Air quality analysis of nitrogen oxides and relationships with ozone pollution

by

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Abstract

Air pollution can harm us when it accumulates in the air in high enough concentrations. Nitrogen oxides (NO*x*), especially nitrogen dioxide (NO_2), are increasingly of concern due to the environmental and health problems they cause. This reviews the recent literature on the reasons and impacts of NO*x* pollution as well as ozone pollution related to NO*x* emissions. A review of the impacts of transportation is provided as it pertains to various types of NO*x* pollution. To improve the air quality, the recent research focuses on how suitable monitoring methods can be used to more economically and precisely collect data on pollution concentrations. Multiple researchers have explored low-cost monitors. Other research explores more convenient ways to eliminate NO*x* pollution to improve air quality. Regarding the impact of transportation on NO*x* emissions, vehicle emission technologies are of concern to an increasing number of people, such as using urea to reduce NO*x* emission for diesel vehicles and developing all-electrical vehicles and plug-in hybrid electric vehicles.

This research focused on the data analysis of NO_2 and ozone concentrations in Chicago from the SASA project. Other analyses also provided some data for states and cities in the U.S. to show the relationship between NO*x* and ozone with transportation. Variations of NO*x* and ozone emissions were explored. First, the hourly variations in NO*x* and ozone emissions each day were studied. Second, the seasonal variation in NO*x* and ozone pollution was analyzed. Third, the differences in NO*x* emissions on working days and weekends were found. The impacts of NO*x* emissions on the variation in the ozone concentration in the air were discussed. The purpose of this research is to help more people, especially residents in the communities of Chicago, related to the SASA project to realize the hazard of NO*x* pollutants to humans and the environment, become aware of the importance and urgency of reducing NO*x* emissions, and provide feasible methods to solve this problem.

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Zixian Wang

Chapter 1 - Introduction

Air pollution can harm us when it accumulates in the air in high enough concentrations. Millions of Americans live in areas where urban smog, particle pollution, and toxic pollutants pose serious health concerns. The federally regulated criteria pollutants under the U.S. National Ambient Air Quality Standards (NAAQS) include particulate matter (PM), ozone (O_3), sulfur dioxide (SO_2), carbon monoxide (CO), nitrogen dioxide (NO_2), and particulate lead (US EPA, 2017b).

Currently, nitrogen oxides (NO*x*), especially nitrogen dioxide, are increasingly of concern due to the environmental and health problems they cause. The air pollution of NO*x* and NO_2 has become a global problem. First, acid rain is precipitation containing harmful amounts of nitric and sulfuric acids. These acids are formed primarily from nitrogen oxides and sulfur oxides released into the atmosphere when fossil fuels are burned. These acids fall to the earth either as wet precipitation (rain, snow, or fog) or dry precipitation (gas and particulates). Some pollutants are carried by the wind, sometimes for hundreds of miles. In the environment, acid rain damages trees and causes soils and water bodies to acidify, making the water unsuitable for some fish and other wildlife. It also speeds the decay of buildings.(“Health and environmental effects of air pollution”, n.d.) Second, Volatile Organic Compounds (VOCs) and nitrogen oxides produce ozone though photochemical reactions. This has also caused VOCs to be recognized as major primary pollutants because of their ozone-forming reactions. Third, NO_2 has a negative impact on human health, particularly on the liver, lung, and spleen functions, and on the blood (US EPA, 2016).

NO*x* and ozone pollution cause environmental degradation and put human health at risk. Most types of NO*x* emissions are formed by complicated processes. The relationship between transportation and NO*x* pollution is significant and about 50% of NO*x* is from vehicles. The NO*x* automobile pollution is caused by combustion of fuel in the engine, which creates exhaust emissions. Exhaust pollutants are emitted from the exhaust pipe of automobiles. These pollutants are particularly harmful to the atmosphere and living things, especially as NO_2 is responsible for both short-term and long-term health effects. Nitrogen oxides are one of the major types of exhaust pollutants. Emissions of nitrogen oxides from Europe and North America have been

nearly equal since the 1980s with each remaining near 25 to 28 million tons/year (Akimoto, 2003). After 1990, because of stringent emission controls in Western European countries, Europe has seen an apparently decreasing trend in NO*x* emissions. In contrast, Asian emissions, which contributed only a minor fraction of global emissions during the 1970s, have increased rapidly since then and surpassed emissions from North America and Europe in the mid-1990s (Akimoto, 2003). Moreover, emissions from Africa and South America will increase, mainly due to their economic growth, which would make air quality a global issue (Akimoto, 2003).

In addition to NO*x*, VOCs emissions from automobiles and other sources are responsible for the formation of photochemical air pollution that causes significant adverse effects in urban areas such as ozone (O_3) pollution. Most O_3 pollution is directly or indirectly due to NO*x* emissions from motor vehicles. Los Angeles, Mexico City, Sao Paulo and Shanghai have serious problems with O_3 (Noll, 1999). New York has moderate to heavy O_3 pollution. The principal concern with NO*x* is that NO*x* contributes to the formation of ozone, O_3, which is a strong respiratory irritant and one of the principal constituents of urban smog. Hydrocarbons will directly react in the atmosphere with nitrogen oxides by photochemical activity to form ozone. Nitrogen oxides react with sunlight, ultraviolet radiation, and oxygen in the air to produce O_3 and NO_2. NO and NO_2 are often treated together as one problem or as a quasi-species and written as NO*x*.

Photochemically derived air pollutants are secondary pollutants. Pollution of the atmosphere by gasoline engines was first observed in Los Angeles and then later in Tokyo in the form of photochemical smog, which can be seen from a distance as a yellow-brown layer in the atmosphere above the city and is caused by the interaction of nitrogen oxides and hydrocarbons in the sunlight to form lachrymatory compounds. This phenomenon causes impairment to health and damage to vegetation. Climatic conditions in Los Angeles and Tokyo retard the dispersion of these pollutants, although the problem is by no means confined to these cities (Harrison et al., 1981).

As for the causes of NO*x* emissions, in addition to transportation, rapid industrialization and urbanization also produce NO*x* pollution. Because several problems have been found with NO*x* and ozone, more and more people wish to focus on NO*x* in the air quality where they live. Air

quality monitors have become significant due to the collection and analysis of air quality data. Besides considering which type of monitors we need to choose to more effectively collect data, how to develop a more effective air monitoring system is also important. One purpose of this review is to provide information on air quality monitoring related to NO*x*. There are two types of approaches: the macro-scale and micro-scale approaches. They include many specific models for monitoring. Selecting suitable scientific methods to collect data on pollutants is the first step to developing a better study of NO*x* pollution.

Reducing NO*x* emissions and improving air quality are significant global challenges. During the 1984 summer Olympic Games in Los Angeles, measures to reduce both vehicle and industrial emissions aimed at combatting Southern California's smog in the city resulted in significantly cleaner air during the Olympics. This experience provides strong evidence that the air quality of the Los Angeles air basin can be improved through aggressive control strategies (Parrish et al., 2016). Similarly, the 2008 Beijing Olympics implemented strict air pollution control measures. In order to avoid medical problems related to air pollution during the Olympics, China banned half of all cars in the city. Due to various emission control measures, such as high emission vehicle restrictions, government vehicle use control, and alternate day driving rules, it is estimated that mobile sources of NO*x* and VOC emissions were reduced by approximately 50% (Wang et al., 2010). The experience of improved air quality during the Olympics prompted political leaders throughout California to further recognize that serious air pollution problems are mainly caused by vehicle emissions and that action can improve air quality (Parrish et al., 2016). Air quality in Beijing improved significantly during the Olympics as a result of actions, too. Observations at Miyun, a rural site 100 km downwind of Beijing’s urban center, indicate that the mean daytime mixing ratio of O_3 was reduced by about 15 ppb in August 2008 (Wang et al., 2009; Shen et al., 2011). During this period, temporary improvement was found in the heart function of healthy young people (Wang et al., 2010). One goal of the review is to include some information on actions that can be taken to control gaseous emissions from motor vehicles. Seeking more scientific air monitoring methods and developing high-efficiency technologies to reduce NO*x* emissions are significant to the environment and human health.

The most important purpose of this review is to help residents of urban communities in their efforts to understand the impacts of the types of vehicle and vehicle technologies on NO*x* emissions. Many residents of large cities do not realize that their different transportation behaviors have been playing important roles in the formation of NO*x* pollutants in the air. In Chapters 4 and 5, detailed data analysis of four communities in Chicago and other compared cities in the U.S. will provide information on the relationship between NO*x* pollution and transportation, as well as the perniciousness of this pollution issue.

At the same time, this report also addresses issues related to pollution related to photochemical smog and ozone, while covering street canyons. Street canyons are a special case of NO*x* pollution in urban environments.

Chapter 2 - NO*x* and Ozone Pollution

2.1 NO*x* Pollution

Nitrogen oxides or oxides of nitrogen (NO*x*) are binary compounds of oxygen and nitrogen (Forano, 2004). Nitrogen oxides are one of the main contaminants of the atmosphere. Nitric oxide (NO)-known as nitrogen monoxide or nitrogen (II) oxide-and nitrogen dioxide are of the most concern in studying air quality. Other nitrogen oxides include nitrous acid and nitric acid. During any high-temperature combustion which breaks the strongly bonded atmospheric N_2 and combines atomic N with oxygen, nitrogen oxides (NO, and to a lesser extent NO_2) are released: power plants are the main stationary sources; automobiles, buses, trucks, trains, and aircraft are the most omnipresent mobile emitters. In 2012, 45% of nitrogen oxide emissions in the European Union (EU) came from transport, and 39% of it from road transport. Transport is thus the second most important source of this pollutant, after energy production (Mally & Ogrin, 2015). In spite of aggressive control efforts, total US emissions of NO*x* have remained above 20 metric tonnes per year, since the early 1980s (Smil, 2001). Because NO_2 is a secondary oxidation product of atmospheric reactions involving NO, the latter of which is directly emitted in combustion, NO*x* is considered a better indicator of traffic pollution than is NO_2 alone (Hamra et al., 2015).

Several oxides of nitrogen are produced in combustion and are considered to be atmospheric pollutants, including NO and NO_2. These gases contribute to the formation of smog and acid rain, as well as affecting tropospheric ozone. Nitrogen oxides and VOCs produce ozone through photochemical reactions. NO*x* and VOC emissions from automobiles are responsible for the formation of photochemical air pollution that causes significant adverse effects in urban areas. Air pollutants resulting from photochemical reactions are considered secondary contaminants. While VOCs are not criteria pollutants, due to their high emissions and important role in ozone-forming reactions, they are recognized as major primary pollutants. NO_2 may cause many serious environmental problems and aggravate illnesses for the human body. For example, nitrate particles make the air hazy and impair visibility, and contribute to nutrient pollution in coastal waters, resulting in eutrophication. NO*x* emissions also contribute to acid rain and eutrophication.

There are many negative effects of NO_2 pollution. The elimination and diminishing of it is an urgent problem. Many people including researchers are concerned because they want to know

what caused the pollution; then they could solve these problems according to sufficient reasons.

Street canyons, as specific polluted areas, have received special attention, because high levels of pollution are observed in street canyons. Street canyons are urban streets with high buildings on both sides (Milosavljevic et al., 2015; Fu et al., 2001). In urban environments, especially in areas with relatively high population and traffic densities, the chances of human exposure to hazardous substances are expected to increase significantly (Fu et al., 2001). Urban areas are not considered to be homogeneous entities, and the largest air pollution is concentrated in street canyons. This is often the case around busy traffic areas in the city centers, where urban topography and microclimates can cause undesirable air quality conditions that can lead to polluted hot spots (Fu et al., 2001). The pollution levels in urban street canyons are higher due to the increased traffic emissions and reduced natural ventilation (Vardoulakis et al., 2003). Although street canyons usually have a lower volume of traffic than arterials on the outskirts of the city or ring roads, they are still quite busy. Because the air's self-cleaning capacity in street canyons has been significantly reduced, primary pollutant levels are very high. Pedestrians, cyclists and motorized transport users are affected, and tenants and workers in nearby buildings are exposed for many hours a day to high concentrations. The air quality along the open space of the street is highly dependent on the amount of traffic, and the pollution on some side can be low when vehicle numbers are small (Mally & Ogrin, 2015). Nonetheless, the air may be severely polluted in street canyons, even if the volume of traffic is quite small, and this pollution will only rise with the increase in traffic density (Mally & Ogrin, 2015). Street canyons are typically a basic geometric unit of urban labyrinth of the city center, i.e. buildings on both sides along the relatively narrow road (Vardoulakis et al., 2003). Pedestrians, cyclists, drivers, and residents in these streets may be exposed to levels of pollutants that exceed current standards for air quality (Fu et al., 2001). From the point of view of population exposure, air quality is of great importance in street canyons, as the highest levels of pollution and the broader targets of effect are often concentrated in this type of road. The so-called canyon effect (i.e. the reduced natural ventilation in urban streets) results in greater health impacts (e.g. indicated by an increased number of respiratory hospital admissions) and cost of damage for the exposed population (Spadaro & Rabl, 2001).

In Branimir's investigation, the influence of traffic flow is one of the key factors affecting the concentration of harmful substances in street canyons, except for the predictive factor

background wind speed (Milosavljevic et al., 2015). They found that the traffic flow has the greatest impact on the NO*x* concentration on the windward side of the street canyon, for background wind speed up to 0.6 ms^{-1} (Milosavljevic et al., 2015). The traffic flow also has the greatest impact on the NO*x* concentrations on the leeward side of the street canyon, for wind speed up to 1.5 ms^{-1} (Milosavljevic et al., 2015). The enhancement of the more open street canyon dispersion ability can be accounted for by increasing the wind speed inside the street canyon (Fu et al., 2001).

Fu et al. (2001) pointed out the Operational Street Pollution Model (OSPM) developed by National Environmental Research Institute (NERI) of Denmark can reflect the basic dispersion pattern in the relatively wide and open streets in Beijing, but gives concentrations that are systematically higher than the actual measurements in their studies. In another study attempting to quantify residential exposure to exhaust gases in Oslo, a correction coefficient was introduced to account for changes in ambient concentrations with height over street level (Larssen et al, 1993). Croxford et al. (1998) have suggested that a side of the street factor should be introduced if the prevailing wind direction is perpendicular or near-perpendicular to the street axis.

In street canyons, ozone concentrations are often too low to react with all the available nitrogen monoxide (Vintar Mally & Ogrin, 2015). NO in the urban environment produces nitrogen dioxide and ozone. In street canyons, this may lead to lower levels of nitrogen dioxide than people might expect. Since nitrogen dioxide is primarily a secondary pollutant, higher concentrations are only expected if there is sufficient NO and oxygen (Vintar Mally & Ogrin, 2015).

2.1.1 NO_2

NO_2 is reddish brown and highly reactive gas. It is one of a group of highly reactive gases known as oxides of nitrogen or nitrogen oxides (NO*x*) (US EPA, 2016). NO_2 primarily gets in the air from the burning of fuel. It is formed by emissions from cars, trucks and buses, power plants, and off-road equipment. NO emissions combine with O_2 to form NO_2. The pollution depends on the traffic intensity and the speed of vehicles. The most polluted air stays at ground level because NO_2 is heavier than N_2 and O_2 (Mally & Ogrin, 2015). Due to rapid industrialization and

urbanization, Western China had a huge change in the spatial and temporal concentrations of nitrogen dioxide (NO_2) pollution. After removing the natural background influences, they find significant anthropogenic NO_2 growth in concentration over Western China between 2005 and 2013 (Cui et al., 2016). They found that anthropogenic emissions are the main driver of the observed NO_2 trends. NO_2 grew the fastest over the city clusters, reflecting rapid economic development, urbanization, and population growth (Cui et al., 2016).

Nitrogen dioxide may cause many serious environmental problems and aggravate illnesses for the human body. First, NO_2 and other NO_x interact with water, oxygen and other chemicals in the atmosphere to form acid rain. Acid rain harms sensitive ecosystems such as lakes and forests (US EPA, 2016). Second, nitrate particles make the air hazy and impair visibility, and contribute to nutrient pollution in coastal waters, resulting in eutrophication (Mally & Ogrin, 2015). Third, breathing air with a high concentration of NO_2 can irritate airways in the human respiratory system (US EPA, 2016). Such exposures over short periods can aggravate respiratory diseases, particularly asthma, leading to respiratory symptoms (such as coughing, wheezing or difficulty breathing), hospital admissions and visits to emergency rooms (US EPA, 2016). Longer exposures to elevated concentrations of NO_2 may contribute to the development of asthma and potentially increase susceptibility to respiratory infections. People with asthma, as well as children and the elderly, are generally at greater risk for the health effects of NO_2 (US EPA, 2016).

Table 1. NAAQS for NO_2 and O_3 (US EPA, 2014)

Pollutant	Primary/ Secondary	Averaging Time	Level	Form
Nitrogen Dioxide (NO_2)	Primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
Nitrogen Dioxide (NO_2)	Primary & secondary	1 year	53 ppb	Annual Mean

Ozone (O_3)	Primary & secondary	8 hours	0.070 ppm	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years

The U.S. Environmental Protection Agency (EPA) has set National Ambient Air Quality Standards (NAAQS) for six principal pollutants, which are called "criteria" air pollutants (US EPA, 2014). Periodically, the standards are reviewed and may be revised (US EPA, 2014). The current standards are listed in Table 1 for NO_2 and O_3. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air ($\mu g/m^3$). One ppm equals 1000 ppb. In NAAQS, 1-hr average NO_2 concentration is 100 ppb; 1-yr average NO_2 concentration is 53 ppb.

2.1.2 NO

Nitric oxide (nitrogen monoxide) is a gas which is colorless, odorless, and nearly insoluble in water with the formula NO. It forms free radicals with bonding structure that includes an unpaired electron. NO has a half-life of 3-6 s. It is readily oxidized to nitrogen dioxide (*Nitric oxide (CHEBI:16480)*, n.d.)

NO constitutes 85-95 % of NO*x* in combustion emission. It is gradually converted to NO_2 in atmospheric air (Reşitoğlu et al., 2015). Exhaust from motor vehicles, chimneys, stacks and other combustion systems produces nitrogen oxides. The decrease in NO in the middle of the day appears to be due to several effects. One of these is meteorological, such as a breaking of the inversion. Another is a thermal reaction, probably with organic matter. In some cases emissions are reduced because of less traffic. The rough parallelism between nitric oxide and nitrogen dioxide concentrations at night suggests that nitrogen dioxide is being formed from nitric oxide (Rogers, 1958).

2.2 Ozone at Ground Level

Ozone is a gas that consists of three oxygen atoms (O_3). Ozone exists in the upper atmosphere of the Earth as well as at ground level. Based on where it is located, ozone can be good or bad. Stratospheric ozone-good ozone-naturally occurs in the upper atmosphere, creating a protective

layer that protects us from the harmful ultraviolet rays of the sun. This beneficial ozone has been partially destroyed by manmade chemicals, causing what is sometimes referred to as a 'hole in the ozone layer'. Because of its effects on people and the environment, ground-level ozone is a harmful air pollutant and the main ingredient in smog (US EPA, 2015).

Ozone (O_3) is a key secondary air pollutant associated with a number of health issues including asthma and premature death. It is expected that changes in the global climate may affect the frequency and magnitude of high O_3 days across much of the United States. The importance of climate change for O_3 air pollution has been highlighted by past studies estimating health impacts of projected O_3 increases over the 21st century (Knowlton et al., 2004). Children are most at risk from exposure to ozone because they are outside playing and exercising in backyards, playgrounds, neighborhood parks, and summer camps during the summer months when ozone levels are at their peak. In addition, children breathe more air per pound of body weight than adults, and because their respiratory systems are still developing, they are more susceptible than adults to ozone related threats. Although there is no evidence that ozone causes asthma or other chronic respiratory disease, individuals with these conditions will generally experience the effects of ozone earlier and at lower levels than less sensitive individuals. In the United States, asthma is a growing threat to both children and adults. Healthy adults who are outdoors and moderately active during the summer months, such as construction workers, landscapers, and joggers, are also among those most at risk because they are exposed to a higher level of ozone than people who are less active outdoors. These individuals are susceptible because during activity, ozone penetrates deeper into the parts of the lungs that are more vulnerable to injury. For environmental aspect, exposure of vegetation to tropospheric ground level ozone causes an alteration in the allocation of resources, which can affect all aspects of plant growth. In particular, it has been found that ozone can cause injury and premature mortality of plant tissues after entering the plant, interfere with the ability of plants to produce and store food, so that growth, reproduction and overall plant health are compromised; and reduce growth and decrease survivability of plant and tree seedlings, etc.

