5 standard in 2006 from 65 $\mu g/m^3$ to 35 $\mu g/m^3$ (Gurjar et al., 2010).

Another group of air pollutants is the so-called secondary pollutants. Secondary air pollutants are not directly emitted from identifiable sources. Rather they are produced in the atmosphere when certain chemical reactions take place among primary pollutants. When fuel is burned, nitrogen oxide and hydrocarbons gases are emitted. These pollutants react with each other under sunlight, which generates atmospheric sulfuric acid (H_2SO_4), photochemical smog or PM, and ground-level ozone (O_3), as shown by the following reactions (Masters and Ela, 2008). The common health effects of ground-level ozone include aggravation of asthma, increased susceptibility to respiratory illnesses such as pneumonia and bronchitis, and permanent lung damage.

$$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3;\ SO_3 + H_2O \rightarrow H_2SO_4$$

$$VOCs + NO_x + Sunlight \rightarrow \text{Photochemical smog (PM and ground-level ozone)}$$

Regarding the sources of air pollutants, in general there are four main types of air pollution sources as illustrated in Figure 2: 1) mobile sources. The primary mobile source of air pollution is the automobile according to the Environmental Protection Agency (EPA) (Masters and Ela, 2008). Mobile sources are motor vehicles such as cars, buses, planes trucks and trains; 2) stationary sources such as coal-fired power plants that are also known as point sources of pollution; 3) area

sources such as agricultural areas, cities, wood burning and fireplaces; and 4) natural sources from erosion and emission of fires, windblown dust, wildfires, volcanoes, and decaying vegetation.

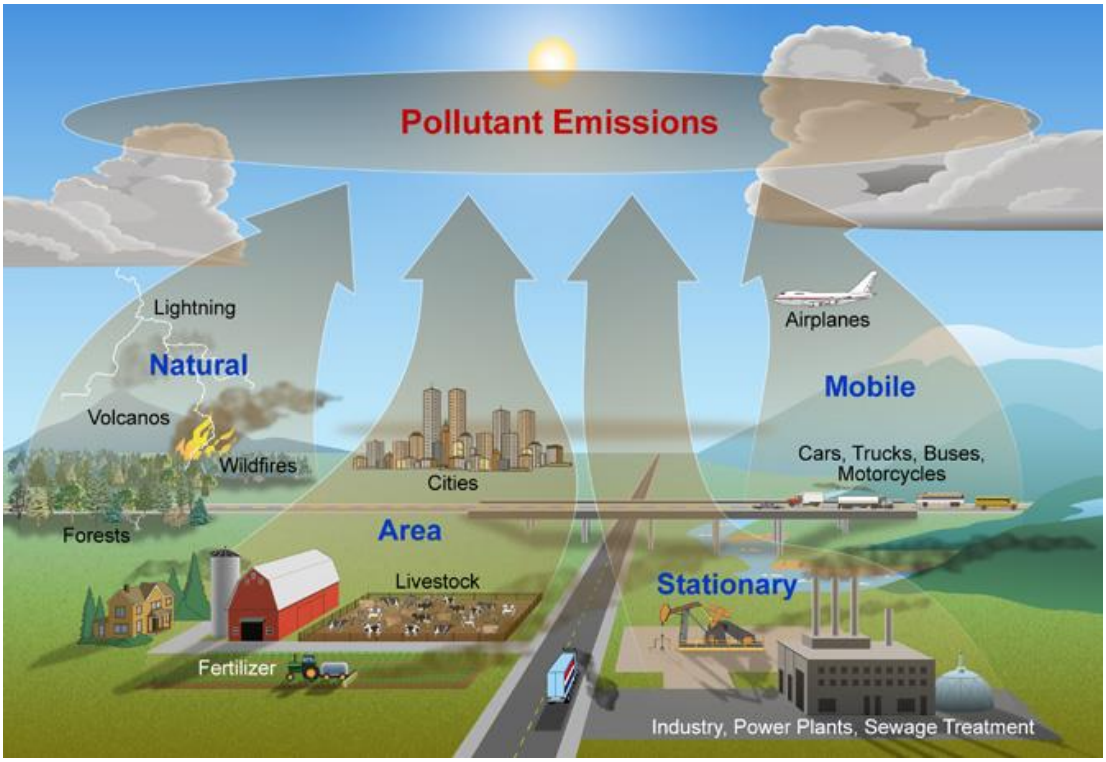

Figure 2. Sources of air pollutants

(source of the figure: https://www.nature.nps.gov/air/aqbasics/images/air_pollution_transport_02-2012.jpg).

The Clean Air Act is the major law in the United States to protect the air quality. The amendment to this law in 1990 allowed EPA to established National Ambient Air Quality Standards for six "criteria" pollutants considered harmful to public health and the environment, including PM and ground-level ozone. According to the standards, the annual average level of PM2.5 from the primary source should be lower than 12 $\mu g/m^3$, and the daily average level of PM2.5 should be lower than 35 $\mu g/m^3$. The 8-hr average level of ground-level ozone should be lower than 0.07 ppm.

1.2. Non-conventional gas and oil production

A boom in non-conventional gas and oil production has tremendously changed the U.S. economy and impacted worldwide energy markets. The United States has succeeded in growing its oil production to over 8 million barrels per day, the highest levels in decades (Omer et al., 2017).

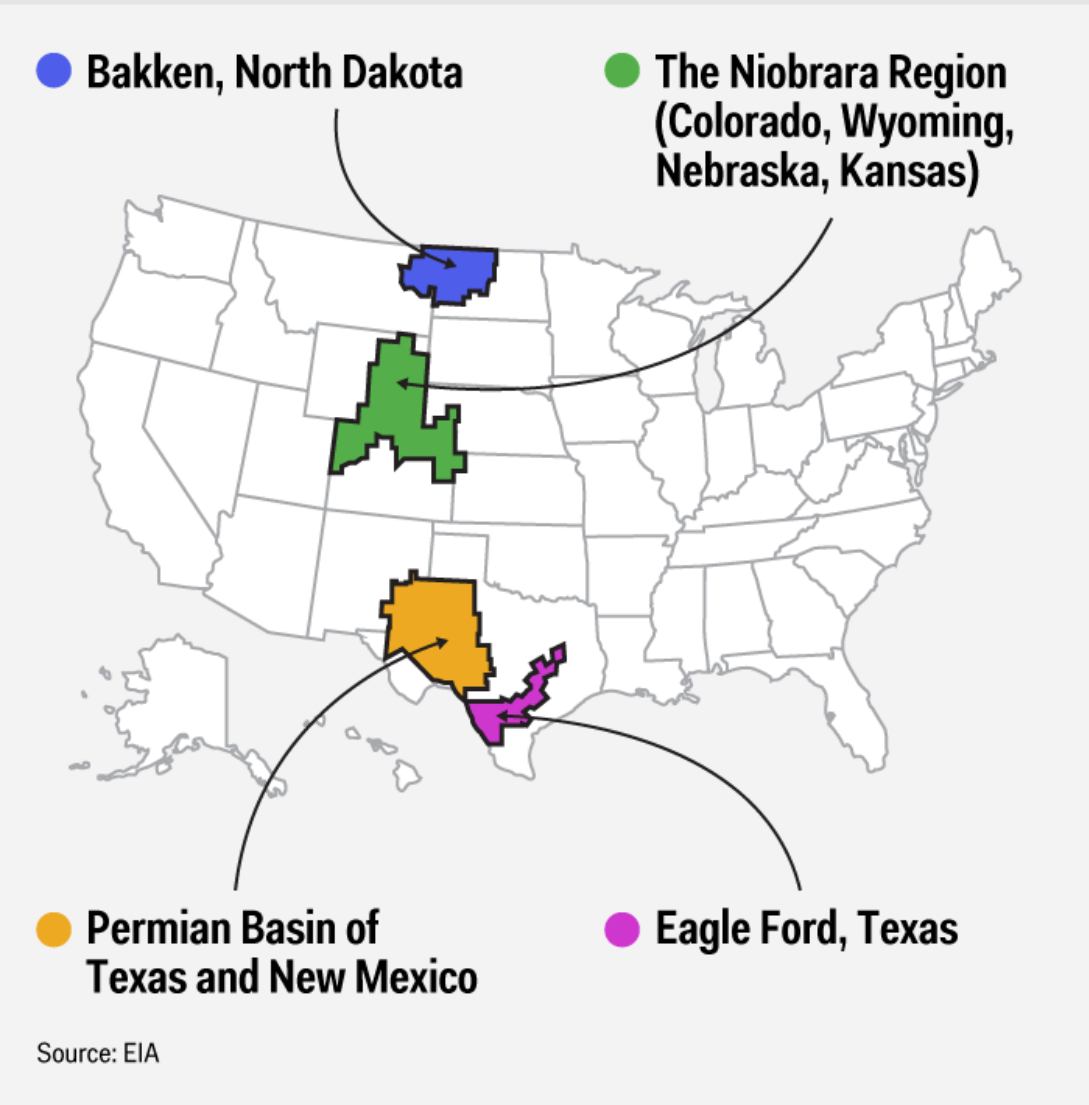

Figure 3. Oil production regions in the United States

(source: https://static-ssl.businessinsider.com/image/555dfaa769bedd5a71fc9711-700-869/map-59.png).

The oil is mainly produced in four areas, Bakken field in North Dakota, Eagle Ford in Texas, Niobrara Region in Wyoming/Colorado/Nebraska/Kansas, and Permian Basin in Texas and New Mexico (Figure 3) (United States. Government Accountability Office. and Rusco, 2012). In 2015, 90% of the U.S. oil production, excluding federal offshore drilling comes from eight states, Texas, North Dakota, California, Alaska, New Mexico, Oklahoma, Colorado and Wyoming. The oil boom is mainly due to the extensive use of horizontal hydraulic fracturing, or fracking, as new technologies give drillers access to some of the largest oil deposits in the world that were once difficult to exploit (Saeed and Sharma, 2012).