In July 1997, EPA revised the former 1-hour ozone standard and replaced it with a more protective 8-hour standard at a level of 0.08 ppm. The 1997 0.08 ppm, 8-hour primary standard is

met at an air quality monitor when the 3-year average of the annual fourth-highest daily maximum 8-hour average ozone concentration is less than or equal to 0.08 ppm (that is, 0.084 due to rounding) (US EPA, 2019). In March 2008, EPA again revised the ozone standard. The 2008 ozone standard was set at a level of 0.075 ppm averaged over an 8-hour period. This standard is met at an air quality monitor when the 3-year average of the annual fourth-highest daily maximum 8-hour average ozone concentration is less than or equal to 0.075 ppm (US EPA, 2019). The latest National Ambient Air Quality Standard for O_3 in 2019 of 0.070 ppm is shown in Table 1.

Hogrefe et al. (2004) report that ozone is likely to increase by an average of 5 ppb over the eastern United States by the 2080s compared to the 1990s due to regional climate change alone associated with a medium / high-growth scenario of climate emissions. In sensitivity studies of five summers in the 2050s, the group found that while pollutant inflows from outside the eastern U.S. would have the greatest impact on the summer average O_3 mixing ratios, peak O_3 values were more affected by climate change than other analyzed factors that included both transportation into the region and changes in anthropogenic O_3-precursor emissions.

Urban heat island phenomenon and the related problem of ozone in Chicago's metropolitan area, IL is also a major problem. The thermal processes that are active in a heat island start early morning with the sunrise, continue throughout the day, and often last through the night (Gray & Finster, 1999).

2.2.1 Pollution of Ozone

Pollution of ozone is caused by the photochemical reaction of precursor volatile organic compounds and nitrogen oxides, with a major source of NO*x* being traffic emissions. To determine the optimal traffic emission control strategy, understanding the complexity of the diurnal ozone process and its relationship to precursors is critical (Gao & Niemeier, 2008). These O_3 precursors are emitted by fossil fuel combustion, agriculture, biomass burning, oil and gas production, and a variety of other industrial processes (Jaffe et al., 2018). According to the American Lung Association (2019), more than 40% of Americans currently live in areas with unhealthy levels of ozone pollution. Due to population growth and reliance on car travel, some

parts of California continue to receive extremely severe ozone warnings; ground-level ozone pollution threatens the health of more than 33 million Californians (Gao & Niemeier, 2008). The experiences of Los Angeles and Beijing during their respective Olympics Games demonstrated that aggressive efforts to control emission could significantly improve air quality in major urban areas, although other factors such as meteorological conditions and local pollution transport also have a significant impact on the concentrations of air pollutants, especially secondary pollutants such as O_3 (Wang et al., 2010).

In recent years, the governments of the world are more concerned about ozone pollution and its harm to human health. They have tried to make policies and management measures to reduce the ozone pollution. For example, the spatial distribution of ozone concentrations within the South Coast Air Basin (SoCAB) has evolved as the absolute and relative magnitudes of ozone precursor emissions have changed, according to the statistics of maximum 1-hour and maximum 8-hour average of measured O_3 concentrations over 5 decades. O_3 exceeded 600 ppb in the 1960s by 1-hour averages and O_3 approached 400 ppb by 8-hour averages (Parrish et al., 2016). Since 1998, neither of these metrics has exceeded 200 ppb. Especially since 2010, they have still decreased generally, and are now close to 100 ppb. The remarkable success of ozone control efforts is clear from the results. The frequency of high pollution episodes has also decreased markedly (Parrish et al., 2016). Over the past three decades ambient concentrations of key pollutants in the SoCAB region have decreased substantially despite a doubling of the population and tripling of vehicle use. Ozone concentrations apparently peaked in the late 1960s, and have declined impressively since then. Although it still violates the NAAQS for ozone, the Los Angeles basin is in compliance with the NAAQS for nitrogen dioxide and carbon monoxide, as well as sulfur dioxide and lead. It is fair to say that this megacity has gone from being one of the most polluted in the world 50 years ago to presently one of the “least polluted” cities of its size. Improvements in air quality are estimated to have saved many thousands of lives in the Los Angeles area ("The Benefits of Meeting Federal Clean Air Standards in the South Coast and San Joaquin Air Basins," n.d.). Despite this progress, Los Angeles ozone concentrations still exceed the US and California air quality standards by a significant margin (Parrish et al., 2016). The national design value for the monitoring stations in the SoCAB didn't achieve the requirement of

the new ozone NAAQS. Thus, significant additional emission control efforts remain to be accomplished to meet this requirement (Parrish et al., 2016).

The change of ozone concentrations has not followed completely the VOC or the NO*x* temporal trends. Peroxyacetyl nitrate (PAN), the pollutant identified as responsible for severe eye irritation in Los Angeles in previous decades, has decreased more rapidly than either precursor. Since PAN has both VOC and NO*x* precursors, its concentration may be expected to decrease at a faster rate than either precursor. Importantly, the ratio of VOC to NO*x* emissions is often taken to be an indicator for the photochemical environment of a polluted atmosphere. The differing temporal trends of VOCs and NO*x* emissions imply that this indicator ratio has decreased by a factor of 12 within the Los Angeles Basin over the 5 decades considered (Parrish et al., 2016).

Since the atmospheric ozone process is a dynamic nonlinear system with spatiotemporal variability, regulated precursor reductions may not necessarily result in ozone reduction (Gao & Niemeier, 2008). For example, the ozone weekend effects seen in many major metropolitan areas have raised important policy issues and sciences on ozone control through precursor reductions. Challenges include transport emissions control (Cleveland et al., 1974; Pont & Fontan, 2001; *The Ozone Weekend Effect in California*, n.d.).

Since all of these underlying factors follow intrinsic daily patterns, a diurnal ozone cycle as a continuous entity constitutes a fundamental unit that most directly incorporates and reflects the effects of these driving factors on ozone dynamics. The forms of diurnal ozone cycles can provide clues as to the formation, scavenging, and transport of ozone at an air monitoring site or within an area (Finlayson-Pitts & Pitts, 1986). In addition to reflecting daily changes in meteorological conditions, diurnal ozone cycles suggest important information about precursor emissions from say transportation activities that are of direct regulatory interest. For example, the shape of the diurnal ozone curve can be used to ascertain if a monitoring site is exposed to locally generated or long-range transported ozone and/or ozone precursor emissions (Böhm et al., 1991). Lefohn et al. (1993) studied diurnal ozone patterns to identify the influence of changes in precursor emissions versus meteorological variation on ozone attainment status. In addition, understanding and characterizing representative diurnal ozone cycles has long been recognized

as crucial for establishing new ozone standards and quantifying health impacts of continuous ozone exposure (Böhm et al., 1991).

A county is defined as out of attainment with the National Ambient Air Quality Standard (NAAQS) for ozone if the 3-year average of the annual 4th highest maximum 8-hour average exceeds 70 ppb (US EPA, 2019). Since the Industrial Revolution, Chicago has struggled with air pollution like many other major U.S. cities. Although emissions of ozone-precursor and summertime ozone levels have decreased significantly since the late 1970's, ozone in Chicago has never complied fully with standards set by the EPA to protect public health. (Holloway et al., 2008; American Lung Association, 2019)

2.2.2 Photochemical Smog and Biogenic VOCs

Photochemical smog is a mixture of ozone, nitrogen oxides and volatile organic compounds (VOCs) that react with sunlight to form mist. Volatile organic compounds and nitrogen oxides are mainly derived from anthropogenic emissions, with traffic emissions being the main factor. Smog formation tends to happen more frequently in the summer because of more sunshine. Most of nitrogen oxides and volatile organic compounds are produced from anthropogenic emissions. It results in photochemical smog. Organic compounds such as peroxyacytyl nitrate (PAN) are formed (US EPA, 2015).

Nitrogen dioxide (NO_2), which is formed in Equation 1, can be broken down by sunlight to form nitric oxide (NO) and an oxygen radical (O) in Equation 2. Oxygen radicals can then react with atmospheric oxygen (O_2) to form ozone (O_3) in Equation 3. Ozone is consumed by nitric dioxide to produce nitrogen dioxide and oxygen in Equation 4. The main source of hydrocarbons is the VOCs. Similarly, oxygenated organic and inorganic compounds (RO*x*) react with nitric oxide to produce more nitrogen oxides in Equation 6. The significance of the presence of the VOCs in these last two reactions is paramount. Ozone is normally consumed by nitric oxide, as in reaction 4. During the day, NO_2 concentration is increasing starting at 6 or 7 am, and it is increasing generally in the morning due to the people's traffic behavior. Automobiles emit NO*x* gases including NO_2 and NO. In daytime, the sufficient sunlight makes more O as shown in Equation 2. O reacts with O_2 to produce O_3 as shown in Equation 3, so the increasing O_3 might happen in the

late morning and afternoon. In Equation 4, NO will be depleted and more NO_2 is produced. Because the mixing ratio of NO is much lower than O_3, Equation 4 does not deplete ozone during the day in background tropospheric air. However, in urban air, Equation 4 can deplete local ozone at night because NO mixing ratios at night may exceed those of O_3 (g) (Jacobson, n.d.).

At the same time, if VOCs are present, nitric oxide and nitrogen dioxide can be consumed as in Equation 5 and 6, allowing the buildup of ground level ozone in Equation 6 (*EPA Information—Photochemical smog—What it means for us*, n.d.).

$2NO + O_2 \rightarrow 2NO_2$ Equation 1

NO_2 + sunlight → NO + O Equation 2

$O + O_2 \rightarrow O_3$ Equation 3

$O_3 + NO \rightarrow NO_2 + O_2$ Equation 4

NO_2 + R → products such as PAN Equation 5

NO + RO*x* → NO_2 + other products Equation 6

There are no serious anthropogenic ozone emissions. Ozone-producing processes involving solar radiation (hv) absorption by nitrogen dioxide and ozone scavenging by nitric oxide (NO) may be characterized in Equation 2 (World Health Organization, 2000). The peak amount of ozone that can be achieved in a polluted environment is not only dependent on the absolute concentrations of volatile organic compounds and nitrogen oxides (NO*x*), but also on their ratio (Jacobson, n.d. ;World Health Organization, 2000). Meteorological conditions are the rate-limiting factor in photochemical processes. Summer conditions favor the formation of ozone primarily. Generally,

concentrations in city centers are lower than those in suburbs, mainly as a result of the scavenging of ozone by nitric oxide originating from traffic (World Health Organization, 2000).

In addition, NO_2 reacts with OH to produce HNO_3 as shown in Equation 1. HNO_3 can keep its lifetime against photolysis 15-80 days. The time depends on the day of the year and the latitude. Nitric acid is red fuming appears as a pale yellow to reddish brown liquid generating red-brown fumes and having a suffocating odor. It is very toxic by inhalation and corrosive to metals or tissue. Prolonged exposure to low concentrations or short term exposure to high concentrations may result in adverse health effects (PubChem, n.d.). And HNO_3 (g) is soluble in water, much of it can be dissolved on cloud drops or aerosol particles.

$NO_2 + OH \rightarrow HNO_3$ Equation 7

The main source of hydroxyl radical (OH) is from the reaction between O_3 and H_2O. The NO_2 is removed from air in Equation 7. At the same time, O_3 also can be removed by producing more OH in Equations 8&9. Therefore, NO_2 and O_3 concentration will decrease in daytime due to Equation 7-10.

$O_3 + hv \rightarrow O_2 + O(^1D)$ Equation 8

$O(^1D) + H_2O \rightarrow 2OH$ Equation 9

More O_3 is formed by Equation 1-3 by more NO_2 in daytime. In nighttime, a lot of ozone production shuts down at night because of lacking O and light. At same time, NO_2 could react with ozone in Equation 10 to consume ozone and reduce ozone concentration.

$NO_2 + O_3 \rightarrow NO_3 + O_2$ Equation 10

Additionally, VOCs also influence the concentration of ozone. NO*x* and VOCs as the precursors of photochemical reactions impact the production of ozone pollutants. Vogel et al. (1995) in Germany found ozone concentration decreased about 18 ppb without BVOC emission during

episodes of high air temperatures. This shows significant effects of biogenic VOC emissions on ozone concentrations at high temperatures. Solmon et al. (2004) also found biogenic emissions increase ozone concentrations at some observation stations in urban and rural areas. Main BVOCs related to transportation emissions included isoprene and monoterpene (MT). Isoprene is mainly from vegetation.

Chapter 3 - Transportation Related to NO*x* emissions

3.1 The Impacts of the Types of Vehicles and Vehicle Technologies for NO*x* Emission

According to Russian national inventory data, road transport accounts for more than 50% of NO*x* emissions, which is due to the continued growth of the fleet (Lozhkina & Lozhkin, 2016). Lozhkina and Lozhkin pointed out that a key gap in understanding these emissions is the impact of changes in vehicle speed and engine load on the average emissions rate of road vehicles (Lozhkina & Lozhkin, 2016). Nitrogen oxides from vehicles are primarily formed in internal combustion engines at temperatures in excess of 170 °C (Fenimore, 1971; Miller & Bowman, 1989). Their chemical processes of formation, transformation and decomposition are complex and complicated. Reducing emissions from diesel and petrol vehicles can help improve air quality in US cities. The US Environmental Protection Agency concluded that air pollution in 2008 was lower than 1990 for NO_2 (35% reduction) nationwide (US EPA, 2010). With the replacement of old vehicles in the road fleet, NO*x* emissions from diesel vehicles will continue to decrease (Wallington et al., 2013).

On the basis of power normalized, the NO*x* emissions of new diesel fleets have dropped by about 60 times in the past 20 years. The NO*x* emission standards for European light-duty diesel engines are significantly less stringent than those for gasoline vehicles (for example, EURO V NO*x* standard for M1 [passenger cars] gasoline is 0.06 g/km and the diesel vehicle is 0.18 g/km) (Wallington et al., 2013). Emissions estimates from May et al. (2014) and Shorter et al. (2005) show that for low-emission vehicles, including hybrid and CNG buses, the median NO_2/NO*x* ratio is less than 0.1, but may be as high as 0.7 for diesel particulate filters and trucks with unknown emission control systems. In addition, biodiesel can result in higher emissions of NO*x*. While biodiesel has received significant attention as an improved fuel for petroleum diesel, its advantages include reduced net carbon dioxide, hydrocarbon, carbon monoxide and particulate matter emissions, and fuel properties similar to petroleum diesel for use in diesel engines. However, one of its limitations is more NO*x* emissions. Diesel engines use highly compressed hot air to ignite the fuel. Air, mainly composed of oxygen and nitrogen, is initially drawn into the combustion chamber. Then, it is compressed, and the fuel is injected directly into this

compressed air at about the top of the compression stroke in the combustion chamber. The fuel is burned, and the heat is released. Normally in this process, the nitrogen in the air does not react with oxygen in the combustion chamber and it is emitted identically out of the engine. However, high temperatures above 1,600 °C in the cylinders cause the nitrogen to react with oxygen and generate NO*x* emissions. So, it will not be wrong to say that the major influences of the formation of NO*x* are the temperature and concentration of oxygen in the combustion process. The amount of produced NO*x* is a function of the maximum temperature in the cylinder, oxygen concentrations, and residence time. Most of the emitted NO*x* is formed early in the combustion process, when the piston is still near the top of its stroke. This is when the flame temperature is the highest. Increasing the temperature of combustion increases the amount of NO*x* by as much as threefold for every 100 °C increase (Lee et al., 2013). Sun et al. (2010) focus on reviewing of higher emissions of oxides of nitrogen. The NO*x* formation mechanism is a complex process that makes it difficult to fundamentally determine how biodiesel affects NO*x* emissions. Several parameters appear to affect the observed differences in biodiesel NO*x* emissions (Sun et al., 2010). Besides, higher NO*x* emissions of light diesel vehicles compared to petrol vehicles are considered (Hu et al., 2012).

For petrol vehicles, Lozhkina confirmed that the NO*x* emission rate of passenger cars without catalytic converters has a gradual increase in NO*x* emissions from 80 km/h to 90 km/h. The NO*x* emission rate of a vehicle equipped with a three-way catalytic converter depends on three main factors: engine speed, vehicle speed, and catalyst recovery efficiency. A particular feature of the NO*x* emission curve for a vehicle equipped with a catalyst is that there are two maximum values: one at 5-15 km / h and the second at high speed at about 100-120 km / h. The lowest value of NO*x* emissions (about 0.15-0.2 g / km) was also observed in the speed range of 20-90 km / h (Lozhkina & Lozhkin, 2016). Lozhkina also found that the NO*x* emission dependence of the Euro I – Euro V petrol powered engines is parabolic, with maximum emissions at <20 km / h at low speeds and > 100-110 km / h at high speeds. The low speed <20 km / h is the residential area or parking area after the start of the journey, or the traffic jam when the car is accelerating/decelerating. Under these circumstances, the ineffective operation of the catalyst at insufficient temperatures in the first case and the temporary violation of the stoichiometric air-fuel ratio in the second case may result in high NO*x* emissions (Lozhkina & Lozhkin, 2016).

Figure 1 shows that Europe has developed Euro standards which have continuously been lowered since 1993 with Euro I to Euro VI. The limits are defined in mass per energy (g/kWh) in this table. Regulations in Euro standards become progressively more stringent in the ensuing years. Compared to Euro I standard, Euro VI standard for NO*x* emissions was decreased, 95 %. The implementation date of Euro VI standard for heavy-duty vehicles was 1st of September 2014 (Delphi, 2012).

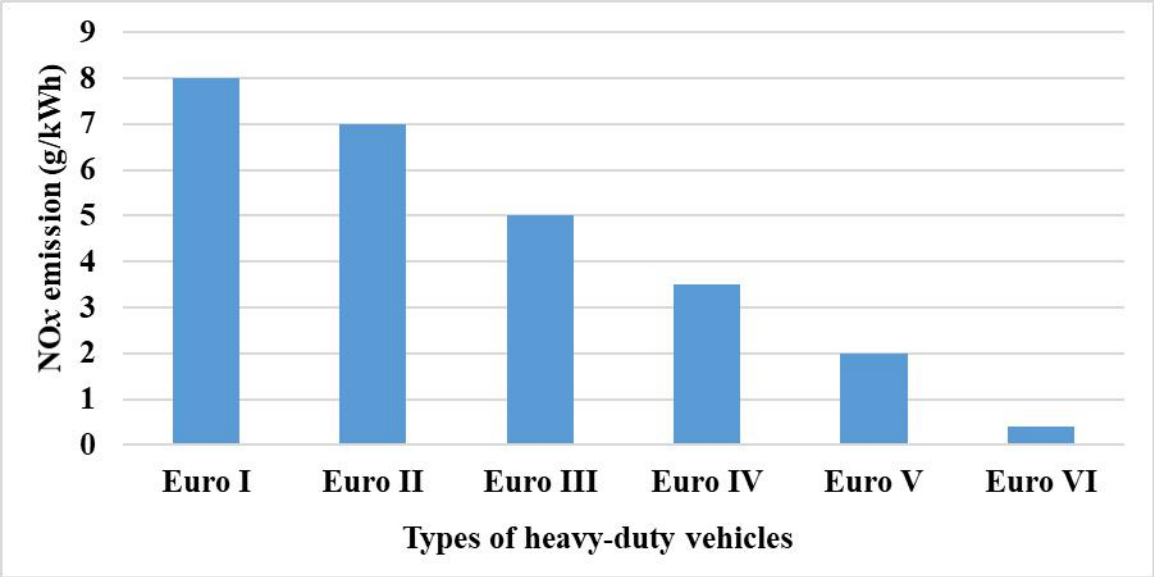

Figure 1.Euro standards of European Union for heavy-duty vehicles (Delphi, 2012).

The results confirm their findings for diesel cars that minimal NO*x* emissions from diesel vehicles correspond to a narrow speed interval with the upper value being 60–65 km/h. Under congested traffic conditions, real life emissions were significantly higher with driving patterns that differed more than when driving at steadier speeds. Modern vehicles with diesel engines emit more NO*x* than the cars of the same emission class with petrol engines. They confirmed previous conclusions of the European investigators (Hagman et al., 2011). Some diesel passenger vehicles may emit in urban traffic up to 40 times more NO*x* than petrol engine cars of the same emission class (Lozhkina & Lozhkin, 2016). Wang et al. (2019) found that diesel taxis have high NO*x* emissions. Diesel taxis have NO*x* emissions that are almost three times that of gasoline taxis. Although light diesel engines have the advantages of energy saving and reduced carbon dioxide emissions, light gasoline vehicles are superior to light diesel vehicles in terms of NO*x*

control. They studied the real-world fuel efficiency and NO*x* emission curves of light diesel vehicles. Compared with similar gasoline models, the average NO*x* emission factor of diesel vehicles is about three times that of gasoline vehicles. Two of the three modern Sonata taxis equipped with exhaust gas recirculation (EGR) + diesel oxidation catalyst (DOC) emission control strategies showed significantly higher levels of nitrogen dioxide emissions and nitrogen dioxide than other diesel taxis. Nitrogen oxide ratio of light diesel vehicles, thus raising concerns about possible adverse effects of urban ozone pollution problems combined with this technology (Hu et al., 2012). Oxidation catalytic converters of modern vehicles facilitating the formation of NO_2 in the exhaust line, especially in diesel cars equipped with original equipment manufacturer (OEM) particle filters, are assumed to be responsible. Highest emissions of NO*x* are recorded for diesel cars equipped with OEM particle filters with mass ratios of NO_2 within NO*x* of up to 70% (Alvarez et al., 2008). Diesel cars are popular in European countries. Although the NO*x* emissions of petrol passenger vehicles have been greatly reduced over the past decade, in order to meet emission standards, NO*x* emissions from diesel vehicles must be reduced within the next few years. It requires a very high degree of technical success in vehicle or fuel industries.

Selective catalytic reduction (SCR) is a technology to reduce NO*x* emissions and especially for high-duty vehicles. Because of low exhaust temperature, it has not been used widely for light duty vehicles. But nowadays, it is being developed for light-duty passenger vehicles and a few light-duty vehicle manufacturers like Audi have been using this technology in their automobiles (Reşitoğlu et al., 2015). SCR is used to minimize NO*x* emissions in the exhaust gas with ammonia (NH_3) as the reductant (Biswas et al., 2009). Water and N2 are released as a result of catalytically conversion of NO*x* in the exhaust gas. Due to the toxic effects of NH3 and to prevent burning of NH_3 in the warm atmosphere before the reaction, NH_3 is provided from an aqueous solution of urea (Moreno-Tost et al., 2008; Hamada & Haneda, 2012) This solution is obtained from mixing of 33 % urea ($(NH_2)_2CO$) and 67 % pure water by mass. In order to get high efficiency, the amount of NH_3 stored on the SCR catalyst should be controlled as well as possible. However, high NH_3 storage can lead to undesired ammonia. Ammonia slip is generally avoided or minimized by the precise injection of urea based on the required ammonia (Majewski & Khair, 2006). By spraying solution on exhaust gas, as a result of the pure water vaporization, solid urea particles begin to melt and thermolysis takes place. SCR has high efficiency in NO*x*

conversion. Unlike Lean NO*x* Trap (LNT) technology, SCR removes NO*x* continuously through the active reductant on the catalyst surface. Otherwise, LNT has a wide operating temperature window and lower desulfurization temperature. Because it leads to an increase in HC and CO emissions and low NO*x* conversion efficiency compared to SCR and LNT, exhaust gas recirculation (EGR) lags behind. In many applications, these technologies can be used as combination to increase NO*x* conversion efficiency (Xu & McCabe, 2012; López et al., 2009).

In addition, diesel oxidation catalyst (DOC) could be used in conjunction with SCR catalysts to oxidize NO into NO_2 and increase the NO_2: NO*x* ratio. Equation 1 is the main reaction related to NO conversion to NO_2 (Zheng & Banerjee, 2009).

NO_2 concentration in the NO*x* is vital for downstream components like diesel particulate filter (DPF) and SCR. A high NO_2 concentration in the NO*x* increases efficiency of DPF and SCR. In the untreated engine exhaust gas, the NO_2 component in the NO*x* is only about 10 % at most operating points. With the function of the DOC, NO_2:NO ratio is increased by inducing thermodynamic equilibrium (Lee at al., 2008; Sampara et al., 2007).

Urea SCR technology for diesel vehicles may decrease NO*x* emission from diesel cars considerably. The detailed description is in Chapter 6. This method has benefits to control NO*x* pollution in urban areas.

3.2 Modeling of Air Quality Monitoring

Different methods and software could be used to assess NO*x* air pollution caused by vehicle emissions and predict short-term and/or long-term air quality values (Wang et al., 2009; Lozhkina & Lozhkin, 2015; Lozhkina & Lozhkin, 2016; Ghude et al., 2013; Milosavljevic et al., 2015). They mention two main types of computing models: Top-down and Bottom-up.

'Top-down' approach is a macro-scale approach. Models are designed to determine major pollutant emissions on the regional or national scale and are based on the statistical information about the vehicle fleet structure (Lozhkina & Lozhkin, 2015). Wang et al. pointed out regional or national-scale vehicle emissions inventories are usually developed using a top-down approach in

China. However, this approach has some limitations (Wang et al., 2009). On the other hand, 'Bottom-up' approach is a micro-scale approach. These models provide data on emission of pollutants from motor vehicles on street scale. The calculations are based on a full-scale survey of the traffic-flow structure and then assess the dispersion of substances near the road (Lozhkina & Lozhkin, 2015).

3.2.1 Top-down Approach

In Ghude's work, they used the Ozone Monitoring Instrument (OMI) tropospheric NO_2 column retrievals in India, using the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) emission inventory to simulate the tropospheric NO_2 column using the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) model. They determined the local relationship between the simulated emissions and the tropospheric column and iteratively applied this relationship to the OMI observations to arrive at an optimized NO*x* emissions inventory. Their top-down inventory captures many of the missing hot spots in the original inventory and indicates that INTEX-B stocks overestimate emissions in India-in the eastern parts of the East and underestimate point sources (Ghude et al., 2013).

WRF-Chem overall captures the spatial features of retrieved Tropospheric Vertical Column Densities (TVCDs) such as higher values over the IG (Indus-Gangetic plain) region and lower values over the central and far northeastern region of India. However, it shows poor agreement for specific spatial features. WRF-Chem overestimates the magnitude of retrieved tropospheric NO_2 column over most of the study domain; the IG region is overestimated. Modeled NO_2 columns are also higher than OMI measurements over the southern tip (Kerala) of India (Ghude et al., 2013). The observed discrepancies between simulated and observed tropospheric NO_2 column are consistent with results from previous studies over India (Kumar et al., 2012; Kunhikrishnan et al., 2004). Ghude et al. (2013) have mapped and derived an independent NO*x* emission estimate for India based on OMI tropospheric NO_2 retrievals and the WRF-Chem model using an iterative inverse technique.

The overall total NO*x* emissions for India in 2005 are comparable with the estimate of EDGARv4.1 and in the INTEX-B inventories (Ghude et al., 2013). However, they found that

there is in general an overestimation of NO*x* emissions in the INTEX-B inventory for the Western and Eastern IG region and the Southern tip of India (Kerala), as well as underestimation over large power plants, cities, and MGIC region. Significant changes in the modeled spatial distribution of daytime maximum O_3 are seen when the optimized top down inventory is used instead of the INTEX-B inventory (Ghude et al., 2013). This method provides a potential basis for mapping and evaluating robust independent NO*x* emissions and trends although there are still remaining uncertainties in the top-down estimate (Ghude et al., 2013).

Wang et al. (2009) compared two approaches for the emission statistics, and they believe that the 'top-down' approach has some limitations for the emission inventory in the city. For example, for 'top-down' approach, the same emission factors for each vehicle at average speed, or emissions from space alternatives from larger geographic scale, may not reflect actual vehicle emission conditions on a local scale (Wang et al., 2009). In their studies, the data on vehicle activity data used in macroscale methods reflect the static level of average vehicle activity throughout the city. There may be significant differences between these data and actual vehicle activity levels on the road (Wang et al., 2009). Travel demand model (TDM) and field investigation are applied to grid-based methods that reflect actual vehicle activity on the road. However, due to its intrinsic drawbacks, the "top-down" approach cannot determine the spatial distribution of accurate Vehicle Kilometers Traveled. It underestimated by 8% and 63% the activity for Passenger Cars and taxies in Wang's studies (Wang et al., 2009).

In the situation, the macro-scale approach has shortcomings because the uniqueness of some cities may affect monitoring results. Wang et al. focused on investigating the air quality in Beijing, China. Due to the importance of Beijing in China, there are many non-local vehicles and military vehicles in the urban area (Wang et al., 2009).

However, these types of vehicles are not included in local statistics. They are excluded from the vehicle emissions inventory used in top-down approach, so this may also result in underestimation of vehicle activity and emissions in the Beijing area (Wang et al., 2009).

Additionally, In Beijing, the use of heavy-duty trucks (HDTs) is limited in urban areas, so most of their activities take place in the suburbs. This contributes to high vehicle NO*x* emissions in the suburbs of Beijing. However, the top-down approach will overestimate 51% and 211% of light vehicle (LDT) and HDT vehicle activity compared to the bottom-up approach. Since trucks are the main source of NO*x* emissions in large cities in China, the top-down approach seems to overestimate NO*x* emissions in Beijing (Wang et al., 2009).

3.2.2 Bottom-up Approach

Air quality in India/Asia has been estimated using traditional bottom-up approaches integrating information about emission source types, fuel consumption, and source specific emission factors (Ghude et al., 2013). The Operational Street Pollution Model (OSPM) and COPERT Methods both are bottom-up approach. OSPM is a well-known semi-empirical model designed to assess the air quality within a street canyon (Milosavljevic et al., 2015). This model developed by the Danish National Environmental Research Institute (NERI) calculates the hourly average concentration of different pollutants on the street, giving the traffic volume on the street (Fu et al., 2001). COPERT is a Microsoft Windows software program aiming at the calculation of air pollutant emissions from road transport and is one of the most common simulation methods for modeling vehicle emission in the European context. A large amount of laboratory data is statistically processed in the COPERT project which has an emission factor that can be expressed as a function of vehicle speed. On the other hand, semi-empirical OSPM is precisely used to evaluate air pollution in canyon streets, where vehicle emissions are modeled using the COPERT method (Milosavljevic et al., 2015). In Branimir's analysis, knowing the final value of the simulated NO*x* concentration, the COPERT method defines the actual emission factor (EF) of the Serbian fleet sample (Milosavljevic et al., 2015). In addition, Wang et al. (2009) pointed out the bottom-up approach of the TDM traffic model and MOBILE5B-China was used to assess traffic-induced emissions in Beijing. MOBILE5B, developed by the US EPA, uses average speed, vehicle fleet characteristics, ambient condition, and other parameters to estimate emission factors. NO*x* for grid-based vehicle emissions is calculated based on grid-based vehicle activity and emission factors, and they show a clear spatial distribution (Wang et al., 2009). Compared to the top-down approach, the bottom-up approach, when vehicle kilometers traveled (VKT) is combined with emission factors, grid-based methods may be more sensitive when measuring

emissions effects caused by specific changes in each grid, especially those at low speeds (e.g., highly congested areas) and high speeds (e.g., the area with freeways) (Wang et al., 2009).

3.2.3 The Selection of Air Monitors and the Development of Air Monitoring Systems

Air quality monitoring systems become significant due to the importance of air quality. The low-cost air quality monitors have been developing rapidly due to research progress. EPA monitors are providing more precise data, but much money needs to be spent to monitor air quality at these sites. However, the precision of its data is still worthy of discussion. In the present, trying to improve the precision of data for low-cost air quality monitors is an important problem. Many researchers focus on the precision of the results. Besides considering which type of monitor, we need to choose methods to obtain more effective data economically. How to use scientific methods to develop a more effective air monitoring system is also important.

According to EPA's Air Sensor Guidebook, the research question and pollutant of interest should govern the size and siting of the sensor network (US EPA, 2016). For instance, if the question involves how air pollutant concentrations vary in the outdoor and indoor environment, a small number of sensors may be needed and siting criteria would include considerations like weather, ventilation, sources, and obstructions (US EPA, 2016). However, if one would like to reliably monitor concentrations over a large area, sensor siting is still important but so is sensor redundancy, pollutant variation, and sensor density within the network (US EPA, 2016). A variety of low-cost air quality sensors and sensor systems are presently available. These sensor systems may measure one or more pollutants and/or environmental parameters, employing one of a variety of measurement techniques. Some sensor systems include onboard algorithms to transform raw data signals into pollutant concentrations. Each uses its own data structure to capture, store, and publish the data. The recent emergence of low-cost micro sensors measuring various air pollutants has significant potential for carrying out high-resolution mapping of air quality in the urban environment. However, the data obtained by such sensors are generally less reliable than that from standard equipment and they are subject to significant data gaps in both space and time. In order to overcome this issue, some researchers present a data fusion method based on geostatistics that allows for merging observations of air quality from a network of low-cost sensors with spatial information from an urban-scale air quality model (US EPA, 2016).

In order to evaluate the current air quality and the effect of air pollution control measures, larger communities maintain monitoring networks. The EPA, as well as most of the states, maintain their own surveillance networks. The ideal objective when installing a monitoring network is to be able to obtain continuous real time data. Continuous monitoring is used with many methods and chemiluminescence reaction with ozone is used for federal reference methods. Coulometric and chemiluminescent reaction with ozone are continuing monitor methods of Nitrogen Dioxide for Federally Regulated pollutants (US EPA, 2016).

Satellite measurements are particularly important when sufficient ground-based measurements are lacking. In Cui's study, a nested GEOS-Chem simulation was used to confirm anthropogenic emissions for NO*x* emissions of western China. The model is run with the full O*x* -NO*x* -VOC-CO-HO*x* gaseous chemistry and online aerosol calculations, and it is driven by the GEOS-5 assimilated meteorology from the NASA Global Modeling and Assimilation Office (Cui et al., 2016).

Minimizing interferences in measurements is necessary but difficult. Many researchers are looking for good methods to get reliable data without interferences. In Xu's study, they conducted roll-around mobile monitoring of NO/NO_2/NO*x* with 1-minute resolution during 14 days of measured activities in and around Chicago, IL, to explore how personal NO/NO_2/NO*x* exposures vary spatially, temporally, and within different microenvironments in an urban environment (Xu et al., 2017). Their measurements were made by new direct UV absorbance NO/ NO_2/NO*x* monitor that is designed to minimize interferences that have been observed in field campaigns using chemiluminescence monitors. They designed monitors to capture data in primary microenvironments: outdoors, indoors inside various building types, and in multiple modes of transportation including walking, personal vehicle, and various modes of public transit. Results are intended to more accurately demonstrate the spatiotemporal variability in personal NO*x* exposures encountered during typical daily activity in an urban environment and to improve knowledge of how personal NO/NO_2/NO*x* exposures correlate with ambient central-site monitors in urban environments. Scripted activities were designed to capture a wide variety of typical behaviors and microenvironments encountered by residents of Chicago, including travel via

multiple modes of transportation (e.g., personal vehicle, city bus, subway, elevated train, regional commuter train, taxi, and walking), residential activities (e.g., inactive periods indoors and cooking activities), work/school activities (e.g., attending class, working in a laboratory, or working in an office building), and dining in restaurants (e.g., both fast food and sit-down). Each activity was scheduled to last at least 10 minutes to ensure adequate data collection in each microenvironment (Xu et al., 2017).

The heterogeneity of urban space is harder to capture by monitored data, because there are many different types of land use in urban areas. It is necessary to set up a dense network of measuring points, and to repeat these measurements many times, in order to gain an accurate picture of spatial pollution patterns and of the change in concentrations in urban space. Heavy pollution of the air in certain parts of the city, and also great variety in the degree of pollution confirms the thesis on the need for a dense spatial network of measurements (Mally & Ogrin, 2015).

Lin et al. (2015) pointed that ow-power, and relatively low-cost, gas sensors have potential to improve understanding of intra-urban air pollution variation by enabling data capture over wider networks than is possible with 'traditional' reference analysers.

The method of diffusive samplers is a method to collect data by passive sampling. The advantages of the method of diffusive samplers is their flexibility and practicality. The samplers are small, lightweight, durable when cared for properly and low-cost (Mally & Ogrin, 2015).

However, the diffusive samplers also have some disadvantages. Warren Spring Laboratory (Campbell et al., 1994) and researchers found that the use of diffusive samplers gave about 30% higher values, with the differences being higher in more heavily polluted environments. Poorly ventilated cities have no steady strong winds. It reduces the self-cleaning capacity of the air. Moschandreas et al. (1990) note that low temperatures (251–283 K) lead to an underestimation of NO_2 concentrations. In addition, the time at which the samplers are exposed can also influence measurement results. Besides, diffusive samplers provide only information about average pollution, and not maximum, hourly, multi-hourly values (Mally & Ogrin, 2015).

In Chapter 4, the data are all collected from Aeroqual monitors. The quality of data with the Aeroqual monitors has been investigated. (Lin et al., 2015; Lin et al., 2017; Masey et al., 2018). The results show that ozone in air impacts the readings when nitrogen dioxide is measured, and that it is beneficial to measure ozone and correct the measured value of nitrogen oxide when ozone concentrations are large. Methods to obtain useful field data are described in these papers.

Lin et al.(2017) thought that to reduce inaccuracies in the measurement of air pollutants by portable monitors it is necessary to establish quantitative calibration relationships against their respective reference analyser. They evaluated some types of portable monitors, including Aeroqual Ltd. (Auckland, New Zealand) S500 O_3 metal oxide and S500 NO_2 electrochemical. Aeroqual NO_2 monitors were sensitive to both NO_2 and O_3 and unresolved biases(Lin et al., 2017). Overall, however, they used the relationship between [Aeroqual_NO_2 −Reference_NO_2] and Aeroqual_O_3 to calibrate the Aeroqual NO_2 monitor concentrations. This effectively constrains the relationship between Aeroqual_NO_2 and Reference_NO_2 to be 1:1 (as may be expected for recent factory-calibration). In this study, they used the following multiple linear regression of Aeroqual_NO_2 on both Reference_NO_2 and Aeroqual O_3 (Lin et al., 2017).

$$\text{Aeroqual\_}NO_2 = k_1 \times \text{Reference\_}NO_2 + k_2 \times \text{Aeroqual\_}O_3 + k_3 \qquad \textbf{Equation 11}$$

This regression is based on the reasonable expectations that the Aeroqual O_3 monitor has a linear response to‘true’,i.e., reference analyser,O_3, and that the Aeroqual NO_2 monitor has a linear response to both NO_2 and O_3, but that its response to O_3 may be different from the Aeroqual O_3 monitor’s response to O_3 (Lin et al., 2017).

We observed significant bivariate linear relationships between Aeroqual O_3 and Reference O_3 concentrations, and significant multiple linear relationships between Aeroqual NO_2 and both Reference NO_2 and Aeroqual O_3 concentrations (Lin et al., 2017).

In addition, Masey et al. (2018) stated that they observed significant bivariate linear relationships between Aeroqual O_3 and Reference O_3 concentrations, and significant multiple linear relationships between Aeroqual NO_2 and both Reference NO_2 and Aeroqual O_3 concentrations.