Texas is the largest domestic producer of oil as this state has had a culture associated with the oil business for more than century. Many historians trace the beginning of the modern oil era to the famous Spindle top well drilled near Beaumont, Texas in 1901. While other states have seen a boom in recent years, Texas is still the epicenter of the U.S. oil industry, with 27 operable refineries, more than any state (Olson and Society of Petroleum Engineers, 2015). With increasing horizontal drilling of the state's Eagle Ford Shale and Permian Basin, Texas is ramping up production averaging 3.6 million barrels a day in 2015, up from 3.1 million in 2014. The Eagle Ford and Permian basins are the main sources of production growth, growing the state's oil output from just over 1 million barrels per day in 2009 to 2.9 million barrels per day in March 2014.

North Dakota is the fastest-growing oil-producing state over the last few years, as it has seen an oil production increase from less than 100,000 barrels per day in 2005 to the 348,367 barrels per day reported in February 2011 (United States. Environmental Protection Agency., 2015). Bakken Shale in North Dakota is one of the largest oil reserves in the world. With oil production increasing by 1,000% between 2003 and 2015, North Dakota has 5.7 billion barrels of proven

reserves and produced 397 million barrels in 2014 (United States. Environmental Protection Agency., 2015). When combined with output from Texas, the two states provide half of the entire U.S. oil output.

The non-conventional gas and oil production activities generate a range of environmental contaminants released to air, soil and water. This thesis focuses on the potential effects on local and reginal air quality. It is known that non-conventional gas and oil production activities generate volatile organic compounds (Gilman et al., 2013, Bunch et al., 2014), which may contribute to the formation of secondary organic aerosols (PM) and ground-level ozone. However, a study on the effects of non-conventional gas and oil production on air quality is nonexistent in the literature.

1.3. Knowledge gap, goal, and objectives

Although numerous studies have been performed on air pollution, we are not aware of a study that focuses on the effects of nonconventional gas and oil production on the regional and local air quality. Such information would be very important for the public and for energy and environmental professionals. The study aims to fill this important knowledge gap. The main goal is to understand the effects of nonconventional gas and oil production on local and regional PM and ground-level ozone. The specific objectives are to 1) investigate the annual and seasonable trends of PM2.5 and ground-level ozone in two oil-producing states (Texas and North Dakota) and two background/control states (Minnesota and Connecticut); 2) understand the effects non-conventional gas and oil production on PM2.5 and ground-level ozone in these four states.

CHAPTER II

METHODOLOGY

2.1. Data collection and analysis

The daily data of ambient air concentration of PM2.5, PM10, and ground-level ozone were downloaded from EPA website (https://www.epa.gov/outdoor-air-quality-data/download-daily-data). The ambient air monitoring data were used in this research as they provide air pollution data to the general public in a timely (daily or hourly) manner. The data were rearranged based on every monitoring station in each year. In Texas alone, there are 112 stations reporting PM2.5 and 103 stations reporting ground-level ozone. The EPA does not specify how a monitoring state was established. From the information collected from the Internet, it seems that the locations for monitoring stations depend on the purpose of the monitoring. Most air quality monitoring networks are designed to support human health objectives. Some of the monitoring stations were established in rural areas to determine background pollution levels, whereas other stations are located in cities.

PM is monitored in these stations by a tapering element oscillating microbalance (TEOM®) as a filter-based measurement system to continuously measure particulate mass (USEPA, 2017a, b). The instrument calculates mass rate, mass concentration, and total mass accumulation on exchangeable filter cartridges that are designed to allow for future chemical and physical analysis. In addition, this instrument provides hourly and daily averages. This system operates on the principal that particles are continuously collected on a filter cartridge mounted on the tip of a tapered hollow glass element. The element oscillates in an applied electric field. With this monitor, particle-laden air enters through an air inlet and then passes to the sensor unit containing the patented microbalance system. The inlet system is equipped with a sampling head

to pre-separate particles. As mass accumulates on the filter cartridge, the resonant frequency of the element decreases, resulting in a direct measurement of inertial mass. Based upon the direct relationship between mass and frequency, the monitor's microcomputer calculates the total mass accumulation on the filter and the mass rate and mass concentration in real-time. The TEOM® monitor is very sensitive to mass concentration changes and can provide precise measurements for sampling durations of 1-h or less.

The most common measurement method for ground-level ozone in these stations is olefin chemiluminescence (USEPA, 2017a). In this method, ozone reacts with olefin to produce electronically excited products, which decay with the emission of light. When ozone reacts with ethylene gas, an olefin, electronically excited formaldehyde is produced. As this excited species returns to the ground state, it gives off light in a band centered at 430 nanometers (nm) in proportion to the amount of ozone present. This chemiluminescence can be measured using a photomultiplier tube, and the concentration of ozone is calculated. The EPA has identified specific monitoring instruments based on gas-phase chemiluminescence for ozone measurement. Any other measurement method or instrument must be compared against the reference method, and must perform on a par with the reference method to be deemed equivalent.

The data downloaded from the EPA's database were first transformed to editable excel spreadsheets, and then analyzed by four major steps.

In the first step, the descriptive statistical parameters, including mean, median, standard deviation, and 25th and 75th percentiles, were calculated for every year from 1999 to 2015. In each state, the number of observations with concentrations greater than 35 $\mu g/m^3$ in each state was calculated by the excel COUNT function. The data from all the stations in a state were then plotted as boxplots.

In the second step, the annual mean of each station in a state in a certain year was calculated. Then the maximum value of the annual means of all the stations in a state in a certain year was identified by the excel MAX function. The maximum annual mean represents a station in a state that contributes to the highest annual mean value of PM or ground-level ozone to this state, which signifies significant local pollution source(s). The maximum annual mean was fit to the classical linear least-squares regression to observe the annual trends in each state.

Furthermore, all the data in each state in a certain year were also arranged and plotted based on the date when the sample was collected from spring (March to May), summer (June to August), fall (September to November), and winter (December to February). The seasonal trends in selected years in each station were described by means of a sine wave time series regression approach:

$$y = y0 + A\sin\left(\pi\frac{x - xc}{w}\right), \quad (1)$$

where y is the measured PM or ground-level ozone, x is the date when the sample was collected, y_0 is modeled average level of PM or ozone, the amplitude A describes the magnitude of the sine wave or the difference between the modeled maximum/minimum value and the modeled average, w describes the width of each sine wave, and C is constant.

In the fourth step, the stations in Texas and North Dakota were separated based on the location to stations in the oil-producing regions and stations in the non-oil-producing regions. It was found that almost all the stations in North Dakota are located in the Bakken area, and thus the separation was only done for Texas. Then the annual means of the two groups were compared based on two-tail *t*-test (paried two sample for means). The default significance level 0.05 was employed. A two-tail significance P less than 0.05 means significant difference between the means. Otherwise, the annual means of the two groups in the oil-producing regions and non-oil-producing regions are not significantly different from each other.

In an additional experiment, the correlations between PM2.5 and PM10 and between PM2.5 and ozone were examined. Finally, to understand the contribution of difference sources to the studied pollutants, data of diesel and fuel consumption (utility source), travel in millions of km (mobile source), and industrial emissions (industrial source) were collected and examined regarding their potential correlations with PM.

CHAPTER III

RESULTS AND DISCUSSIONS

3.1. Annual trends of PM2.5 and ground-level ozone.

In this chapter, we first present the annual trends of PM2.5 and ground-level ozone. The daily PM2.5 and ozone monitoring data in all the stations in Texas in were collected and presented as a boxplot that includes the maximum, mean, median and minimum of data collected from all the Texas stations in a certain year. Figure 4 shows such boxplots of PM2.5 in Texas from 1999 to 2015. As shown, a majority of the PM2.5 data were below the NAAQS standard (35 $\mu g/m^3$). The number of observations with PM2.5 > 35 $\mu g/m^3$ remain between 20 to 40 between 1999 and 2012, except for 2003 when a significant number of observations (n > 100) having PM2.5 > 35 $\mu g/m^3$. The annual trend of maximum annual mean is also given in Figure 4. In general, the data show a decline in PM2.5 in Texas from 1999 to 2015. By average, the maximum annual mean declined by 0.37 $\mu g/m^3$ each year. Overall, the data indicate a significant improvement in the air quality in Texas in terms of the reduction in PM2.5 level.

The ground-level ozone also declined in Texas. The maximum daily 8-hr mean of ozone declined at a rate of 0.008 ppm per year. Noticeably, a significant observation 1999 to 2004 (~1200 to 1500) have the ground-level ozone greater than 0.07 ppm, which declined quickly since 2004 and dropped to less than 600 in recent years.

The red dotted lines for PM2.5 in boxplot diagram represent standarads whose value is 35 $\mu g/m^3$ and for annual mean standards whose value is 12 $\mu g/m^3$, for ozone standarad value is 0.0070 $\mu g/m^3$ for both boxplot and annual mean diagram. This standard value is given by National Ambient Air Quality Standards (Sources: https://www.epa.gov/criteria-air-pollutants/naaqs-table)