Sensors for NO_2 have been shown to be cross-sensitive to O_3, meaning that both pollutants must be measured simultaneously to allow correction of the NO_2 sensor response (Masey et al., 2018)

Chapter 4 - Data Analysis on SASA project

4.1 The SASA Project and 4 Communities in Chicago

Shared Air/Shared Action (SASA) is Community Empowerment through Low-Cost Air Pollution Monitoring, an EPA Air Pollution Monitoring for Communities Grant (*Shared Air/Shared Action (SA2): Community Empowerment through Low-Cost Air Pollution Monitoring | Center for Hazardous Substance Research*, n.d.). Kansas State University (KSU) and seven partners proposed addressing air monitoring needs in South Chicago through the creation of the Shared Air/Shared Action (SASA) project. The project has monitored the air quality of 4 communities in Chicago using various low-cost monitors. In addition, the investigations also collected some data in different areas of the U.S. through the EPA. Data on NO*x* and ozone that have been collected was searched for and the data analytics and statistics were used for the purpose of gaining a better understanding of the sources, air quality, and health. Finding ways to use data to improve air quality and health is important. The project focused on 4 main communities: Little Village (LV), Northbrook (NB), Southeast (SE), and South Loop (SL). Low-cost monitors "Aeroqual" for the SASA project (SASA_AQ) were utilized to monitor NO_2 and O_3 concentration in the communities, and many regulatory monitors from EPA also were used to monitor the neighborhood of the communities.

In January 2019, a three-day conference was held with video recording of the presentations (Erickson, 2019). The most recent progress report is available on the U.S EPA Internet site (Griswold, n.d.). There are STI reports that provide some results following an analysis of the data (STI Report, 2018a, STI Report, 2018b). The data is available at http://fingolfin.kdd.cs.ksu.edu:8080/airquality/download/.

Figure 2 Satellite map of the LV community from Google Maps. (The green spot is the position of the sensor of SASA_AQ1 for monitoring NO_2 and the sensor of SASA_AQ2 for monitoring ozone.)

Figure 2 shows the detailed geographical distribution of Little Village (LV). It is a dense human settlement. There are many restaurants and stores, including auto shops. The commercial activities tend to attract more vehicles in this area. Transportation can influence the NO_2 concentrations. Busy traffic means more NO_2 emissions from automobile exhaust. In addition, the monitors are located near the main streets such as S Spaulding Ave and W 25 St. This makes the NO_2 concentrations higher due to the emissions from transportation. SASA project involved 525 hours to monitor NO_2 concentration of Little Village by sensor "Aeroqual" from 4/18/2017 16:00 to 6/28/2017 10:00. Regulatory monitor close to Little Village is site "17_31_4002", which collect 1674 hours of NO_2 concentration from 4/18/2017 16:00 to 6/28/2017 10:00 (STI Report, 2018b).

Figure 3. Satellite map of the NB community from Google Maps. (The green spot is the position of the sensor of SASA_AQ1 for monitoring NO_2 and the sensor of SASA_AQ2 for monitoring ozone.)

Figure 3 shows the detailed geographical distribution for Northbrook (NB). It obviously has more greenery than the LV community. There are few human settlements and few shops. This area is not a commercial zone; thus, the level of transportation activities is lower than in the LV community. In addition, the monitors are located far away from the main transportation road: Dundee Rd. It means NO_2 concentrations are lower because it could monitor less emissions from transportation. It can be predicted that the average level of NO_2 concentrations measured were lower than in the LV community.

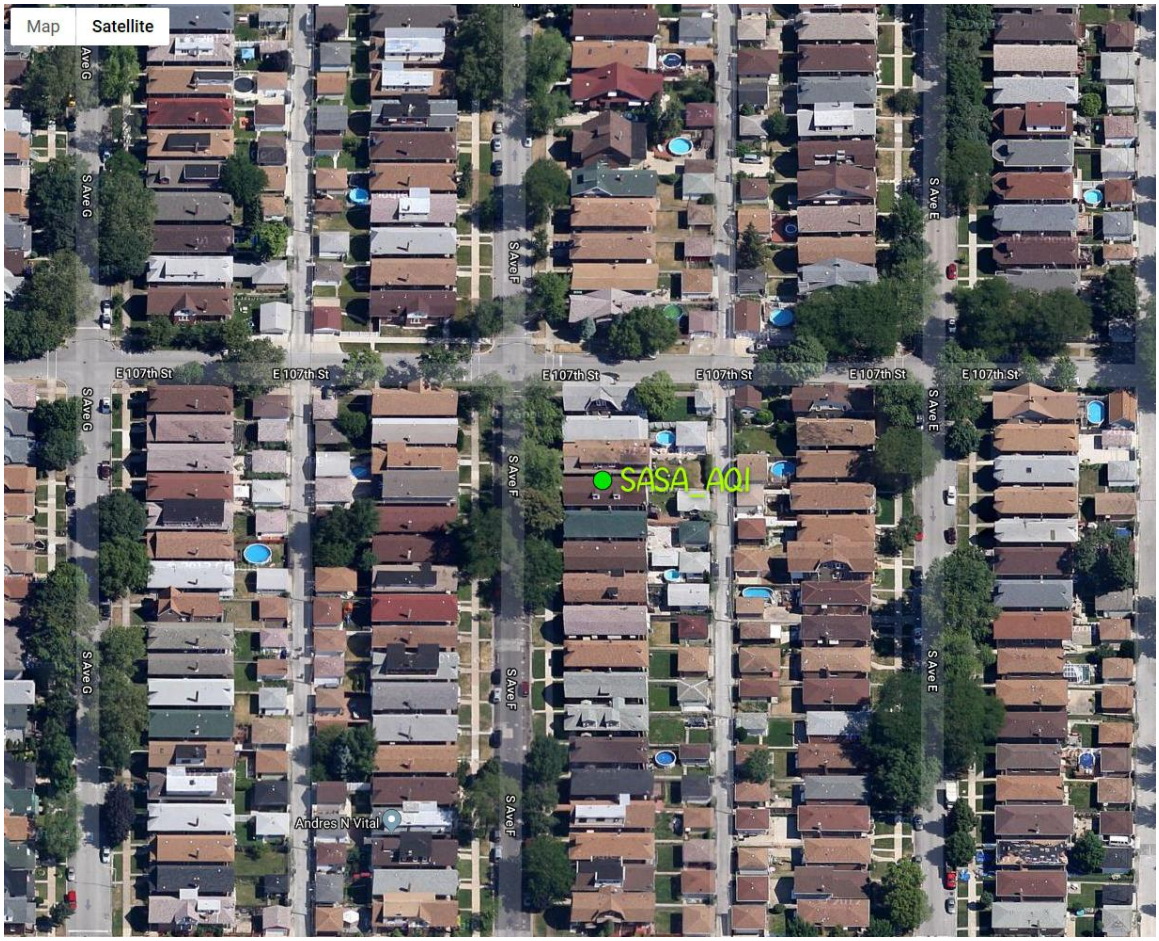

Figure 4. Satellite map of the SE community from google map (The green spot is the position of the sensor of SASA_AQ1 for monitoring NO_2.

Figure 4 shows the detailed geographical distribution of Southeast (SE). There are many houses and apartments but few shops. This area is also not a commercial zone; thus, the transportation activity is lower than in the LV community. However, many people who live in this area need to leave by vehicles, so the intensity of traffic in this area is not very low. Additionally, the monitors are close to the intersection of S Ave F and E 107th ST. It makes the concentration higher due to the emissions from transportation. SASA project involved 213 hours to monitor NO_2 concentration of Southeast by sensor "Aeroqual" from 7/30/2017 11:00 to 3/24/2017 13:00. Regulatory monitor close to Southeast is site "17_31_0076", which collect 5365 hours of NO_2 concentration from 7/30/2017 11:00 to 3/24/2017 13:00 (STI Report, 2018b).

Figure 5. Satellite map of the SL community from Google Maps. (The green spot is the position of the sensor of SASA_AQ1 for monitoring NO_2.)

Figure 5 shows the detailed geographical distribution of South Loop (SL). This area is an education zone because there are many schools like Daystar Academy, Perspectives Charter Schools, South Loop Piano Lessons, and Forward Momentum. Thus, the transportation activities will be influenced by the students' traffic behavior and school hours. There will be more regular variations of NO_2 concentrations due to emissions from transportation. Additionally, there are also some shops. They also can bring much traffic to the area. Moreover, the monitoring sensors are close to the Perspectives Charter schools and other schools, so the data collected on NO_2 concentrations has time variations, as they are influenced by school hours. SASA project involved 390 hours to monitor NO_2 concentration of South Loop by sensor "Aeroqual" from 9/13/2017 13:00 to 10/2/2017 17:00. Regulatory monitor close to South Loop is site "17_31_0063", which collect 460 hours of NO_2 concentration from 9/13/2017 13:00 to 10/2/2017 17:00 (STI Report, 2018b).

All of the communities involved in the SASA project are impacted by diesel exhaust. Little Village is a Latino neighborhood and the Southeast Side is a mixed Latino/European immigrant community. Both these neighborhoods are heavily impacted by industrial activity. South Loop, the non-environmental justice community, is a gentrified neighborhood bordering transportation areas. The area has heavy construction activities and considerable vehicle emissions during rush hours (STI Report, 2018b).

4.2 Data Visualization and Analysis

Data were provided to Sonoma Technology, Inc. (STI) by Kansas State University (KSU). This included raw and hourly data from Aeorqual ozone and NO_2 at multiple fixed locations. Low-cost air pollution sensors were deployed in these communities to monitor air pollution and foster a shared understanding of community exposure. STI organized the data by deployment (summer 2017, winter 2018) and by community. They then examined each data set to confirm sensor locations and data collection periods were valid. They provided KSU with recommended quality control (QC) procedures; KSU subsequently provided a QC'd dataset. Regulatory monitoring data were examined for negative values and extreme outliers which were removed (STI Report, 2018b). As part of QC, STI examined a diurnal box plot of each sensor at each location. STI then examined scatter plot and correlation matrices of the sensor data paired with data from nearby regulatory monitors. The goal was to identify if there were any clear biases for an individual sensor, and whether the inter-site variability appeared to be typical of ambient air pollution. NO_2 sensor measurements had very unusual variability, indicating likely interference of the NO_2 measurement from ozone or other gases with reactive oxygen, which is not unusual for this type of sensor (STI Report, 2018a).

Ambient air pollutant measurements were made in the Little Village area with sensors during 6/1/2017 – 8/10/2017 (summer) and 3/11/2018 – 3/31/2018 (winter) by SASA. Sensor "Aeroqual (SASA_AQ1)" was used to monitor NO_2 pollutant, and Sensor "Aeroqual (SASA_AQ2)"was used to monitor O_3 pollutant (STI Report, 2018b).

Table 2. Summary statistics of daily averages from sensors deployed in Little Village in the summer (6/7/17-8/10/17) time period (STI Report, 2018b).

Pollutant	N Hours	N Days (Complete)	Summary Statistics using Complete Daily averages (ppm)				
			Mean	Minimum	Median	Maximum	St. Dev.
NO_2	509	19	0.0294	0.0168	0.0301	0.0456	0.0078
O_3	576	24	0.0309	0.0193	0.0318	0.0403	0.0062

According to the statistics of Table 2, the mean of NO_2 concentration in Little Village in summer is 0.0294. It is lower than the regulatory level of 1-hr average NO_2 concentration in NAAQS (0.1 ppm), and also lower than the regulatory level of annual average NO_2 concentration in NAAQS (0.053 ppm). The data of NO_2 contains results for 509 hours, and the data of O_3 contains results from 576 hours. Although there are some inferences in some days, the time is enough to avoid large error by using average values. Medians are very close to means in Table 2, but they are a little more than means.

Table 3. Summary statistics of daily averages for NO_2 pollutants measured at the regulatory monitors from nearby fixed site air monitoring locations in the summer (6/7/17-8/10/17) time periods (STI Report, 2018b).

Monitor Code	N Hours	N Days (Complete)	Summary Statistics using Complete Daily averages (ppm)				
			Mean	Minimum	Median	Maximum	St. Dev.
17_31_0063	1553	65	0.0132	0.0032	0.0124	0.0309	0.0069
17_31_0076	1530	65	0.0099	0.0039	0.0095	0.0202	0.0036
17_31_3103	1548	65	0.0152	0.0038	0.0143	0.0297	0.0057
17_31_4002	1545	65	0.0135	0.0048	0.0129	0.0241	0.0049

In Table 3, the regulatory monitors by EPA have more hours of data than in the SASA sensors. The times are all more than 1500 hours. It makes average values more precise. The mean values in Table 3 are smaller than the mean value for NO_2 in Table 2 which is to be expected because the SASA data is from closer to the road. The standard deviation in Table 2 is larger than the values in Table 3, which is to be expected because the mean value is larger.

The monitor "17_31_0063" is monitoring NO_2 in 321 S. Franklin, Chicago, Cook County. The monitor "17_31_0076" is monitoring NO_2 and O_3 in 7802 Lawndale, Chicago, Cook County. The monitor "17_31_3103" is monitoring NO_2 in Schiller Park, Cook County. The monitor "17_31_4002" is monitoring NO_2 and O_3 in Schiller Park, Cook County.

Table 4. Summary statistics of daily averages for O_3 pollutants measured at the regulatory monitors from nearby fixed site air monitoring locations in the summer (6/7/17-8/10/17) time periods (STI Report, 2018b).

Monitor Code	**N Hours**	**N Days (Complete)**	**Summary Statistics using Complete Daily averages (ppm)**				
			Mean	**Minimum**	**Median**	**Maximum**	**St. Dev.**
17_31_0032	1542	65	0.0389	0.0212	0.0373	0.0613	0.0094
17_31_4002	1260	51	0.0337	0.0187	0.0350	0.0525	0.0080
17_31_4201	1522	64	0.0351	0.0188	0.0352	0.0584	0.0094
18_89_2008	1545	65	0.0326	0.0176	0.0323	0.0536	0.0081

The data from the SASA project appear to have some values that are larger for NO_2 than some data collected from EPA monitors. From the literature review, the data for NO_2 are larger when they are near the road, and this may explain why some of the SASA values are larger.
Ozone concentrations from SASA sensors were similar to those at nearby regulatory monitors, but they still have some differences. The EPA monitor "17_31_4201" was used to collect data of O_3 concentration from nearby fixed site of Little Village. The site "17_31_4201" is 750 Dundee Ed., Northbrook, approximately 20 miles north of the Little Village Environmental Justice organization (STI Report, 2018a). Compared with data from Table 2, the mean, minimum,

median, and maximum of EPA monitors are larger than values from the SASA sensors in Little Village in same time period. However, the EPA monitor "17_31_4002" which was collected data of NO_2 and O_3 concentration from nearby fixed site of Little Village has some concentrations lower than the SASA sensor. The site "17_31_4002" is at 1820 S. 51st Ave, Cicero., near W 16th and S Laramie, approximately 3.5 miles west of the Little Village Environmental Justice organization (STI Report, 2018a). The agreement for ozone is better than the agreement for NO_2 when the EPA data is compared to the SASA data. The value of standard deviation is smaller for ozone for the SASA compared to the EPA data.

Figure 6 shows the collected data in all monitoring times. The monitors collected data in 1-hour intervals. According to the recorded measurements, the monitoring data collected on LV and SL is from the summertime period, and the data on NB is during the winter period. There are data for SE in March, July, and August. In the LV community, the sensor "SASA_AQ1" was used to monitor NO_2 pollutants from April 18 to June 28 in 2017. In the LV neighborhood, the regulatory monitor close to LV, EPA sensor "17_31_4002," was used to monitor NO_2 pollutants from April 18 to June 28 in 2017.

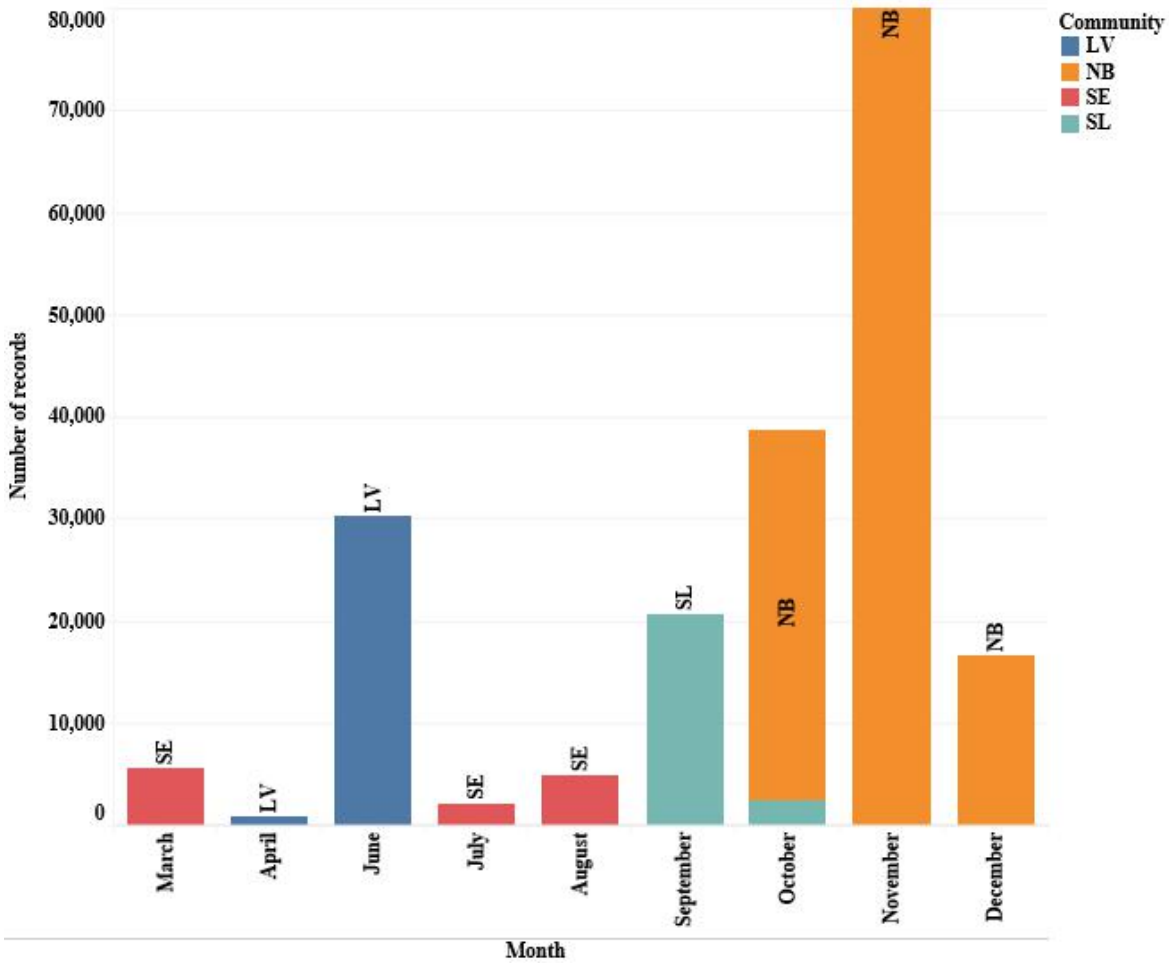

Figure 6. Number of the records of measurements in the LV, NB, SL, and SE communities for NO_2.

In the SL community, sensor "Aeroqual (SASA_AQ1)" was used to monitor NO_2 pollutants from September 13 to October 13 in 2017. In the SL neighborhood, the regulatory monitor close to South Loop, sensor "EPA17_31_0063," was used to monitor NO_2 pollutants from September 13 to October 13 in 2017. The locations of the monitors are shown in Figure 7.

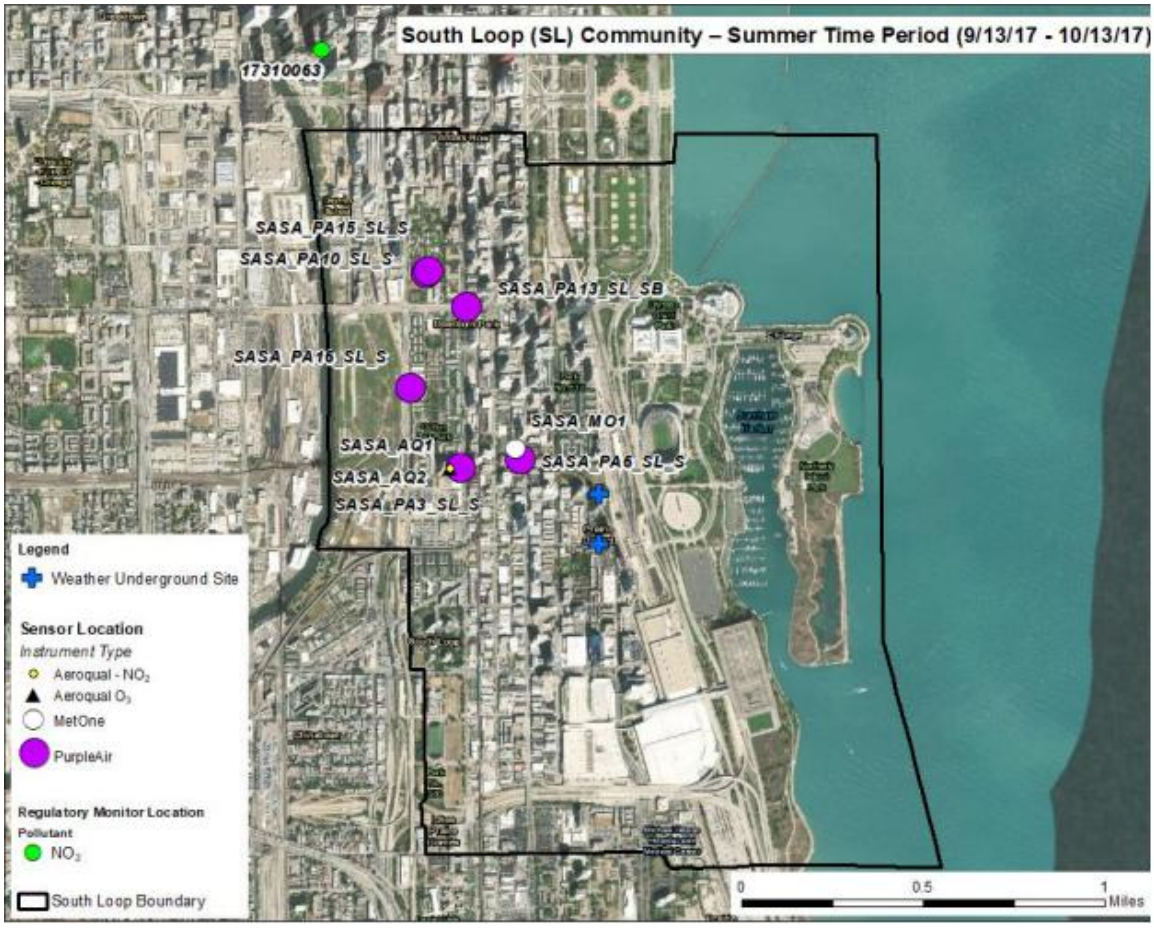

Figure 7. 2017 (9/13/2017 – 10/13/2017) sampling locations in South Loop including the sensors (yellow) plus regulatory monitor (green) locations. (Meteorology was obtained from Weather Underground sites; data were downloaded from the Weather Underground website.)

In Figure 7, EPA monitor "17-310-0063" is at 321 S. Franklin, Chicago. It can monitor NO_2 concentration.

In the Southeast (SE) community, Monitor "Aeroqual (SASA_AQ1)" was used to monitor NO_2 pollutants on some days from July 30, 2017 to March 24, 2018. In the SE neighborhood, the regulatory monitor close to the Southeast, EPA Monitor "17-310-076," was used to monitor NO_2 pollutants from July 30, 2017 to March 24, 2018. They are shown in Figure 8.

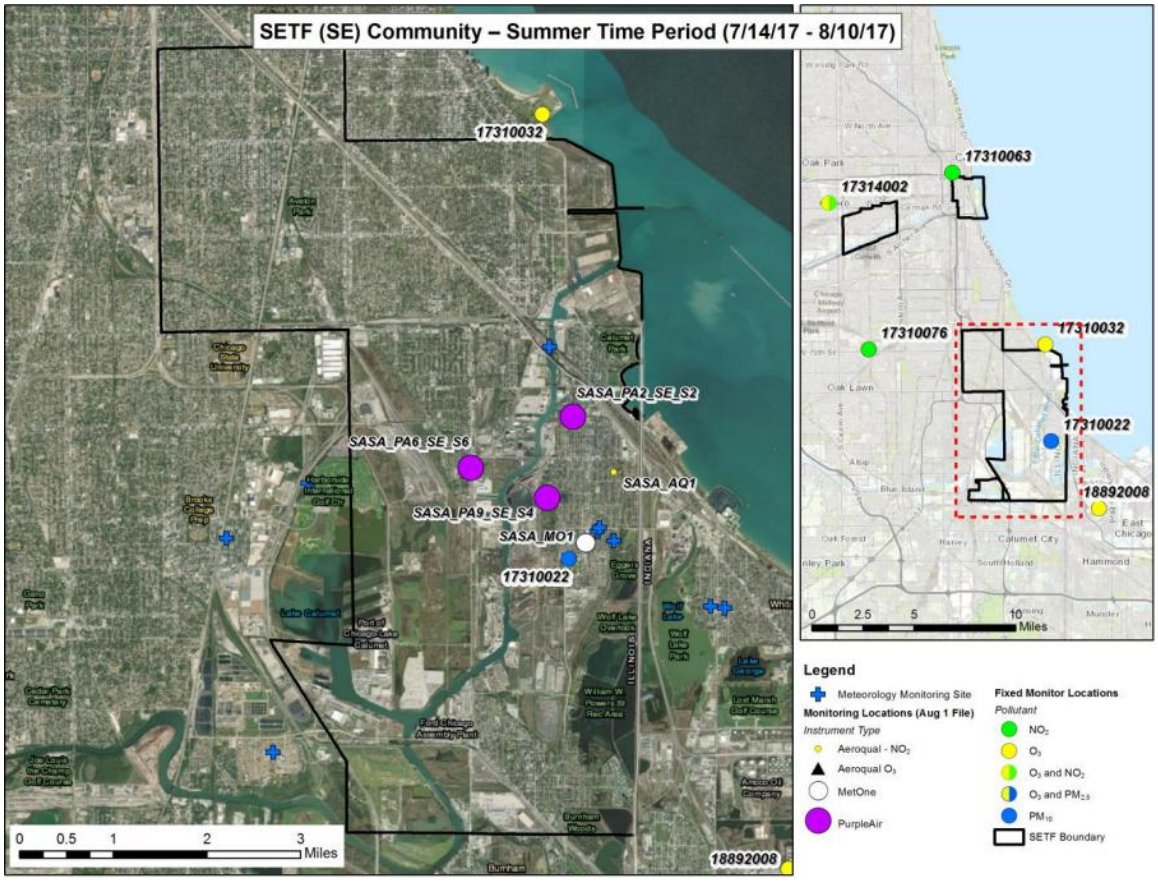

Figure 8. 2017 (7/14/2017 – 8/10/2017) sampling locations for Southeast. (The green sensors show monitor locations of NO_2 pollutant. The yellow sensors show monitor locations of ozone pollutant.)

For Little Village (LV), Monitor source "Aeroqual (SASA_AQ2)" was used to monitor ozone concentrations from April 18 to April 19, and from June 2 to June 28 in 2017. The address is LVEJO 2445 Spaulding. For South Loop (SL), Monitor source "Aeroqual (SASA_AQ2)" was used to monitor O_3 pollutants from September 13 to October 2 in 2017.

For the Northbrook (NB), Monitor source "Aeroqual (SASA_AQ2)" was used to monitor ozone concentrations from October 6 to October 27 in 2017.

4.2.1 Results for NO_2

Figure 9 compares the average concentrations of NO_2 pollutant in the LV, NB, SE, and SL communities in 2017. South Loop has the highest average NO_2 concentration, and the NB community has the lowest. Actually, the NO_2 concentrations are all at good levels. South Loop is an education zone because there are many schools and also many stores. It brings much traffic volume. More vehicles produce more NO_2 emissions. It makes the average NO_2 concentration in the SL community higher than in other communities. On the contrary, the NB community has greater green space. Less commercial activities exist in this area. The traffic volume is obviously lower, resulting in lower NO_2 emissions and NO_2 concentrations in the NB community.

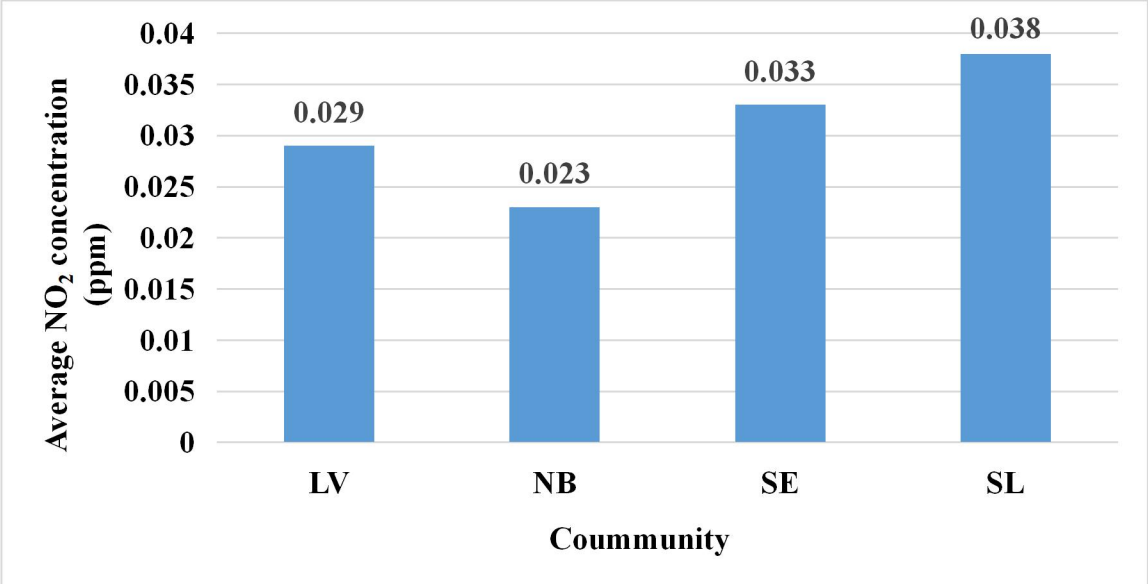

Figure 9. Average reading for NO_2 pollutant for the LV, NB, SE, and SL communities in 2017.

Figure 10's data is the hourly average data of SASA NO_2 pollutants. All collected data in Chapter 4 are from SASA Tables in Shared Air, Shared Action. The data could be found at http://fingolfin.kdd.cs.ksu.edu:8080/airquality/download/. The average values of NO_2 concentration in each hour were collected by the SASA sensors from 2017 to 2018. They contain Little Village's data from April 18, 2017 to June 28, 2017; Northbrook's data from October 6, 2017 to December 8, 2017; Southeast's data from July 30, 2017 to March 24, 2018; South Loop's data from September 13, 2017 to October 2, 2017.

In Figure 10, from 7:00 to 10:00 am, the trends for all communities are for NO_2 concentrations to go up. The average NO_2 concentrations increase in the mornings. However, they also have some differences. The rates of increase for the LV, SL, and SE community are more similar than in the NB community. Especially, the SL community is very similar to the SE community. They rapidly increase and reach the maximum around 10:00, but NB has the highest value around 16:00. More interestingly, the LV community has the second lowest around 16:00. Although the time of the second highest peak in the LV community is different from the other communities, it shows the downward trend obviously slows down, even increasing from 13:00 to 14:00 and from 15:00 to 17:00. It is noteworthy that there are lower NO_2 concentrations in the nighttime (from 19:00 to 7:00) than in the daytime.

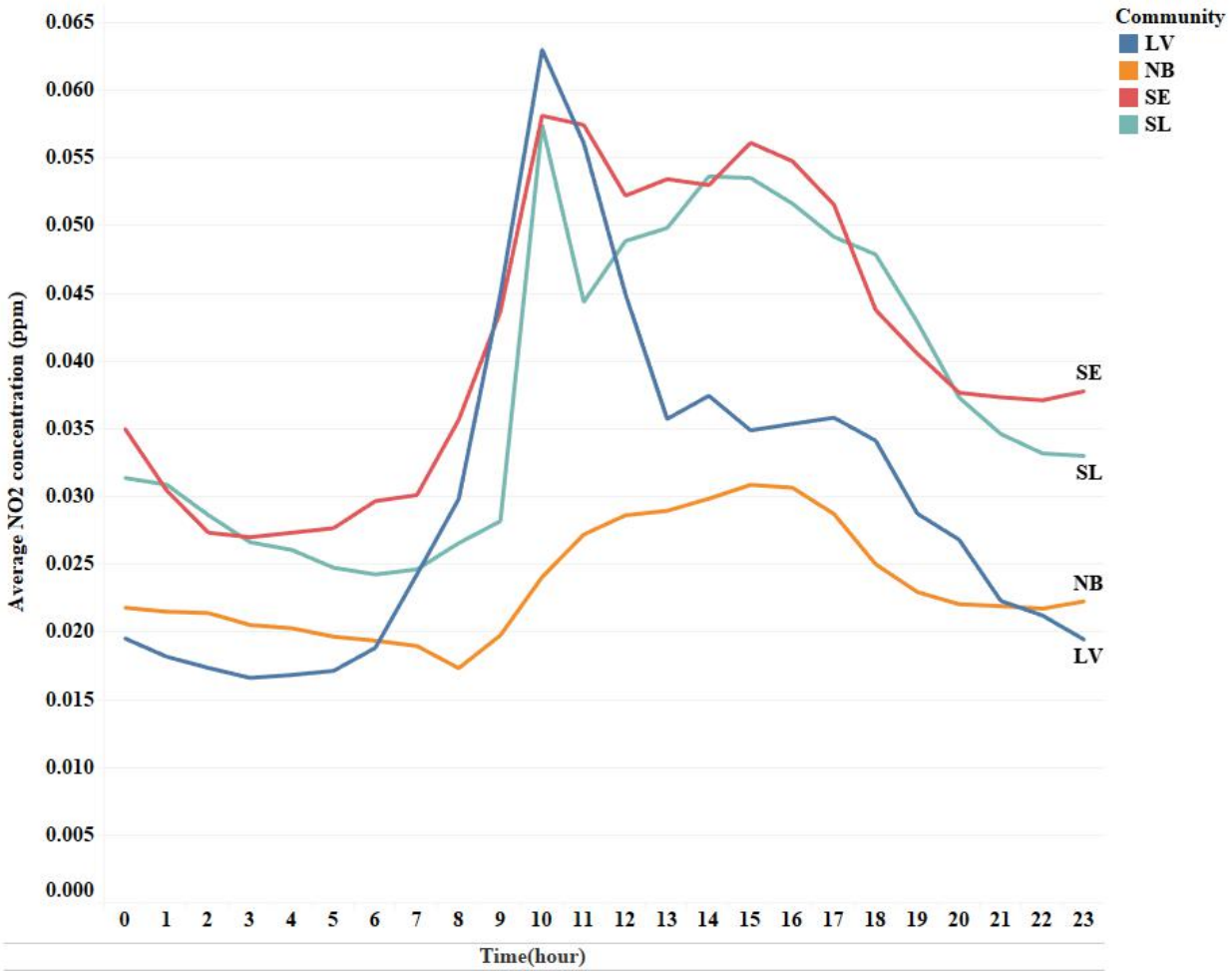

Figure 10. Hourly variations of 1-hr average NO_2 concentration for LV, SL, SE, and NB communities (SASA)

Nitrogen oxides are highly reactive gases emitted from transportation exhaust, industrial processes, and residents' daily life at home. In particular, NO_2 can react with other chemicals to form other pollutant compounds. Because much of the NO*x* in the air is emitted by motor vehicles, concentrations tend to peak during the morning and afternoon rush hours (New Jersey Department of Environmental Protection, 2016). Conversely, the NO_2 concentrations are lower in the nighttime due to there being less traffic. The variations in NO_2 concentrations in these communities fit the pattern of NO_2 concentrations within a 24-hr period.

In Figure 10, the NB community has the lowest concentrations among these 4 communities, not only because the NB community has more green space and less traffic, which is the reason provided in Chapter 4.1, but also because the data collected for the NB community was during the winter. Figure 6 shows that the data for the NB community is from October, November, and December. On the one hand, the seasonal variation is obvious in the NO_2 emissions due to people's behaviors like using more heat during the winter.

In addition, NO_2 readings by Aeroqual sensors are sensitive to ozone concentration. In the afternoon, one of main reasons for NO_2 decreasing in Figure 10 is the reaction shown in Equation 2. The sunlight is more sufficient in the afternoon, so more NO_2 transfer to NO.

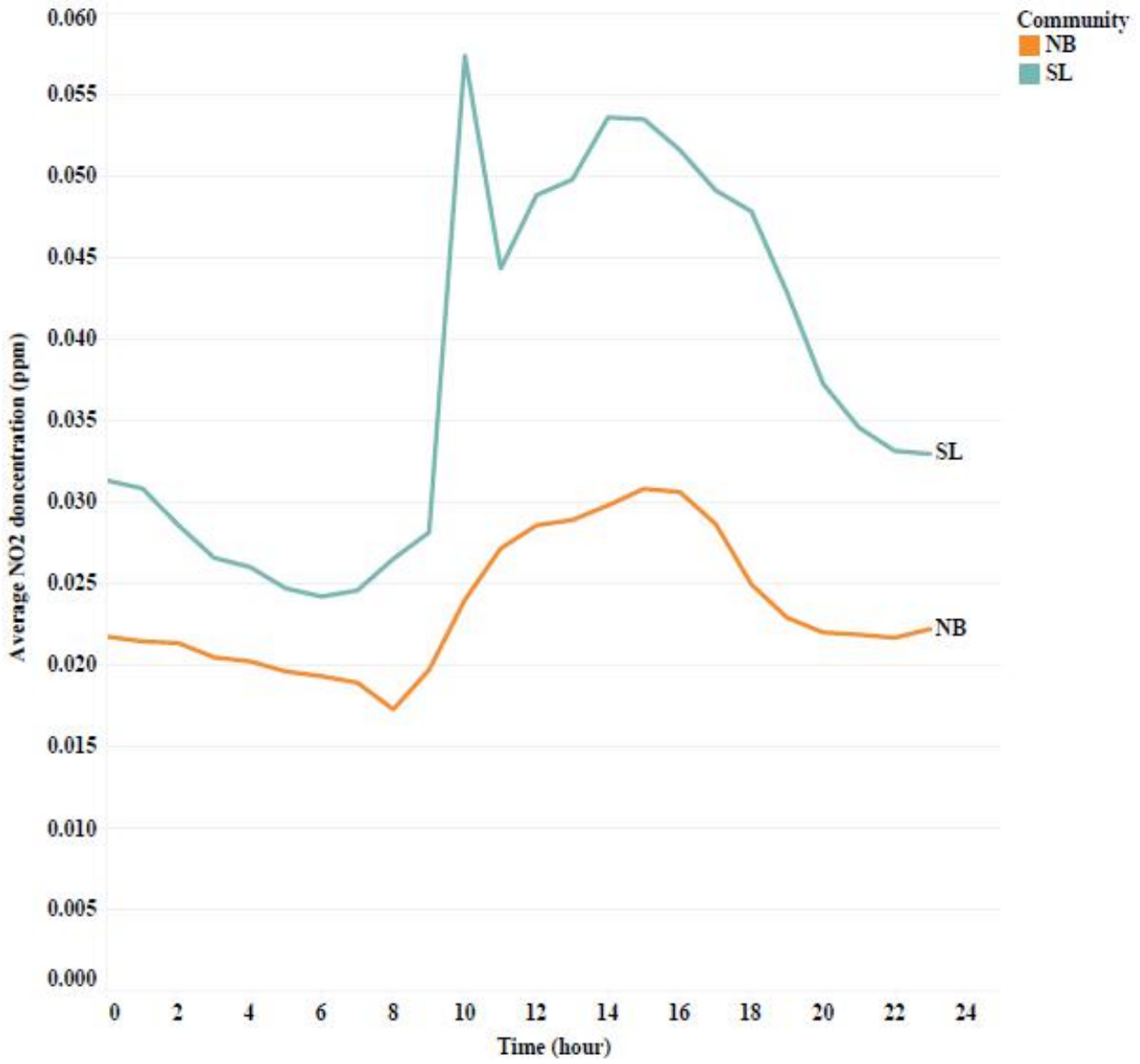

Figure 11. Hourly variations of 1-hr average NO_2 concentrations for the SL and NB in September, October, and November.