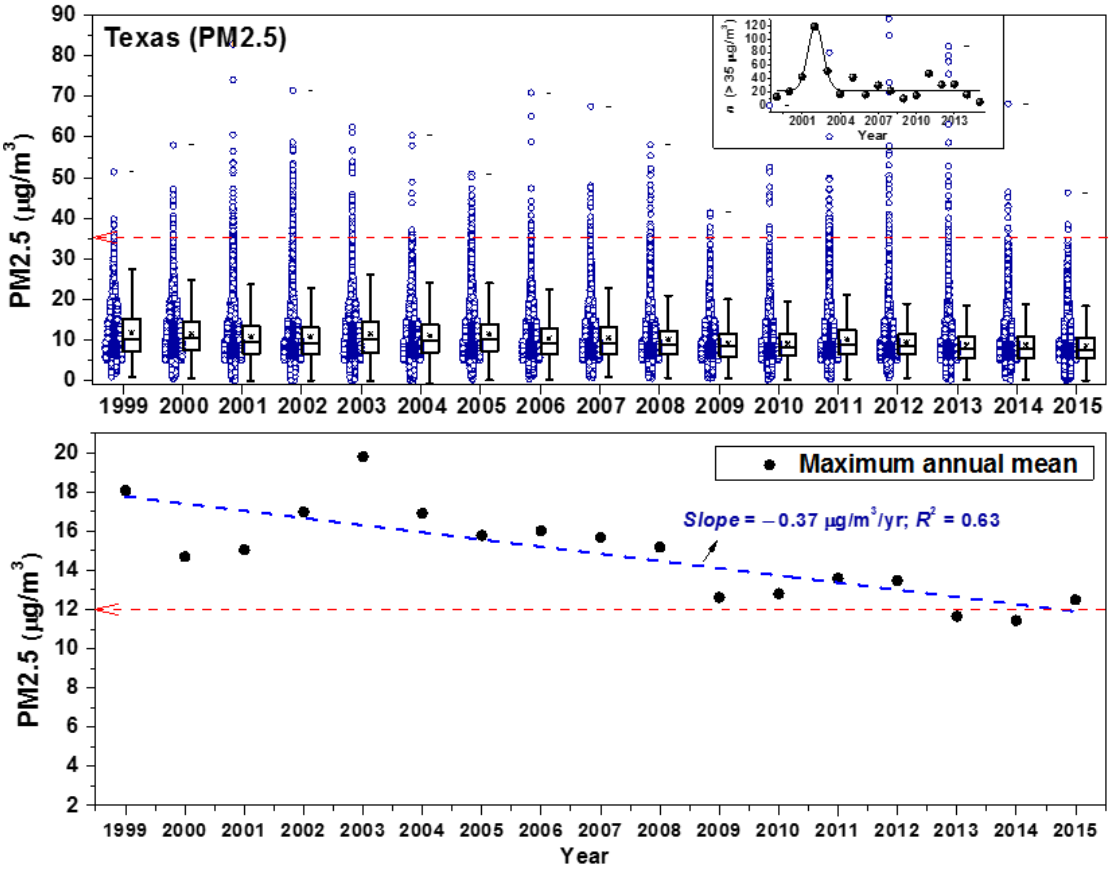

Figure 4. PM2.5 levels in Texas from the year 1999 to 2015

Figure 4. shows PM2.5 levels in Texas from the year 1999 to 2015 (up figure) and annual trends of maximum means of all the stations (bottom figure) The solid line in the up figure is a guide for the eye, and the dashed, blue line in the bottom figure represents a linear least-squares regression fit.

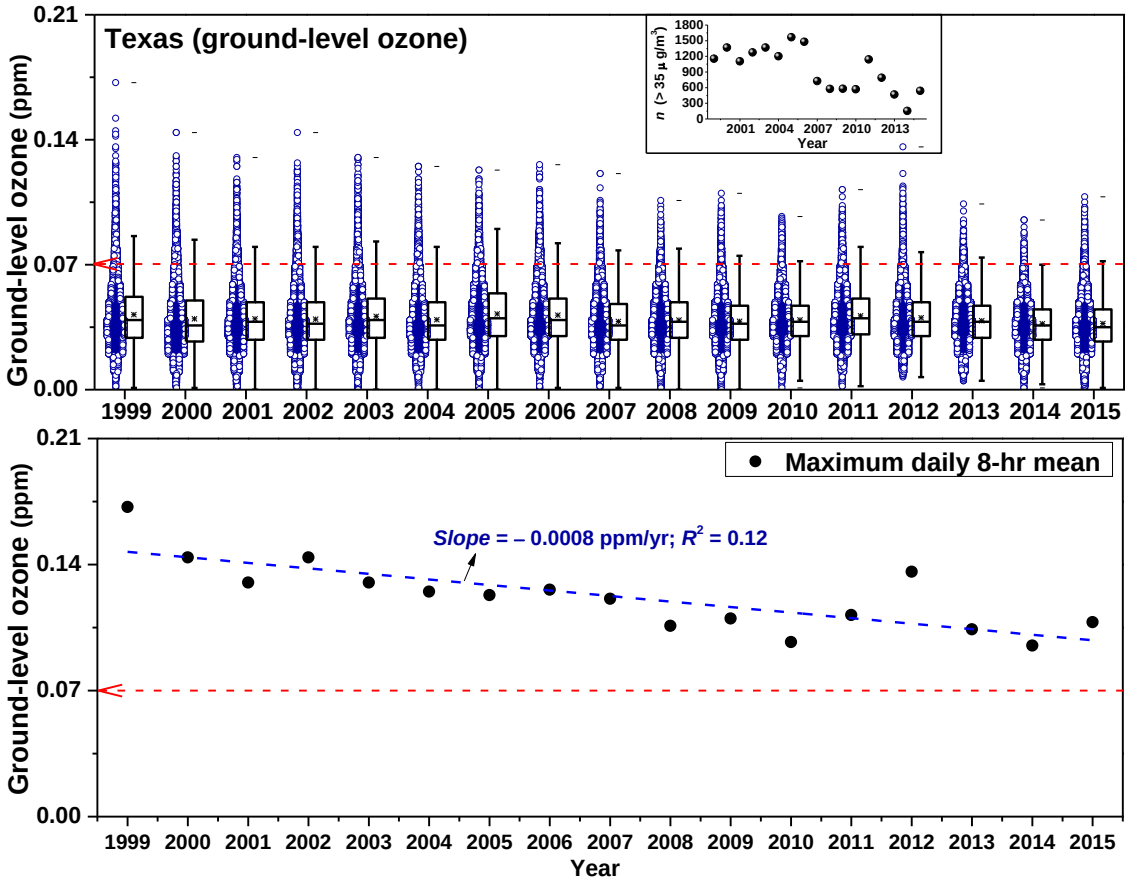

Figure 5. Ground-level ozone in Texas from the year 1999 to 2015

Figure 6. shows ground-level ozone in Texas from the year 1999 to 2015 (up figure) and annual trends of maximum means of all the stations (bottom figure). The solid line in the up figure is a guide for the eye, and the dashed, blue line in the bottom figure represents a linear least-squares regression fit.

Figures 6 and 7 present the annual trends of PM2.5 and ground-level ozone in North Dakota, another oil producing state. In contrast to Texas, the maximum average levels of PM2.5 and ground-level ozone remained stable from 1999 to 2015, at 8.4 μg/m^3 (PM2.5) and 0.069 ppm (ozone). One noticeable exception is that the number of observations with PM2.5 > 35 μg/m^3 jumped to 63 in 2015 form less than 10 between 1999 to 2013. It remains unclear with such change.

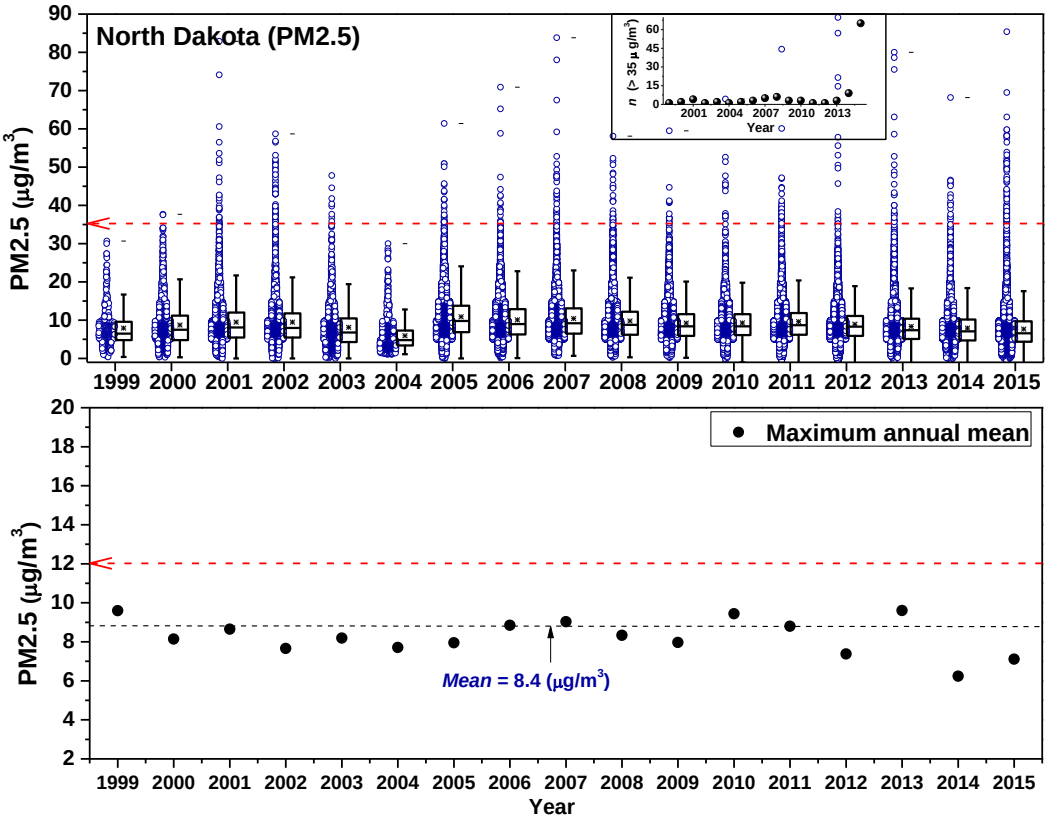

Figure 7. PM2.5 levels in North Dakota from the year 1999 to 2015

Figure 8. shows PM2.5 levels in North Dakota from the year 1999 to 2015 (up figure) and annual trends of maximum means of all the stations (bottom figure). The solid line in the up figure is a guide for the eye, and the dashed, blue line in the bottom figure represents a linear least-squares regression fit.