Because the collected data is from different months in Figure 10, so the data comparison was influenced by the seasons. To minimize or eliminate the seasonal interference, Figure 11 shows how hourly NO_2 concentrations vary by sensor across the South Loop neighborhood and NB, both collected during the fall. The data in Figure 11 contains South Loop's data from September 13, 2017 to October 2, 2017 and Northbrook's data from October 6, 2017 to November 30, 2017. There is variability in the NO_2 measurements, which could be due to differences in the locations

and nearby localized emissions sources, measurement biases between the sensors, or both. NO_2 concentrations in the SL community are obviously higher than in the NB community. The SL community has many schools and shops, so people's traffic behavior obviously influences the variation in the NO_2 concentrations in this area.

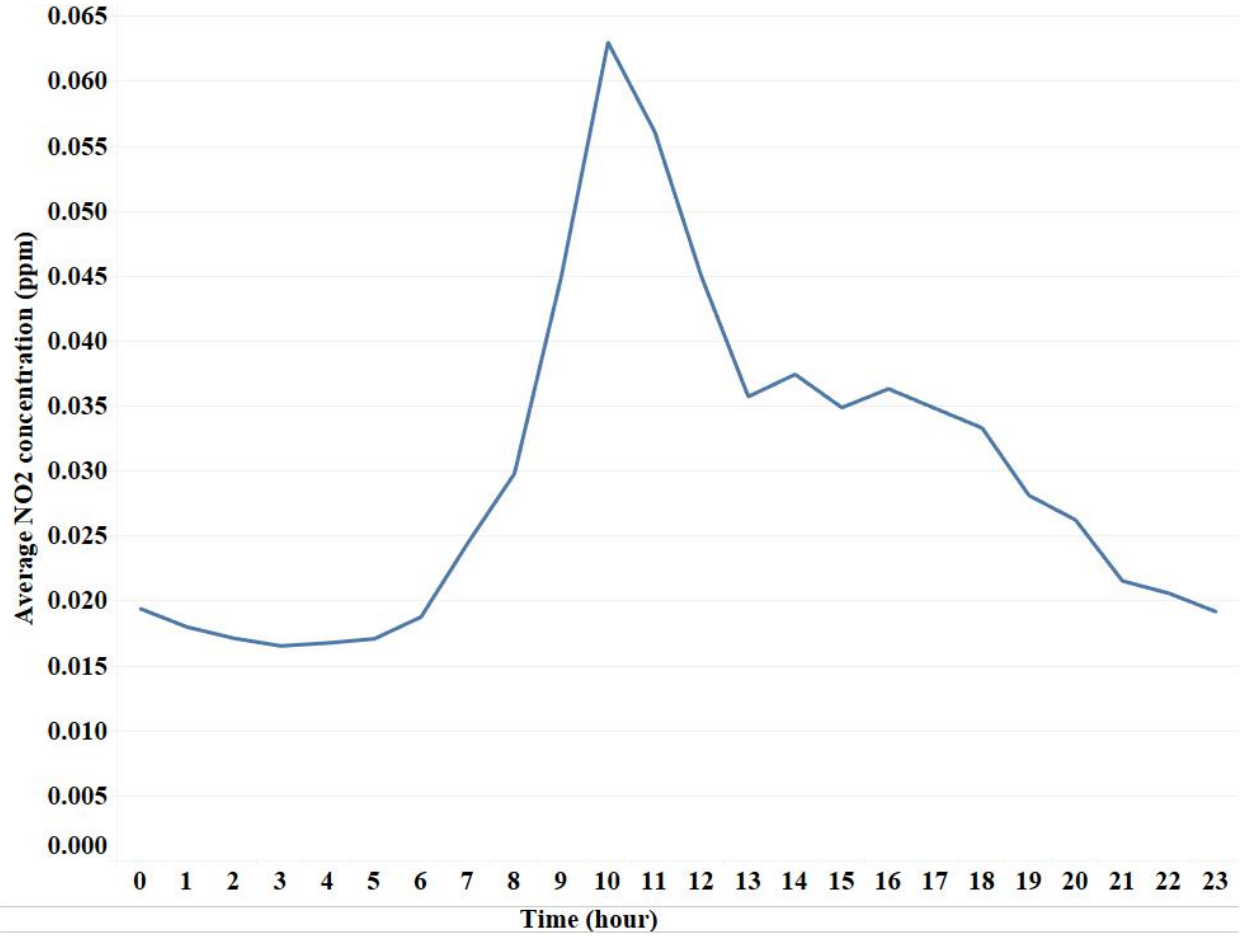

Figure 12. Hourly variations of 1-hr average NO_2 concentration for Little Village in June 2017.

Figure 12 shows the hourly variations of the 1-hr average NO_2 concentrations in LV in June. The data was collected from the summer monitoring SASA_AQ1. The concentrations have lower value in the nighttime due to there being less traffic at night, but it begins rapidly increasing from 5:00 to 10:00 because people are starting to go out early in the morning, using more transportation methods. The highest peak is around 10:00. The concentration dramatically decreases from 10:00 to 13:00. After 13:00, although the concentration is still decreasing, the

reduced speed is much slower than in the morning, as there is even a slight upswing from 13:00 to 14:00.

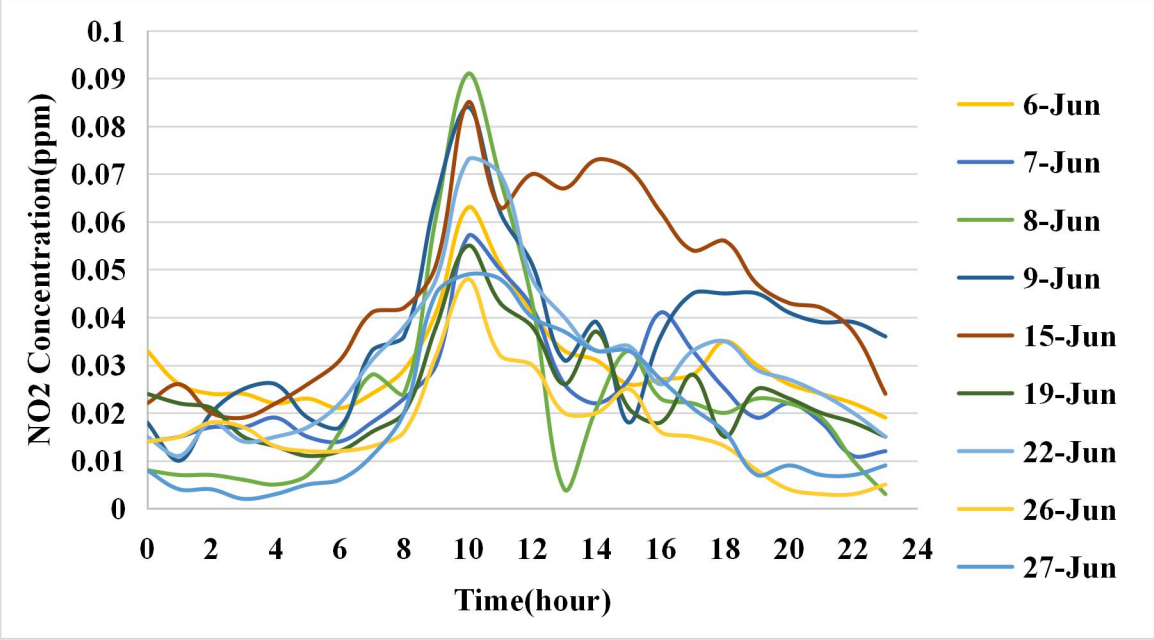

Figure 13. Hourly variations of 1-hr average NO_2 concentration on workdays for Little Village in 2017

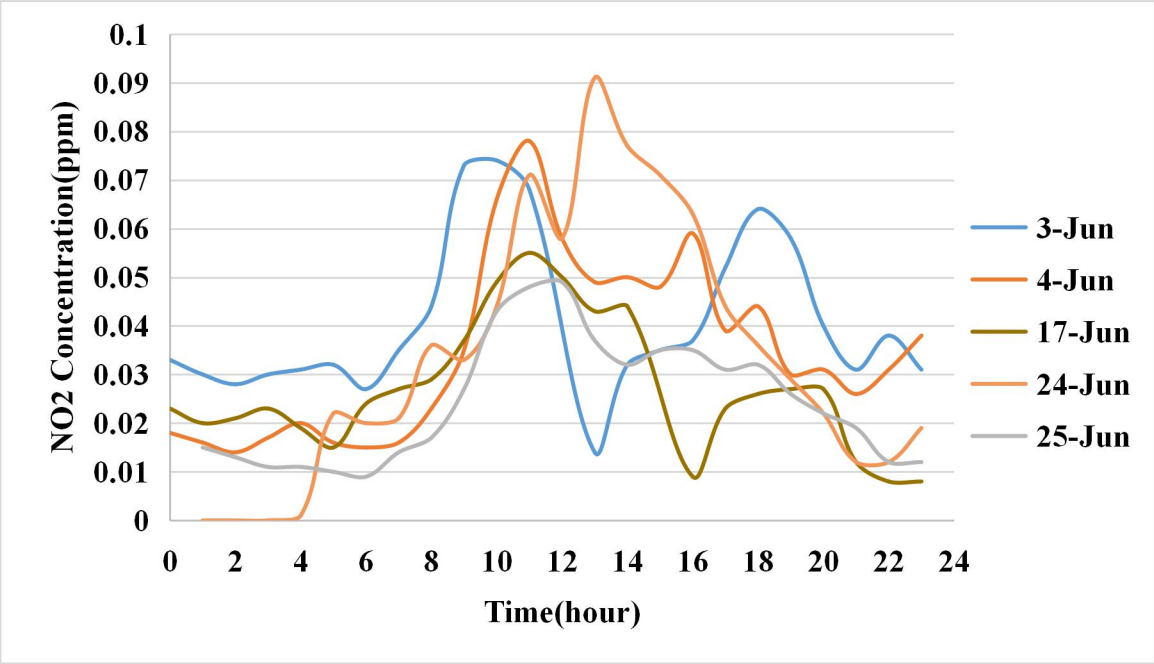

Figure 14. Hourly variations of 1-hr average NO_2 concentration on Weekends for Little Village in 2017.

The NO_2 concentration varies with the traffic intensity. Figures 13 and 14 show the details of the hourly variations on the workdays and weekends in LV during the summer of 2017. Workday includes Monday, Tuesday, Wednesday, Thursday, and Friday. Figure 13 shows the NO_2 concentrations obviously increase starting at 6 am. The maximum is at 10 am. It seems related to people's traffic when it is time to go to work on the workdays. At night, the concentrations are lower because most of people don't go outside. In Figure 14, on the weekends, the concentrations at night are also low but they don't have a consistent moment of peak value. This indicates that people's behavior differs from during the workdays. People like to go outside at any time instead of focusing on traffic hours associates with work.

The workdays and Sundays differ in terms of the highest value of the 1-hr average NO_2 concentrations. On workdays, there are obvious peaks at 10:00. However, on some Saturdays and Sundays, there are two peaks within a day. There are two possible reasons for these two peaks: 1. Dining time produces more traffic. More vehicles emissions on the road cause higher NO_2 concentration. For example, there is one peak at 11:00 while the other peak is at 13:00 on June 24, 2017. This is more likely caused by reason: 1. because it's lunch time, two small peaks mostly exist during lunch and dinner on Sundays. 2. traffic jams lead to traffic stagnation; less traffic flow creates fewer NO_2 emissions, thus, there is a period of low concentration between two close peaks.

Table 5. Comparison of values of mean and standard deviation of NO_2 concentration between workdays and weekends at 10:00 and 13:00 from 6/3/2017 to 6/27/2017 in Little Village.

Time	**10:00**		**13:00**	
Type	**Workdays**	**Weekends**	**Workdays**	**Weekends**
(Mean ± Std)_avg value	0.0672 ± 0.0165	0.0552 ± 0.0140	0.0316 ± 0.0170	0.0468 ± 0.0280
(Mean ± Std)_max value	0.0853 ± 0.0161	0.0806 ± 0.0174	0.0493 ± 0.0196	0.0682 ± 0.0345
(Mean ± Std)_min value	0.0468 ± 0.0162	0.0286 ± 0.0171	0.0158 ± 0.0154	0.0238 ± 0.0195

The obvious different hourly variations between workdays in Figure 13 and weekends in Figure 14 exist. In Table 5, the mean and standard deviations (Std.) of NO_2 concentration at 10:00 and at 13:00 from 6/3/2017 to 6/27/2017 in Little Village are shown. The time interval for measurement is 1 minute, so there are 60 times of records per hour. The value at the hour is related to the records of the 60 closest minutes. For example, the average value at 10:00 is mean value from 9:30 to 10:30; the maximum value at 10:00 is the largest value from 9:30 to 10:30; the minimum value at 10:00 is the smallest value from 9:30 to 10:30. At 10:00, the mean value of average values on workdays is larger than on weekends. It shows the NO_2 concentration at 10:00 on weekends is usually less than on workdays. It indicates that there are less emission on weekends. At 13:00, the mean value of average values on workdays is smaller than on weekends. It shows the NO_2 concentration at 13:00 on weekends is usually higher than on workdays. It indicates that there are more emissions on weekends at 13:00, a normal lunch time. In addition, at 10:00, the standard deviation of average values on workdays is larger than on weekends. It shows the data of NO_2 concentration at 10:00 on weekends is more stable. However, at 13:00, the standard deviation of average values on workdays is less than on weekends. It shows the data of NO_2 concentration at 13:00 on workdays is more stable.

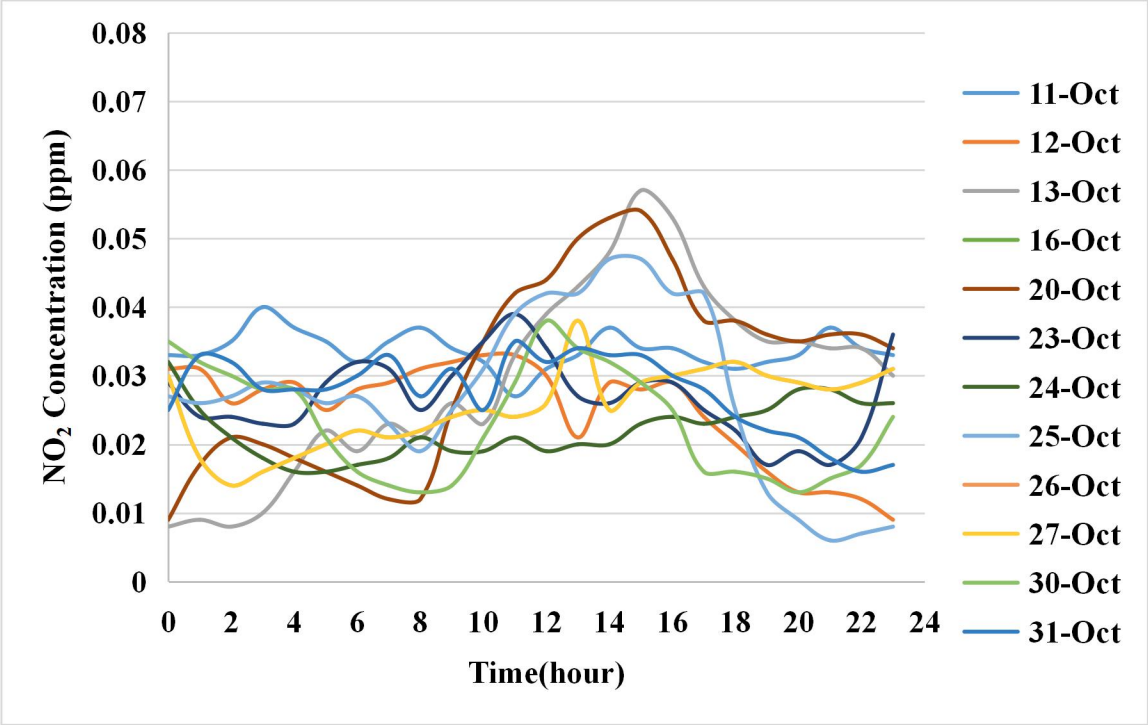

Figure 15. Hourly variations of 1-hr average NO_2 concentration on Workdays for NB in October 2017.

In Figures 15 and 16, the distribution of NO_2 concentrations in NB don't have an obvious pattern of change, which could be related to people's traffic behavior in this community. Geographic variations can be considered for the NB community. The NB community has much more green space and fewer main transportation roads. This community displays the least influence from transportation. Thus, the changes are smaller with time during each day.

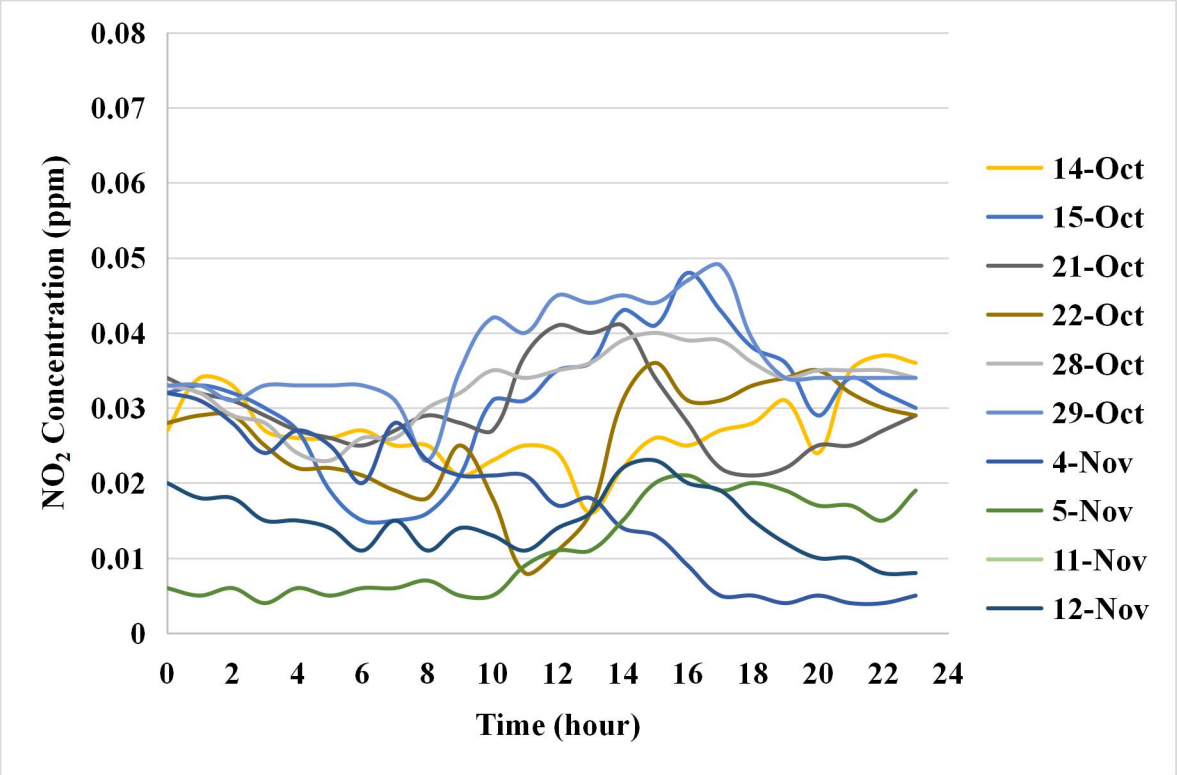

Figure 16. Hourly variations of 1-hr average NO_2 concentration in Weekends for the NB community in 2017.