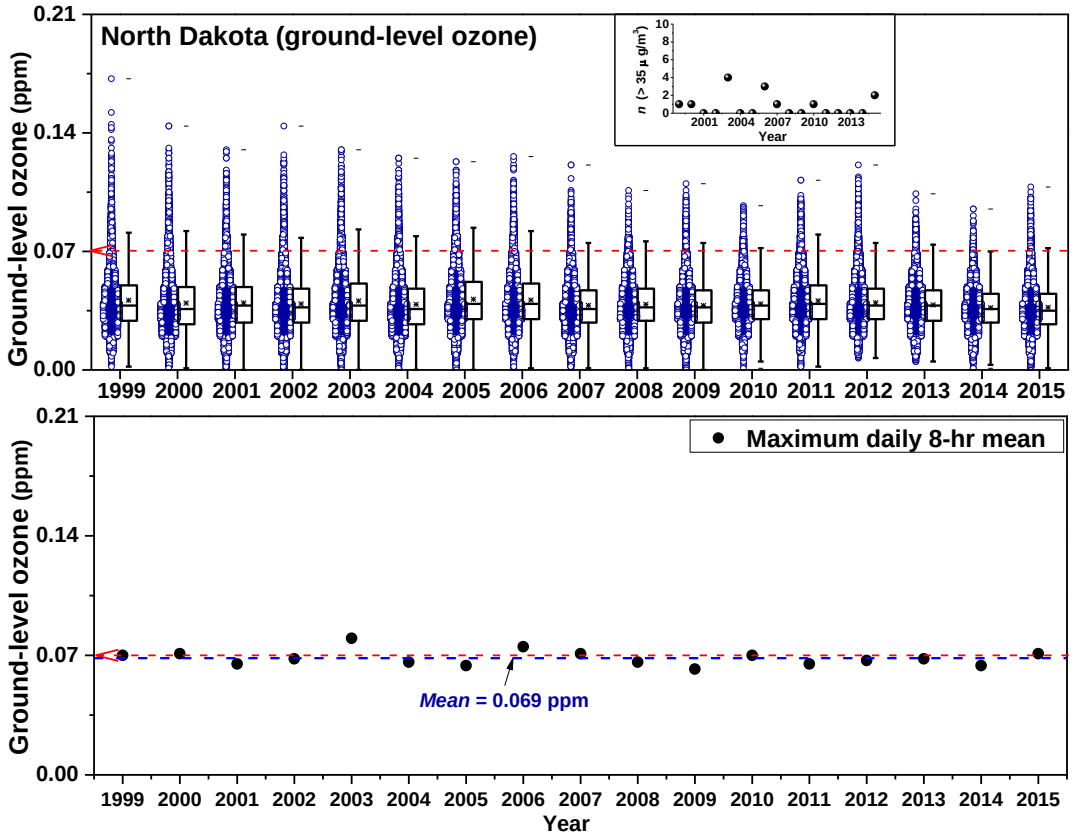

Figure 9. Ground-level ozone in North Dakota from the year 1999 to 2015

Figure 10. shows ground-level ozone in North Dakota from the year 1999 to 2015 (up figure) and annual trends of maximum means of all the stations (bottom figure). The solid line in the up figure is a guide for the eye, and the dashed, blue line in the bottom figure represents a linear least-squares regression fit.

North Dakota is the only state in the four that has a stable annual mean of PM2.5 and ground-level ozone. In one of the control, non-oil-producing state, Minnesota, the maximum annual mean of PM2.5 decreased by 0.19 μg/m^3 per year from 1999 to 2015 (Figure 8). The number of observations with PM2.5 greater than 35 μg/m^3 reached the highest (~40) in 2008, but remained <20 in most of other years. The ground-level ozone in Minnesota also declined, by a rate

of 0.0008 ppm per year (Figure 9). The number of observations with ozone level greater than 0.07 ppm was 10–40 between 2007, and remained less than 20 in recently years. In comparison with North Dakota, Texas and Minnesota are relatively urbanized states, which may have multiple sources of PM2.5 and ground-level ozone. The emissions from these sources, especially from industrial sources (see the following) may have reduced, which contribute to the apparent decline in PM2.5 and ground-level ozone in Texas and Minnesota.

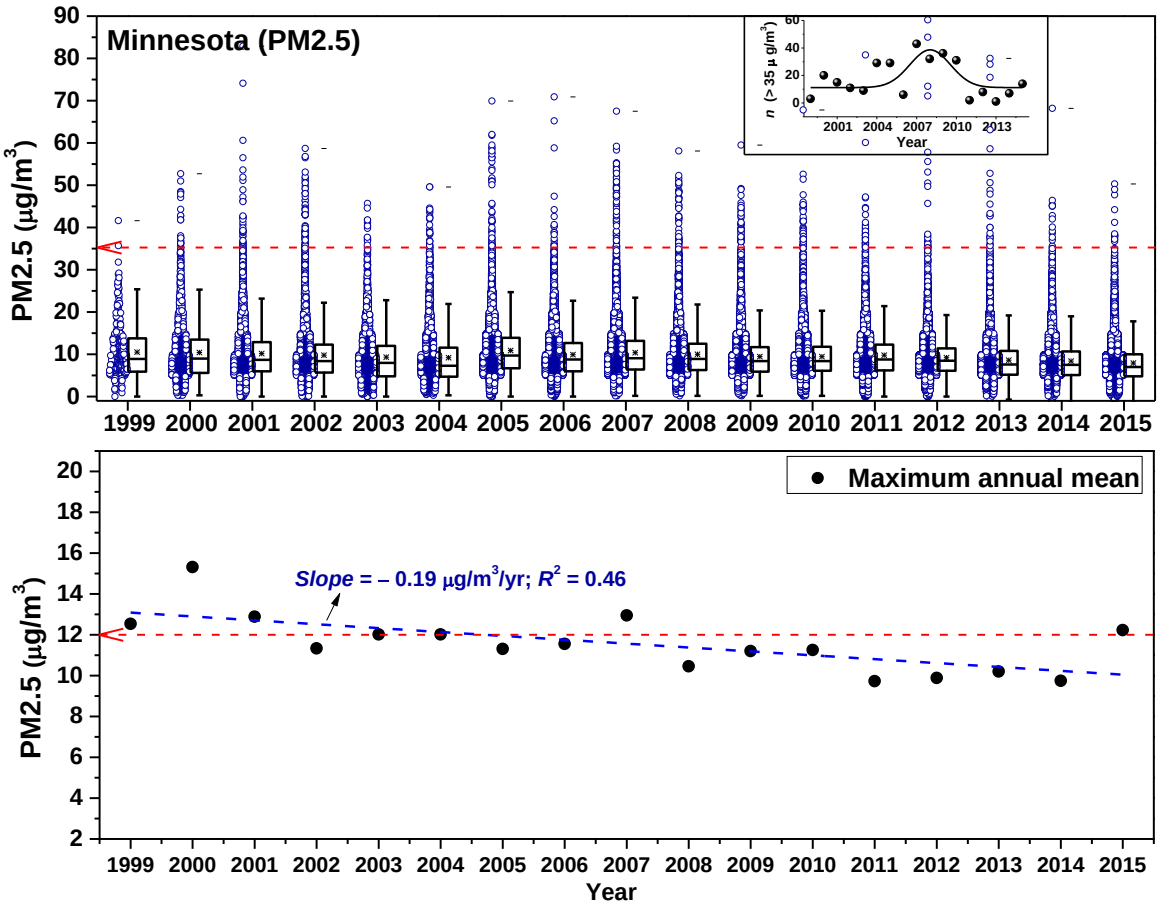

Figure 11. PM2.5 levels in Minnesota from the year 1999 to 2015

Figure 12. shows PM2.5 levels in Minnesota from the year 1999 to 2015 (up figure) and annual trends of maximum means of all the stations (bottom figure). The solid line in the up figure is a

guide for the eye, and the dashed, blue line in the bottom figure represents a linear least-squares regression fit.

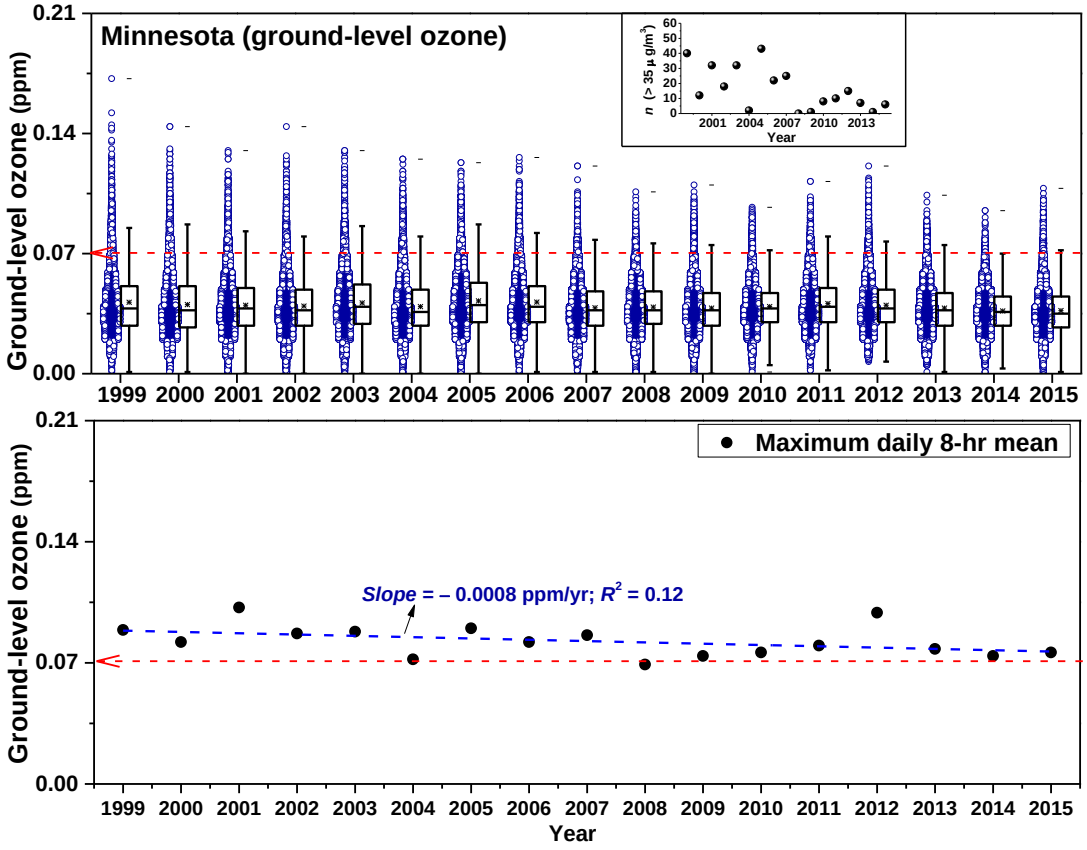

Figure 13. Ground-level ozone in Minnesota from the year 1999 to 2015

Figure 14. shows PM2.5 levels in Minnesota from the year 1999 to 2015 (up figure) and annual trends of maximum means of all the stations (bottom figure). The solid line in the up figure is a guide for the eye, and the dashed, blue line in the bottom figure represents a linear least-squares regression fit.