Compare Figure 14 to Figure 16, although they both show data on weekends, most of standard deviations of NO_2 concentration at NB are less than standard deviations of NO_2 concentration at LV shown in Table 6. It means the 1-hr average NO_2 concentration in a day at the LV community changes greater than the 1-hr average NO_2 concentration in a day at the NB community.

Table 6 shows the mean and standard deviation of 1-hr average NO_2 concentration in a day at LV in June, and at NB in October and November in 2017. The time interval for measurement is 1 minute, so there are 60 times of records per hour. A completed day has 1440 times of records. The mean in Table 6 is mean of all values in 24 hours for each day. The standard deviation in Table 6 is calculated by average value at each hour in a day.

Table 6. Mean and standard deviation of 1-hr average NO_2 concentration in a day at LV and at NB

Time	Mean ± Std (ppm)	Community
6/3/2017	0.0407 ±0.0162	LV
6/4/2017	0.0347 ± 0.0186	LV
6/17/2017	0.0269 ± 0.0136	LV
6/24/2017	0.0326 ± 0.0276	LV
6/25/2017	0.0240 ± 0.0127	LV
10/14/2017	0.0271 ± 0.005	NB
10/21/2017	0.0295 ± 0.0058	NB
10/22/2017	0.0255 ± 0.0076	NB
10/28/2017	0.0329 ± 0.0048	NB
11/4/2017	0.0168 ±0.0096	NB
11/5/2017	0.0114 ± 0.0062	NB
11/11/2017	0.0253 ± 0.0033	NB
11/12/2017	0.0147 ± 0.0042	NB

In Table 6, the standard deviations of 1-hr average NO_2 concentration at the NB community are all smaller than values at the LV community. It indicates that the 24-hr variation for NO_2 concentration is more stable at the NB community in the winter. However, the seasonal reason could influence the NO_2 concentration. It would have been better to use same date or season to compare these two communities' variation of NO_2 concentration.

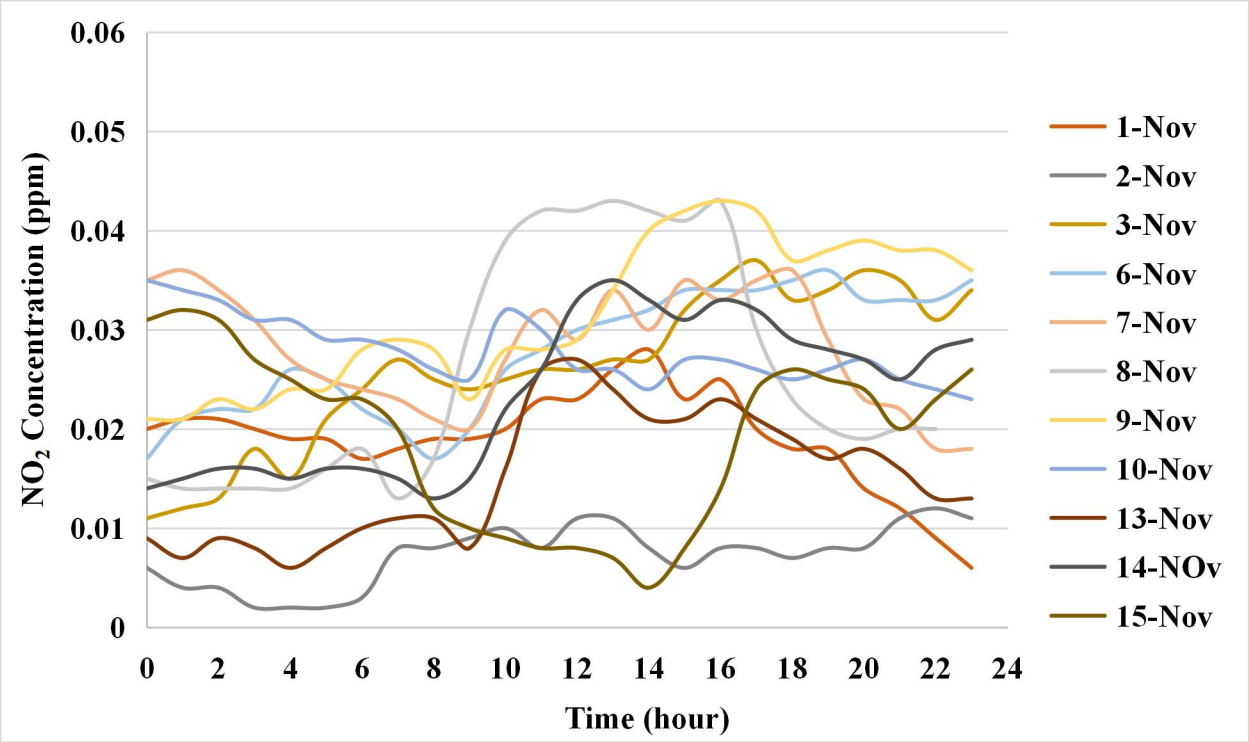

Figure 17. Hourly variations of 1-hr average NO_2 concentration on Workdays for the NB community in November 2017.

In Figures 15, 16, and 17, there is no obvious consistent peak or lowest value of NO_2 concentration in these days. Workdays and weekends all have fluctuating NO_2 concentrations. It shows the NB community was less influenced by emissions from transportation.

The data in Figure 18 contains average NO2 concentrations in each day at Little Village from April 18, 2017 to June 28, 2017.

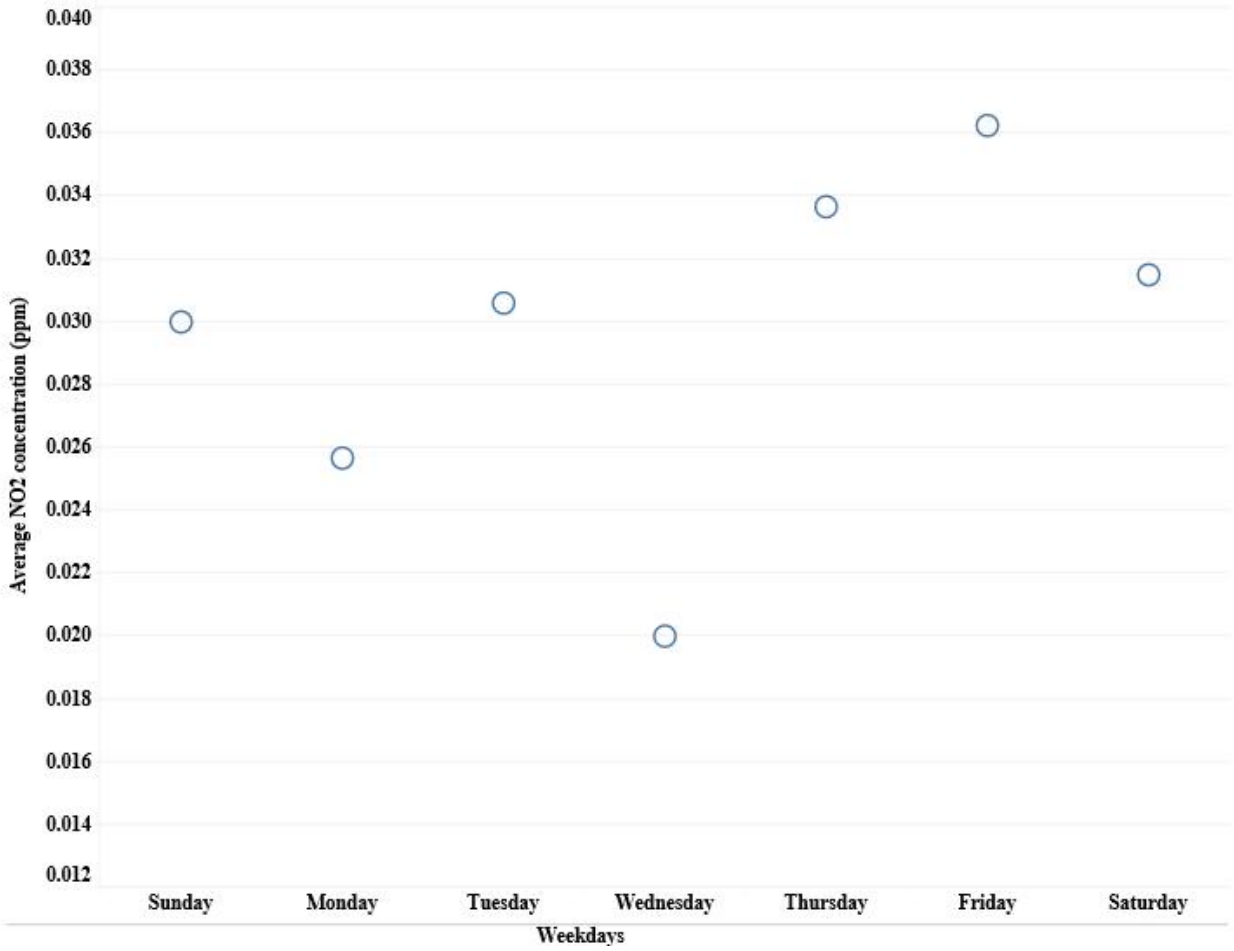

Figure 18. Weekday variation of 24-hr average NO_2 concentrations in LV.

Figure 18 shows that the lowest average concentrations are on Wednesdays. Also, Thursdays, Fridays, Saturdays, and Sundays have higher concentrations than Mondays, Tuesdays, and Wednesdays. The Little Village community has many leisure facilities such as restaurants, shopping centers, and other stores. In people's leisure time, the traffic intensity will be greater. Thus, more traffic means more NO_2 emissions from vehicle exhaust. The NO_2 concentration on the weekends, Thursdays, and Fridays should be higher.

4.2.2 Results for O_3

Figure 19 shows that there are higher ozone concentrations during the daytime and lower O_3 concentrations at nighttime. Transportation is the main reason. More traffic exists during the

daytime. The other source of NO_2 emissions come mainly from some industrial plants, which usually run in the daytime. Ozone concentration increases in daytime when NO*x*, VOCs and solar radiation are present. Sunlight is needed to produce ozone; see Equations 2 and 3. The data for Little Village in 2017 collected from the SASA project is the most complete as 1-hr average and 8-hr average ozone concentrations are both provided. Figure 19 shows that the LV, NB, and SL communities have similar trends in the hourly variations of 1-hr average ozone concentrations. The average values of O_3 concentration in each hour were collected by the SASA sensors from 2017 to 2018. They contain Little Village's data from April 21, 2017 to April 26, 2017 and from June 2, 2017 to June 27, 2017; Northbrook's data from October 6, 2017 to October 27, 2017; South Loop's data from September 13, 2017 to October 2, 2017.

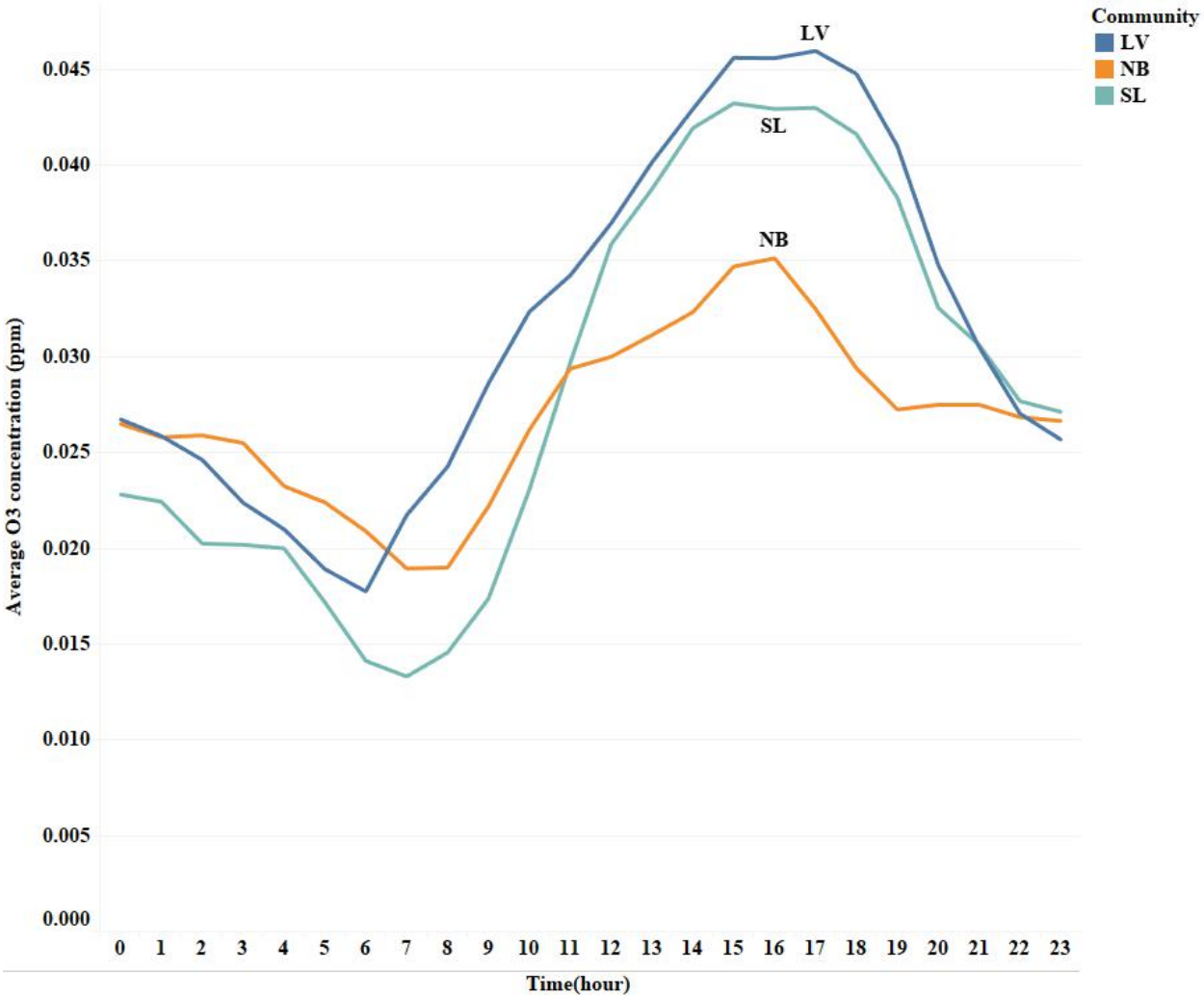

Figure 19. Hourly variation of 1-hr average O_3 concentration in the LV, NB, SL communities.

In Figure 19, for the LV community, the minimum is at about 5:00. After the sun comes up, the ozone concentration rapidly increases until 18:00 as the peak value is at 18:00. The SL and the NB communities have similar change patterns for the average 1-hr concentrations of ozone during the summer; see Figure 19. Their maximum average ozone concentration is at around 15:00. The minimum average ozone concentration is at about 7:00. From 7:00 to 15:00, the ozone concentrations substantially increase during the daytime. From 15:00 to 6:00 the next day, ozone concentrations dramatically decrease at night. Although these communities have similar change patterns, the NB community is more stable or shows smaller fluctuations, and it has lower concentration at its peak time.

In addition, compare Figure 19 to Figure 10. There is a negative correlation between ozone readings and NO_2 readings in the early afternoon, because NO_2 is decreasing to produce ozone. In the early morning, ozone can be produced with NO_2 concentration increasing by Equation 2, so NO_2 has positive impacts on ozone. At night, NO_2 can react with ozone in Equation 10 to reduce both NO_2 and ozone. They change in the same direction at night in Figure 10 and 19.

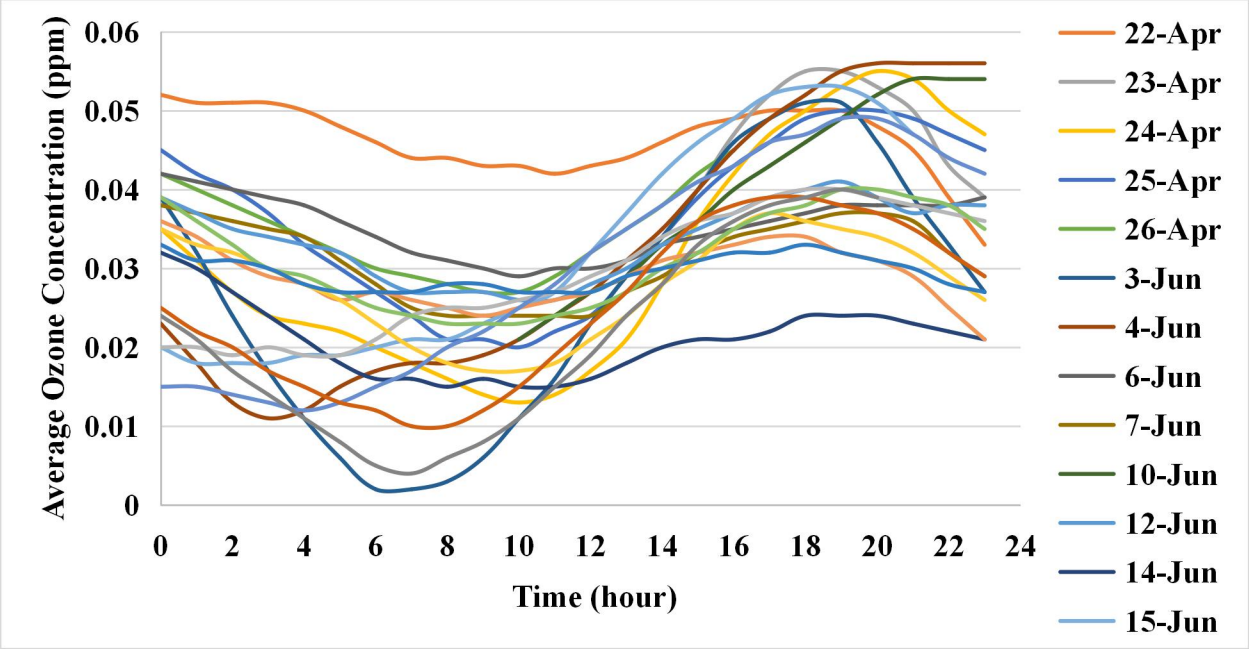

Figure 20. 8-hr average ozone concentration for Little Village in 2017 from SASA.

There is a valley from 5:00 to 7:00. The lowest concentrations occur after 20:30, during the night. The peak values are after 15:00 and before 20:30 in Figures 19, 20 and 21.