In another highly-urbanized state, Connecticut, PM2.5 declined by a fate of 0.8 μg/m^3 per year that is much faster than Texas and Minnesota (Figure 10). In Connecticut, the number of observations with PM2.5 greater than 35 μg/m^3 sharply dropped to <20 in 2012 from a maximum

of ~80 in 2003. Therefore, the data suggest that before the period of 2003–2006 urbanization activities are the major contributors to PM2.5 and ozone in the three states (Connecticut, Texas, and Minnesota). After 2006, the emissions from these sources declined since 2006, thus contributing the decline in PM2.5 and ground-level ozone.

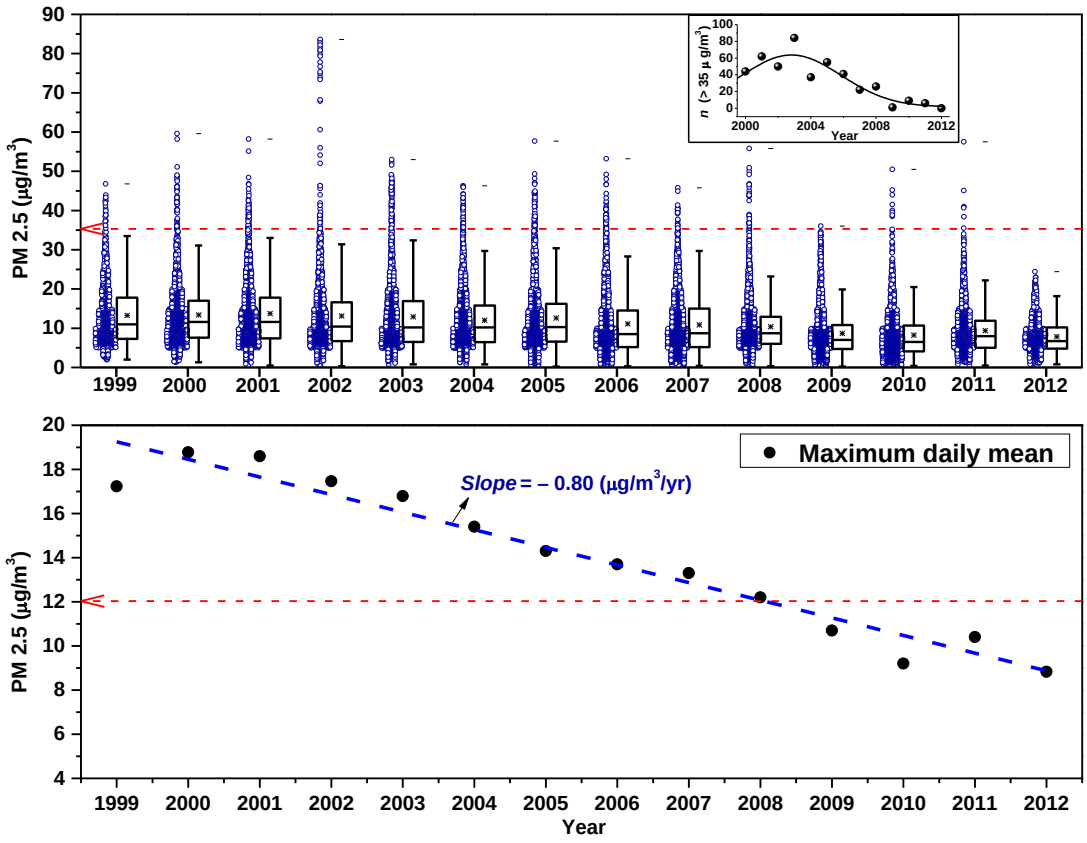

Figure 15. PM2.5 levels in Connecticut from the year 1999 to 2012

Figure 16. shows PM2.5 in Connecticut from the year 1999 to 2012 (up figure) and annual trends of maximum means of all the stations (bottom figure). The solid line in the up figure is a guide for the eye, and the dashed, blue line in the bottom figure represents a linear least-squares regression fit.

3.2. Seasonal trends of PM2.5 and ground-level ozone.

This study also examined the seasonal trends of the two criteria air pollutants in the studied states. Figure 11 shows the PM2.5 data in the highly-urbanized state (Connecticut) in six selected years. The data were modeled by a sine wave function (Eq. (1)). The difference between the modeled highest value and the average value was described by a coefficient of A (the amplitude). The larger the value of A, the greater is the seasonal variation. A strong seasonal trend was observed. In all the studied years, the PM2.5 data show two peaks, one in summer and another one in winter. As given in Figure 11, the seasonal variation (A) remained as high as 3.8–4.5 μg/m^3 between 1999 and 2008, which dropped to 2.6 in 2010. Consistent with the maximum annual mean presented in the previous section, the modeled y_0 (the annual mean) gradually declined from 1999 to 2010. W value is not relevant.

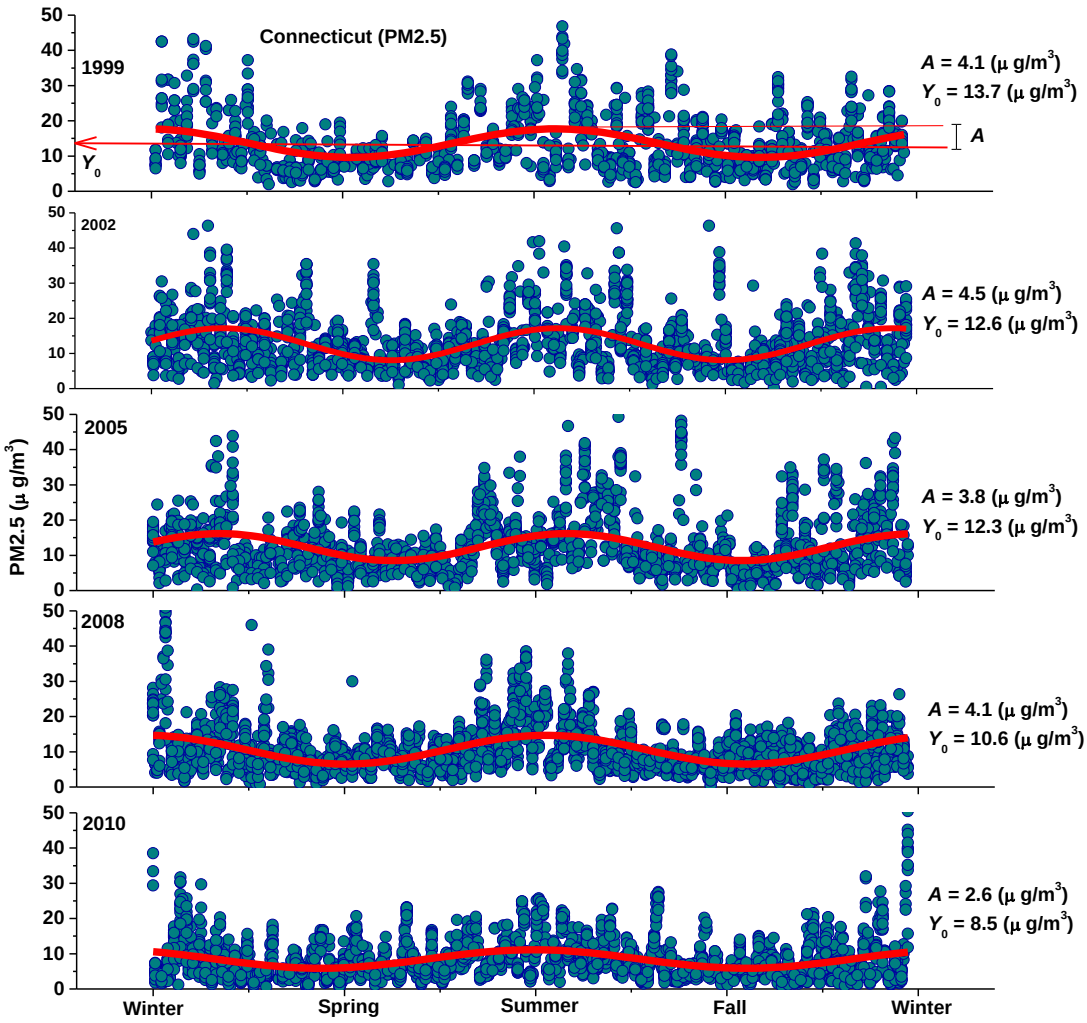

Figure 17. Seasonal variations of PM2.5 in Connecticut in the year 1999, 2002, 2005, 2008 and 2010

Figure 18. shows seasonal variation of PM2.5 in Connecticut in five selected years. The red lines represent a nonlinear fit by a sine wave function.

In comparison with Connecticut, other three states show much less variations in the seasonal trends of PM2.5 (Figures 12-14). For example, in Texas (Figure 12), the hot season (summer) also shows a higher PM2.5 than the spring and fall; however, the value of *A* was small, ~1.3–2.1 μg/m^3. In the rural state (North Dakota), the amplitude remained less than 2.0 μg/m^3

(Figure 14). A noticeable exception is North Dakota in 2015. In this year, PM2.5 in a number of days in the mid-summer and early fall was much greater than the average in North Dakota (Figure 14), which was not captured by the sine wave model.

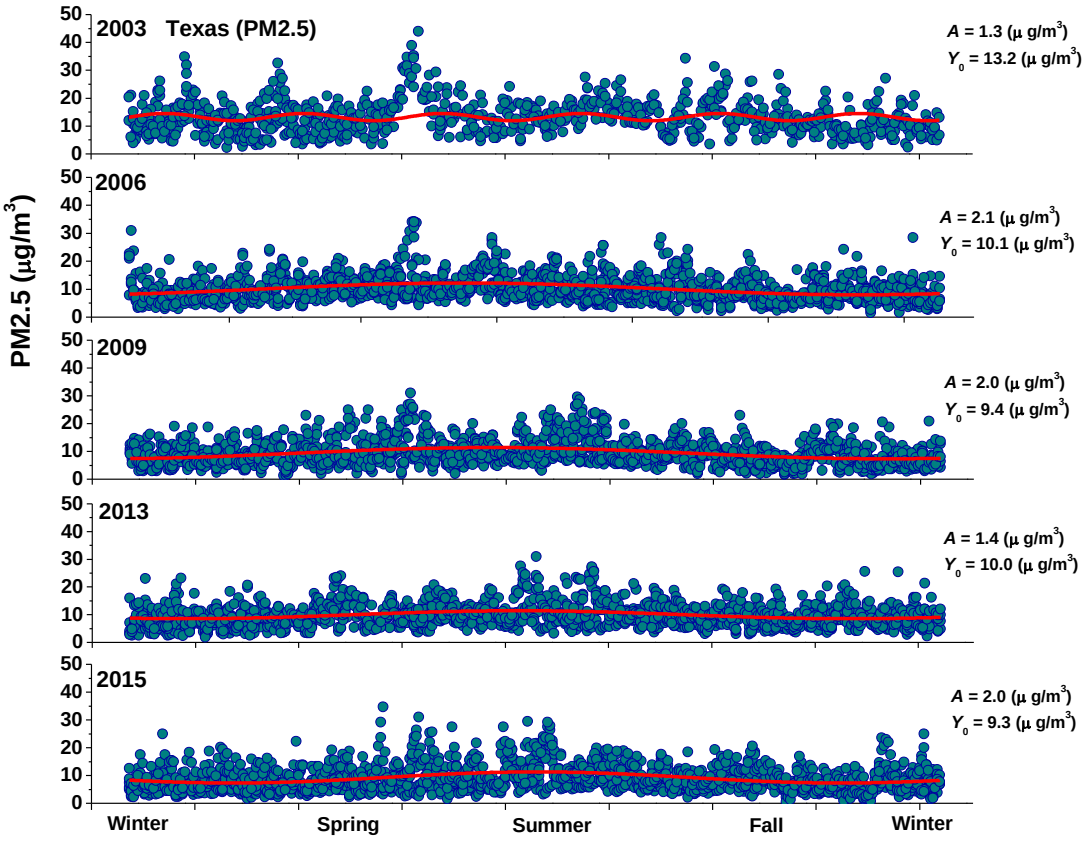

Figure 19. Seasonal variations of PM2.5 in Texas in the year 2003, 2006, 2009, 2013 and 2015

Figure 20. shows seasonal variation of PM2.5 in Texas in selected years. The red lines represent a nonlinear fit by a sine wave function.

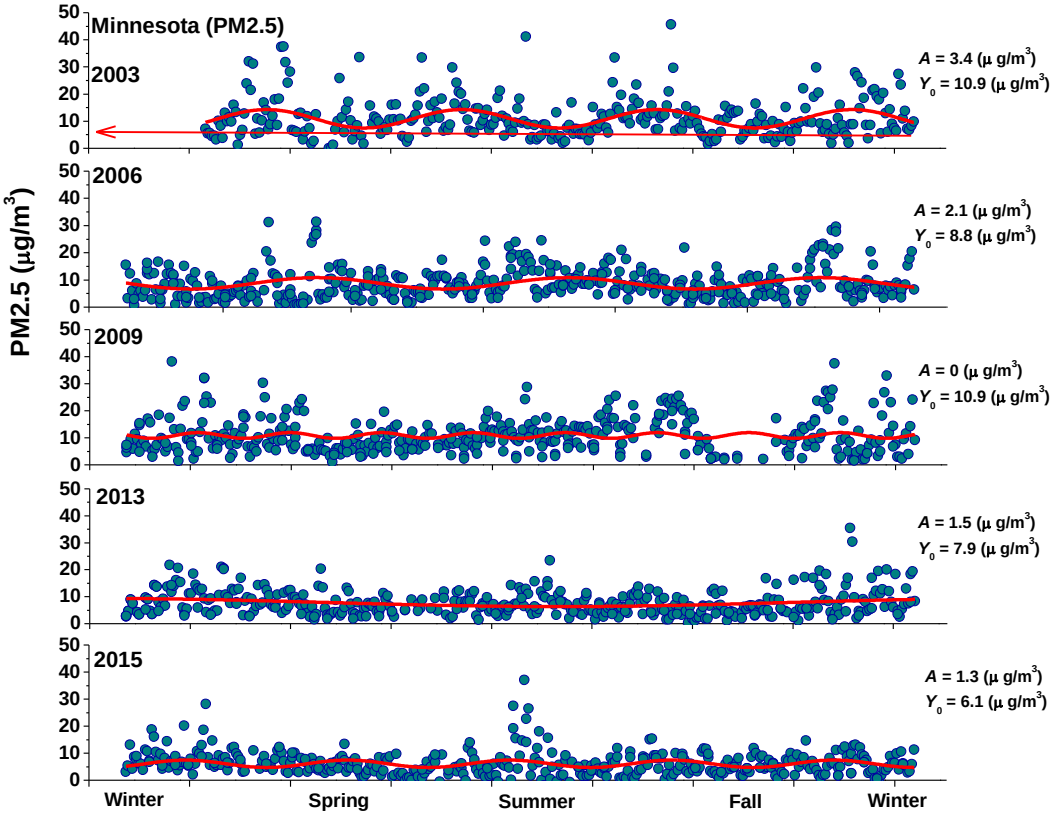

Figure 21. Seasonal variations of PM2.5 in Minnesota in the year 2003, 2006, 2009, 2013 and 2015

Figure 22. shows seasonal variation of PM2.5 in Minnesota in selected years. The red lines represent a nonlinear fit by a sine wave function.

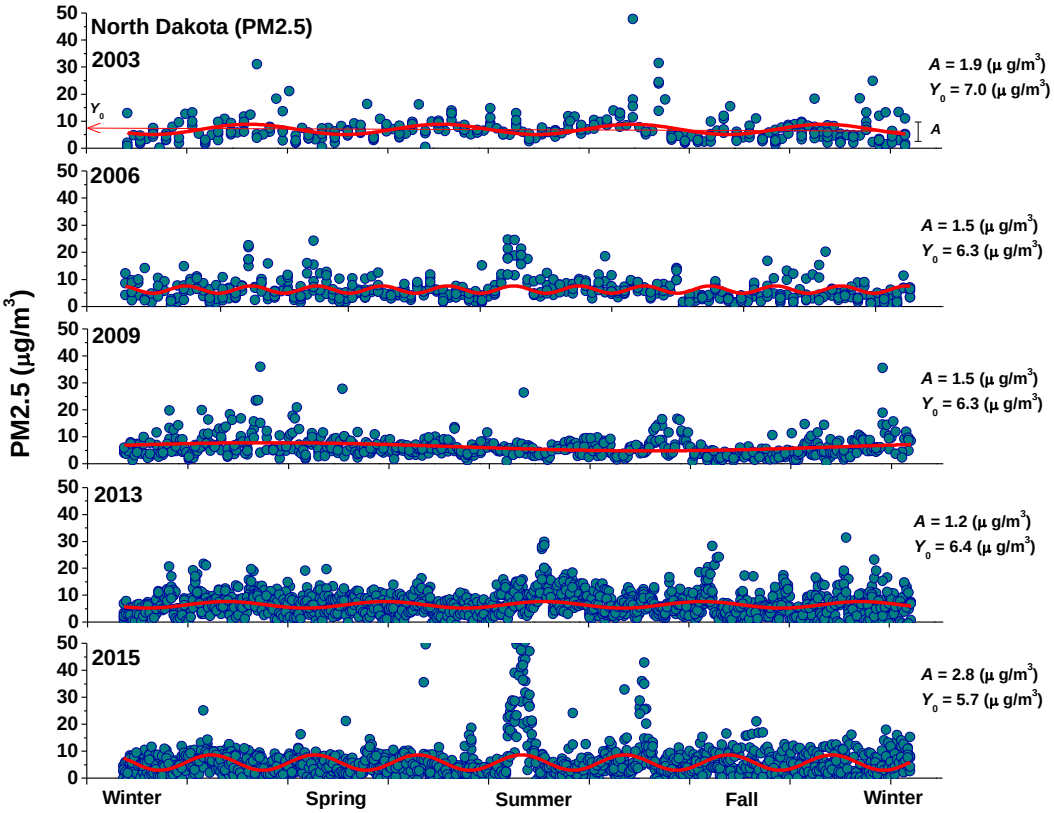

Figure 23. Seasonal variations of PM2.5 in North Dakota in the year 2003, 2006, 2009, 2013 and 2015

Figure 24. shows seasonal variation of PM2.5 in North Dakota in selected years. The red lines represent a nonlinear fit by a sine wave function

The seasonal variations of ground-level ozone in these states have been presented in Figures A1-A3 in the Appendix. As shown, in general the ozone level reaches the highest in summer and the lowest in winter. The amplitude *A* remained stable at ~0.01 ppm from 1999 to 2015 in all the studied states.

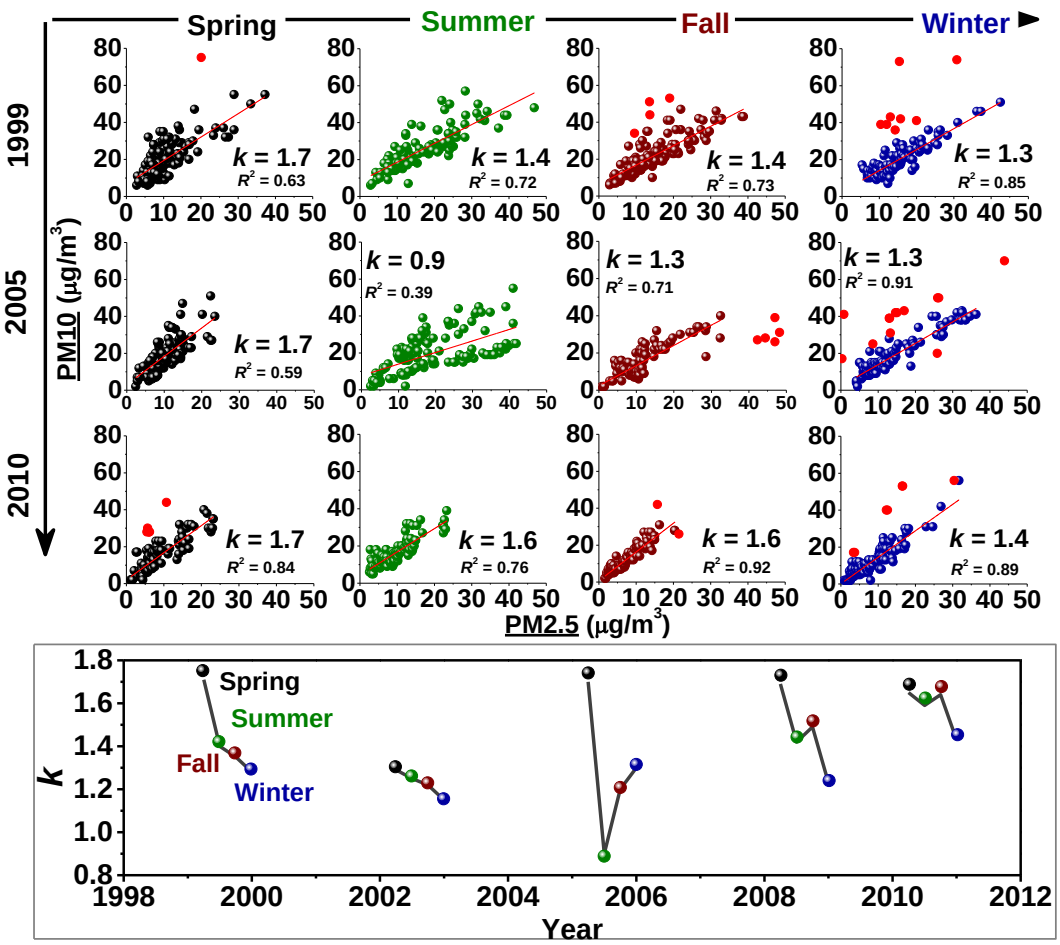

Figure 25. Correlation between PM2.5 and PM10 in different seasons in the year 1999, 2005 and 2010 in Connecticut

Figure 26. shows correlation between PM2.5 and PM10 in different seasons of selected years in Connecticut. The red lines represent a nonlinear fit by a linear least-squares regression fit.

We also attempted to analyze the annual and seasonal trends of PM10 in these states. However, it has been well known that PM2.5 and PM10 are strongly correlated with each other (Marcazzan et al., 2001, Querol et al., 2001). Therefore, we expected PM10 data in these four states have similar trends as PM2.5. To prove it, we examined the correlation between PM2.5 and

PM10 in Connecticut in 20 seasons (or five years). As shown in Figure 15, PM2.5 is strongly correlated with PM10 in all cases, which can be represented well by a simple linear function:

$$PM10 = k\ PM2.5, \qquad (2)$$

The coefficient of determination (R^2) ranging up to 0.89. Also, shown in this figure, PM10 is 1.3 to 1.7 times greater than PM2.5, which is reasonable since the size of PM10 particles is greater than PM2.5 particles. The strong correlation some PM2.5 and PM10 particles come from the same source. Furthermore, the values of k did not change greatly from year to year but did change significantly from season to season. The strongest correlation was found in spring when pollen may contribute to both PM2.5 and PM10. No significant correlation between PM2.5 and ozone was found.

As mentioned in the beginning of this thesis, there are multiple sources contribute to PM and ozone. To understand the decline of PM2.5 in these states, we collected the annual data of diesel and fuels consumption (utility source), travel in millions of km (mobile source), and stack and fugitive emissions from the industry (industrial source) in one of the states (Connecticut), which are plotted in Figure 16 along with the annual PM2.5 data in this state. As shown the fuel consumption and travel in millions of km remained relatively stable in the years studied. Therefore, it is apparent that the utility and mobile sources are not the cause for the decline in PM2.5. On the other hand, strongly correlations were observed between PM2.5 and stack/fugitive emissions. The results suggest that PM2.5 mainly comes from industrial sources. According to the data, a reduction of 1.9×10^5 kg from stack emission or 6.4×10^6 kg form fugitive emission may contribute to a decline in PM2.5 by 1 $\mu g/m^3$.

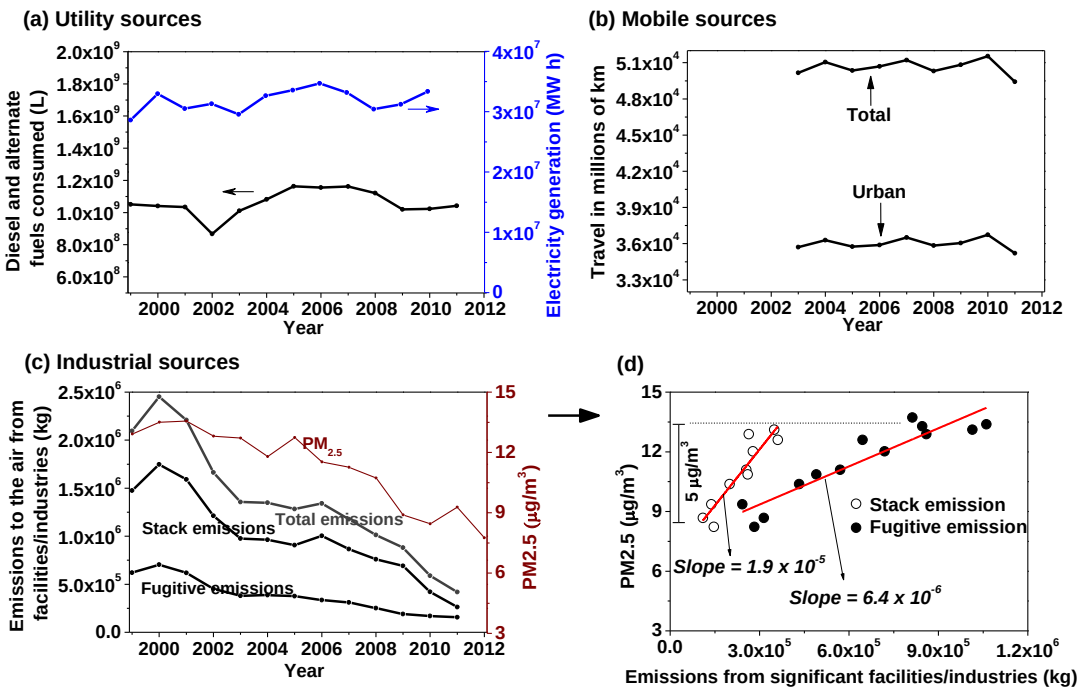

Figure 27. Potential sources of PM2.5 and the correlation between PM2.5 and industrial emissions.

3.3. Effects of non-conventional gas and oil production on regional and local air quality.

One of the major objectives of this study is to understand the effects of non-conventional gas and oil production on regional and local air quality. We first separate the stations in the oil-producing regions from those in the non-oil producing regions in Texas (see Figure 17). Then the annual means of PM2.5 and ground-level ozone in each year in each group were calculated and presented as bar graphs in Figure 18. Then a two-tail *t* test was performed to compare the means between the two groups.

Figure 28. Stations included in the study on the effects of gas and oil production activities on PM2.5 and ground-level ozone in Texas.

Figure 29. shows stations included in the study on the effects of gas and oil production activities on PM2.5 and ground-level ozone in Texas. The blue and red symbols represent the stations in the oil-producing and non-oil-producing regions, respectively.

The first impression from Figure 18 is that the difference in the annual means between the two groups is small. The *t* test results also confirmed that the difference is not significant. The results clearly show that the non-conventional of PM2.5 and ground-level ozone. It should be noted; however, we focus our attention to PM and ground-level ozone. Future studies are recommended to understand the effects of gas and oil production activities on other air pollutants, including volatile organic compounds or semi-volatile organic compounds, as well as soil- and water-borne contaminants. gas and oil production activities have minimum effects on PM2.5 and ground-level ozone in Texas. In North Dakota, almost all the stations are located in the oil-

producing regions. However, the annual trends discussed in Section 3.1 that show a relatively stable and low levels of PM2.5 and ground-level ozone in these stations also support the conclusion that non-conventional gas and oil production activities are not a significant source

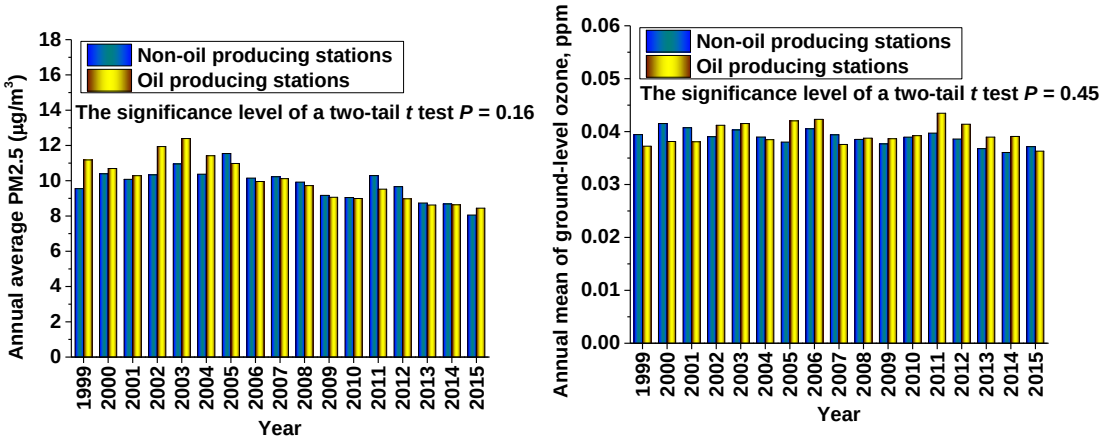

Figure 30. Comparison of the annual average of PM2.5 and ground-level ozone from the year 1999 to 2015 in Texas

Figure 31. shows comparison of the annual average of PM2.5 and ground-level ozone in Texas air monitoring stations in oil-producing and non-oil-producing regions.

CHAPTER IV

CONCLUSION

This thesis concerns with two criteria air pollutants (PM2.5 and ground-level ozone) that have known adverse health effects to the public. We download the data from EPA's database and analyzed the data by different approaches. The major goal is to identify the potential effects of non-conventional gas and oil production on local and regional air quality. Based on the results of this thesis, the following conclusions can be made.

Our analysis has shown that non-conventional gas and oil production has no significant effects on PM2.5 and ground-level ozone in the two-major oil-producing states (Texas and North Dakota), which seems to be counterintuitive. Non-conventional gas and oil production and combustion activities are known to generate CO_2, CH_4, and volatile organic compounds. However, CO_2 and CH_4 are greenhouse gases, not air pollutants based on EPA's definition. Based on our analysis, the volatile organic compounds generated form non-conventional gas and oil production and combustion appear not able to contribute to significant increase in PM2.5 and ground-level ozone in the oil producing regions.

Furthermore, the data analysis has shown a clear difference between urbanized and rural states. In Connecticut and other two relatively urbanized states (Texas and Minnesota), a significant decline in PM2.5 was observed in the past 15 years. In the rural state (North Dakota), however, PM2.5 and ground-level ozone remained to be stable and a relatively low level.

Another major finding is the strong seasonal trends of PM2.5 and ozone. In general, PM2.5 is greater in summer and winter than in spring and fall. The strong sunlight in summer and the

heating/combustion activities in winter contribute to the greater PM2.5. Ground-level ozone, on the other hand, is high in the summer but low in the winter because of the seasonal variation of sunlight radiation.

We have also observed the strong correlation between PM2.5 and PM10, suggesting a majority of PM2.5 and PM10 particles come from the same source(s). No significant correlation between PM2.5 and ground-level ozone was observed.

In the source-identification study, we found strong correlation between PM2.5 and industrial emissions. Utility and mobile sources, on the other than, were not correlated with PM2.5.

APPENDIX A

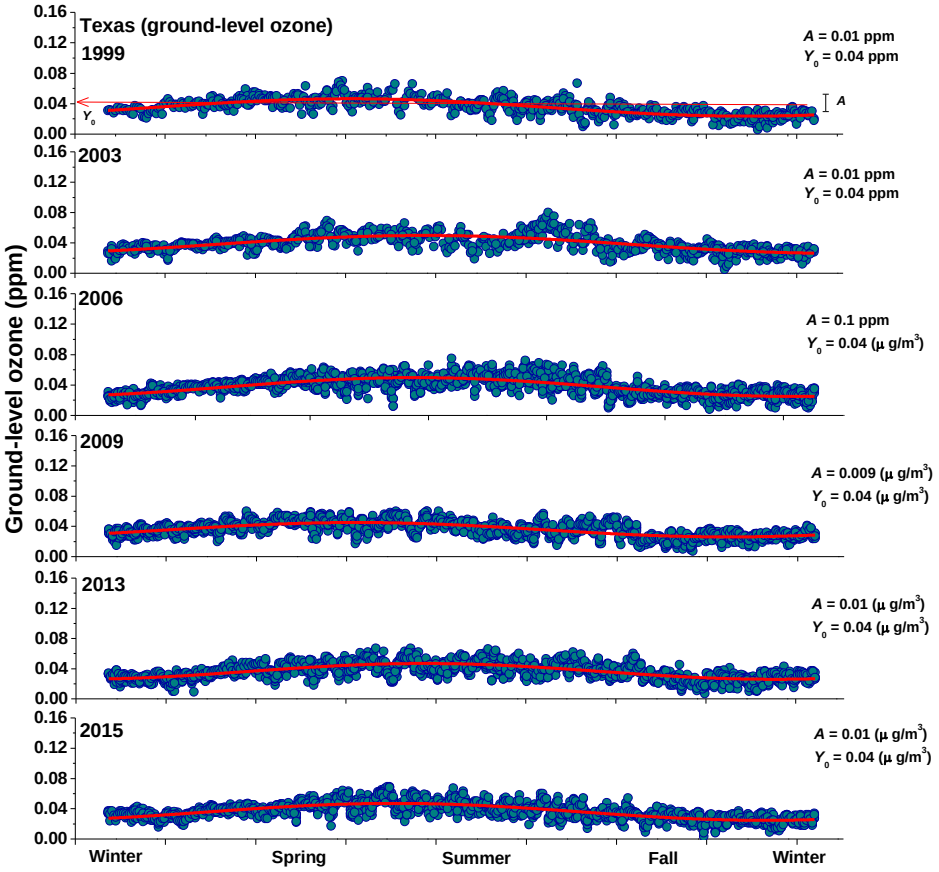

Figure A1. Seasonal variation of ground-level ozone in Texas.

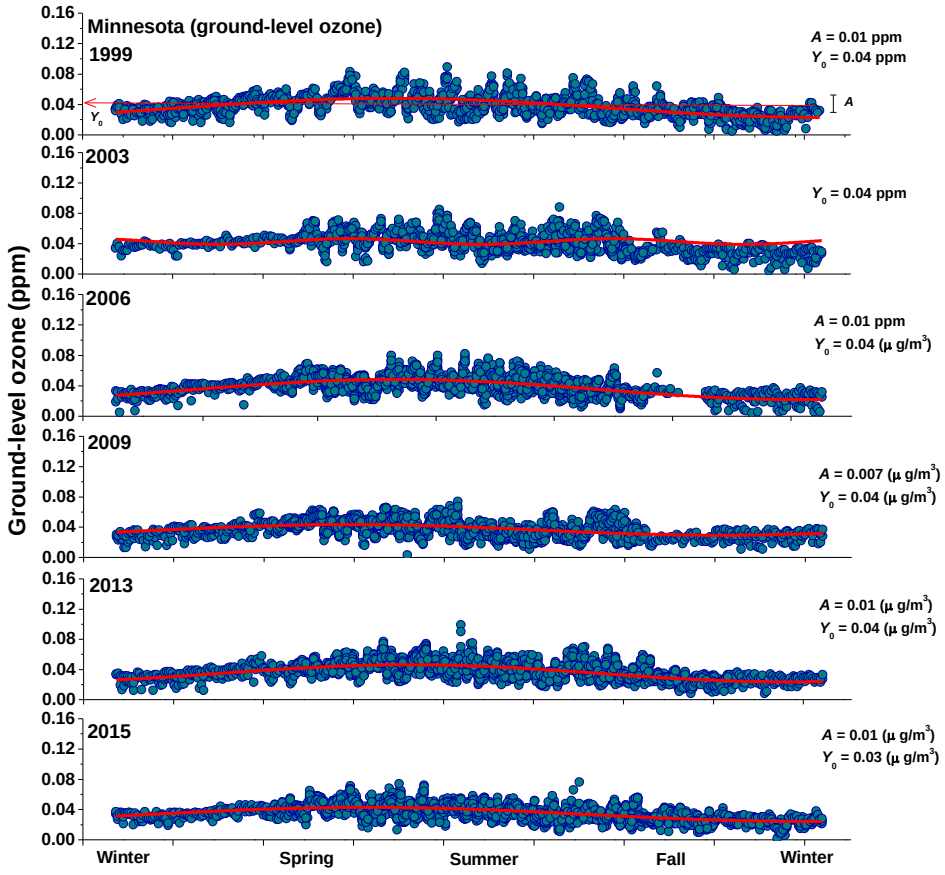

Figure A2. Seasonal variation of ground-level ozone in Minnesota.

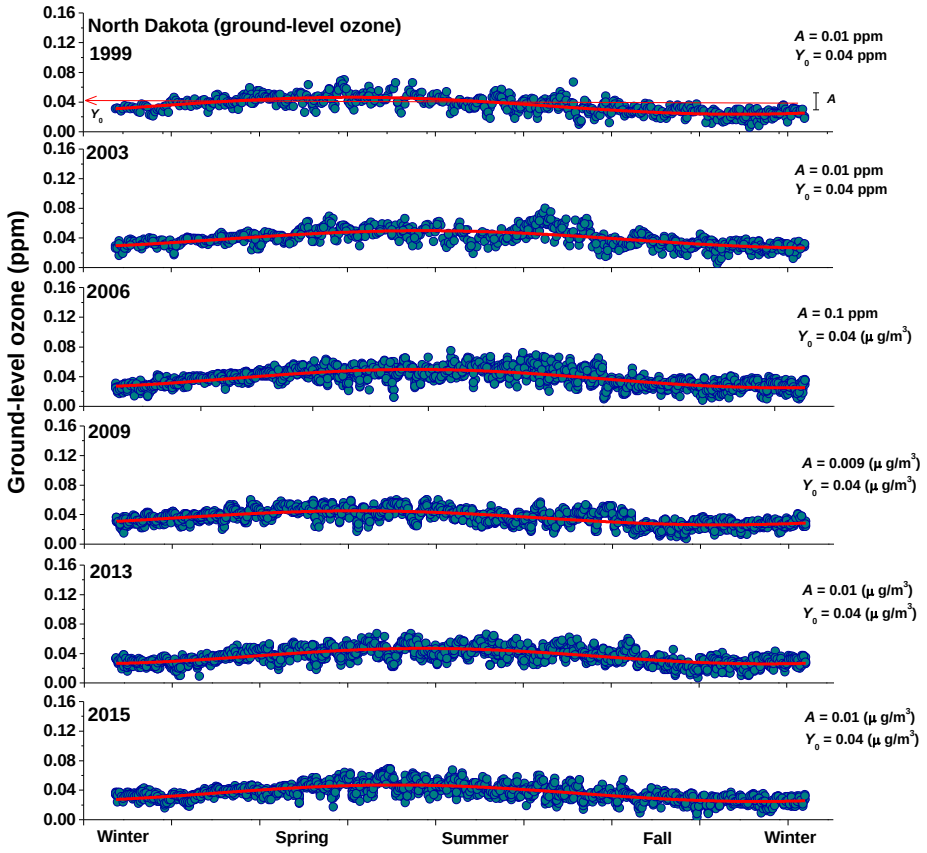

Figure A3. Seasonal variation of ground-level ozone in North Dakota.

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