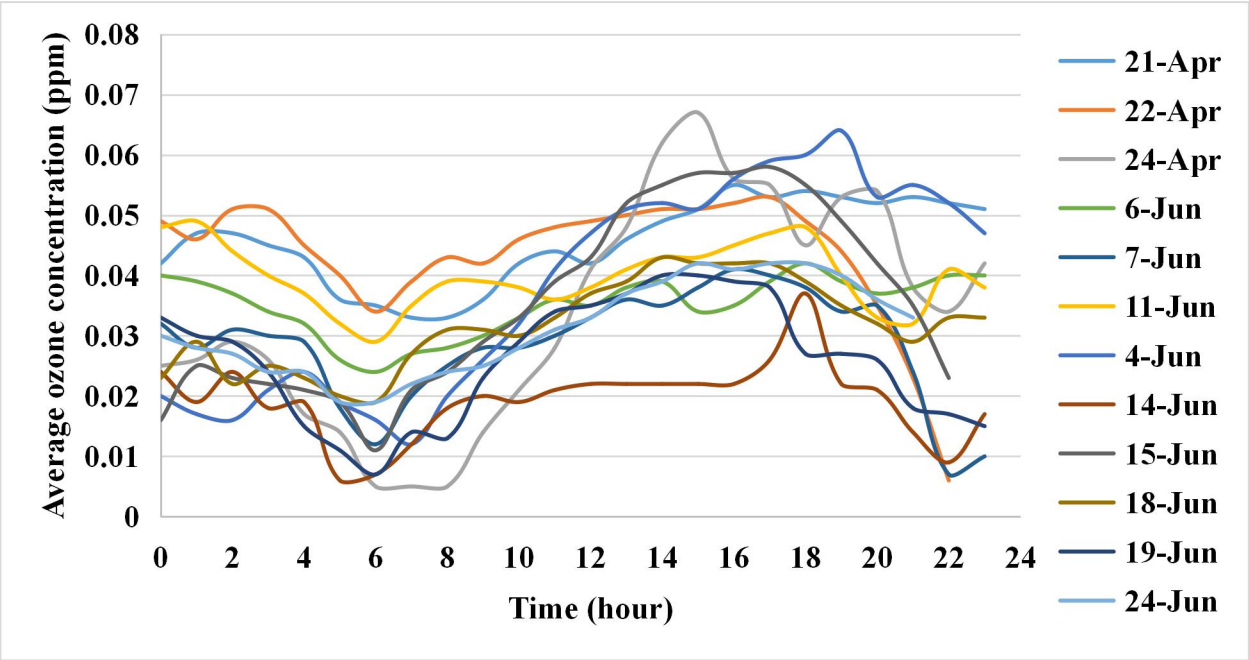

Figure 21. 1-hr average ozone concentration for Little Village in 2017 from SASA.

Comparing the data on the 1-hr and 8-hr average O_3 concentrations, the 1-hr average concentrations are more suitable to use for analysis of the variations within a day. See Figures 20 and 21. There are some regularities about the daily changes in the 8-hr ozone concentration in Figure 20. Many days in the statistics have the lowest values around 7:30. The highest concentrations are around 19:00. There is an obvious growth stage because NO_2 can produce ozone according to Equations 2 and 3. Daily changes in NO_2 concentrations are obviously influenced by traffic. Ozone concentrations decrease during the period from 19:00 to 7:00.

During the day, NO_2 concentrations increase starting at 6 or 7 am because of people's traffic behavior. Automobiles emit NO*x* gases such as NO_2 and NO. Equation 1 happens in the daytime traffic when NO is produced and converted to NO_2. Because the mixing ratio of NO is much lower than O_3, Equation 4 does not deplete ozone during the day in the background tropospheric

atmosphere. However, in urban air, Equation 4 can reduce local ozone levels at night because NO mixing ratios at night may exceed those of O_3. Equation 2 does not produce O at night, which is needed in Equation 3 for ozone production.

NO_2 reacts with OH to produce HNO_3. HNO_3 can keep its lifetime against photolysis for 15–80 days. The time depends on the day of the year and the latitude. HNO_3 (g) is water soluble, so much of it can be dissolved in cloud drops or moist aerosol particles.

In Equations 8& 9, the main source of hydroxyl radical (OH) is from the reaction between O_3 and H_2O. NO_2 could be removed in Equation 7; at the same time, O_3 can also be removed to produce more OH. So, NO_2 and O_3 concentrations may decrease in the daytime according to Equations 7-10. More O_3 creates more NO_2 in the daytime. This shows that increasing O_3 concentrations in the daytime causes increasing NO_2 concentrations. At night, much of the ozone production shuts down because of a lack of O. At the same time, NO_2 can react with ozone in Equation 10. It can consume ozone and reduce ozone concentrations.

Focused on the data in Figure 21, not only standard deviation of 1-hr average O_3 concentration at 4:00 is larger than 10:00, but also standard deviation of 1-hr max O_3 concentration at 4:00 is larger than 10:00. In Table 7, there are mean and standard deviation values of all measured average and maximum concentrations at 4:00 and at 10:00 on April 21, April 22, April 24, June 4, June 6, June 7, June 11, June 14, June 15, June 18, and June 19 in 2017 at Little Village. The mean of average value at 10:00 is larger than the mean of average value at 4:00, and the mean of maximum value at 10:00 is also larger than the mean of average value at 4:00. The values are reasonable because there is more traffic for NO_2 emissions at 10:00, and this produces more ozone. The smaller standard deviation at 10:00 shows better collected data at that point than at 4:00, because more close values means less interference from unknown reasons in different days.

Table 7. Mean and Standard deviation of O_3 concentration at 4:00 and 10:00 from 4/21/2017 to 6/18/2017

Time	(Mean ± Std)_average value (ppm)	(Mean ± Std)_max value (ppm)
4:00	0.0277 ± 0.0104	0.0325 ± 0.0103
10:00	0.0319 ± 0.0081	0.0377 ± 0.0075

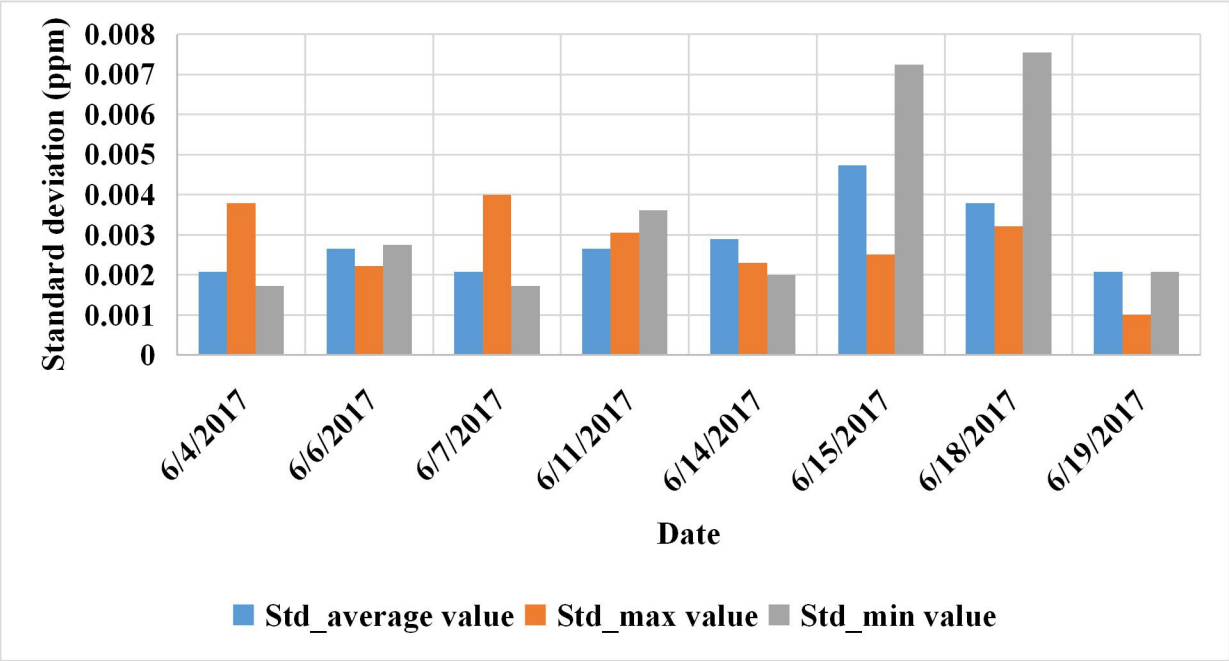

Figure 22. Standard deviation of O_3 concentration from 0:00 to 2:00 on different dates

In Figure 22, values are shown for the standard deviation of O3 concentration from 0:00 to 2:00 on June 4, June 6, June 7, June 11, June 14, June 15, June 18, and June 19 in 2017. These days are the days which have measured records in June 2017. The time interval for measurement is 1 minute, so there are 60 times of records per hour. The value at the hour is related to the records of the 60 of closest minutes. For example, the average value at 2:00 is mean value from 1:30 to 2:30; the maximum value at 2:00 is the largest value from 1:30 to 2:30. The standard deviation of average value from 0:00 to 2:00 is calculated by the standard deviation of average values at 0:00,

1:00, and 2:00. The standard deviation of maximum value from 0:00 to 2:00 is calculated by the standard deviation of maximum values at 0:00, 1:00, and 2:00.

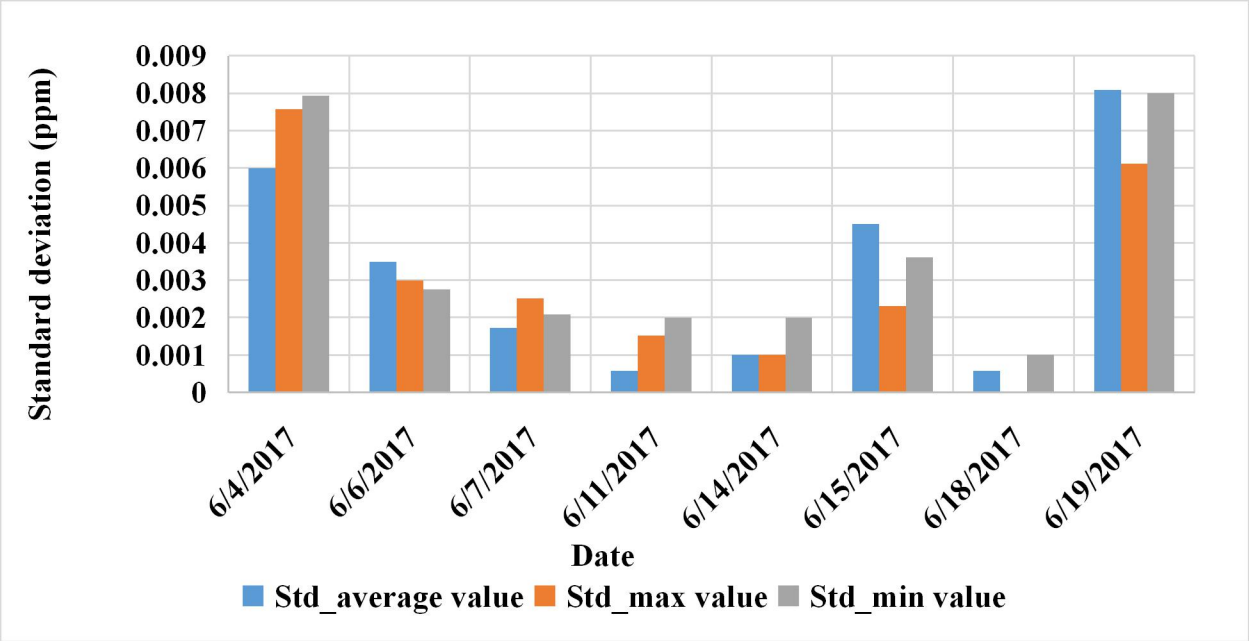

Figure 23. Standard deviation of O_3 concentration from 8:00 to 10:00 on different dates

In Figure 22 and Figure 23, most of standard deviations of 1-hr average O_3 concentration are lower than the standard deviations of 1-hr max and 1-hr min O_3 concentration. Lower standard deviation means more stable data. It indicate 1-hr average data is more suitable to use to analyze in this research.

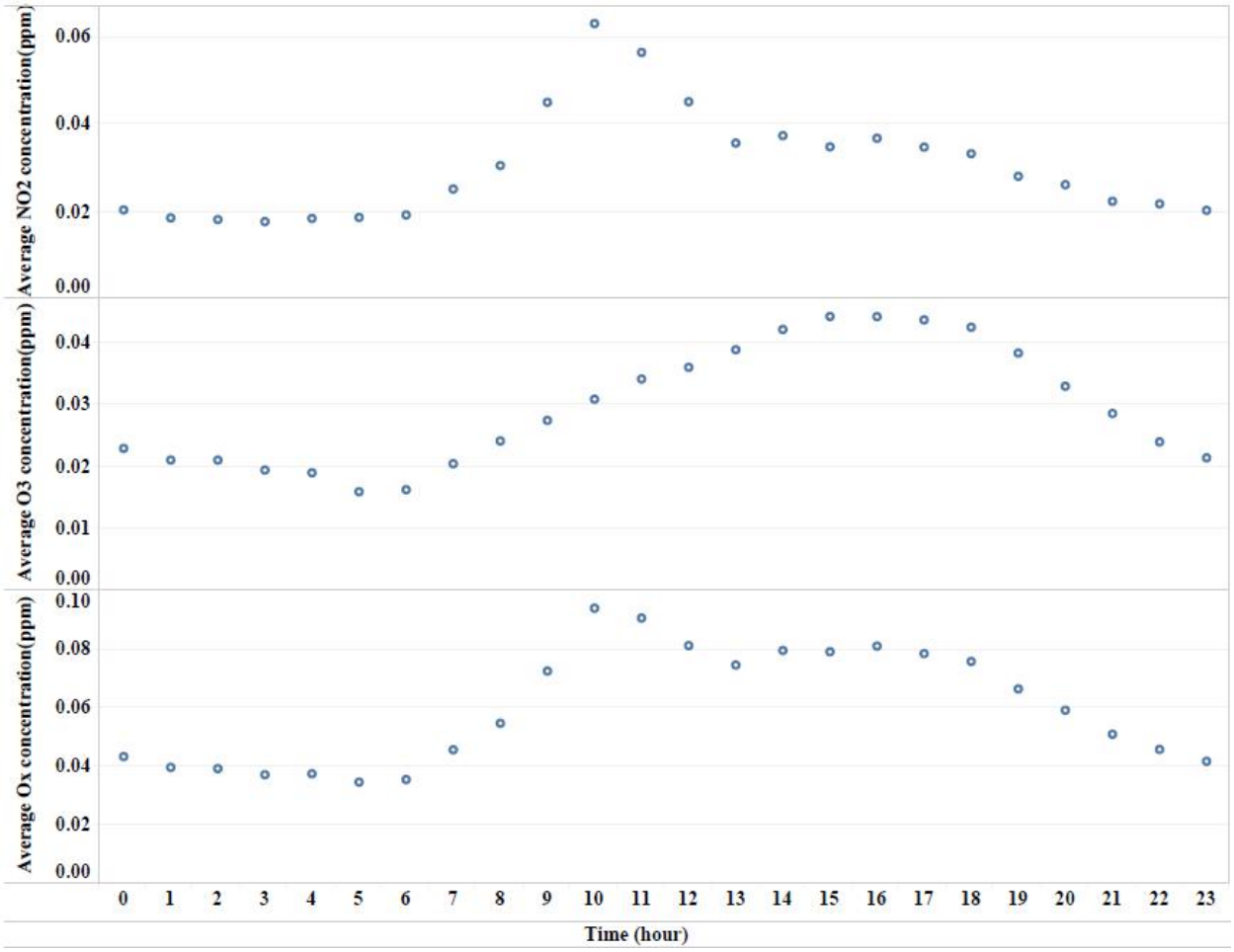

Figure 24. Average of measured values for a daily period of 1-hr average NO_2, O_3, and Ox concentrations for the LV community. The period is from 16:00 June 2, 2017 to 20:00 June 27, 2017.

Figure 24 shows values of 1-hr average of NO_2, O_3, and O*x* for a period of time in June where the measured values for several days are averaged for each time of day. O*x* concentration is the sum of NO_2 concentration and O_3 concentration. The highest NO_2 concentration is around 10:00, but the highest O_3 value is around 15:00. The ozone peak is about 5 hours after the NO_2 peak. The formation of ozone is deeply influenced by NO_2. The tendency of change between NO_2 and O_3 is not the same. An obvious time lag exists. The time period for high values is different because the reactions (shown in Equation 2& 3) need time to happen in the LV community. With the increasing O_3 concentration in the afternoon, NO_2 concentration is decreasing because most

of NO_2 takes part in the reactions to form O_3. O*x* concentration shows the sum of the two pollutants' concentration. The highest value of O*x* concentration is around 10:00, the same as NO_2 concentration.

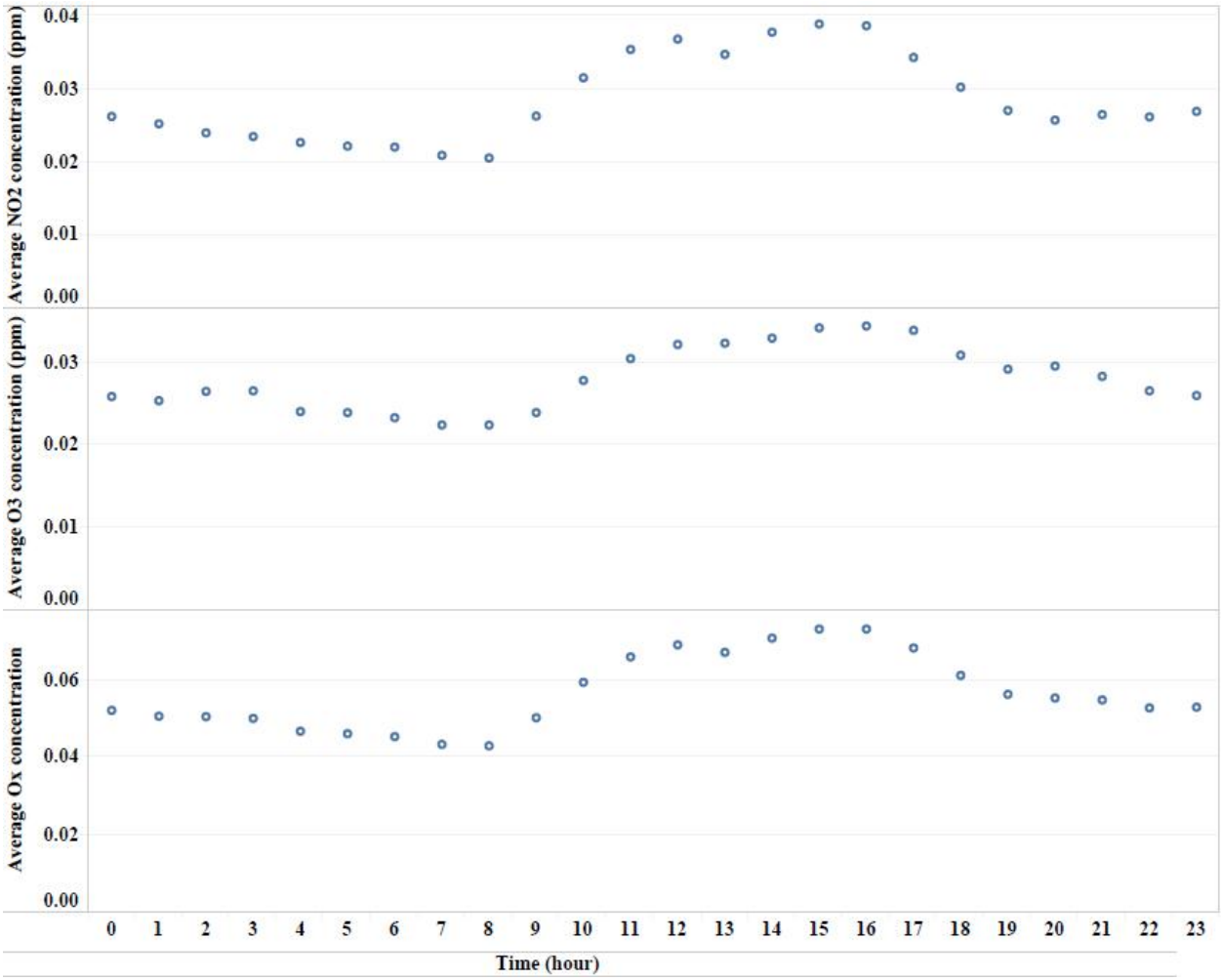

Figure 25 Average of measured values for a daily period of 1-hr average NO_2, O_3, and Ox concentrations for the NB community. The period is from 13:00 October 6, 2017 to 13:00 October 27, 2017.

Figure 25 shows average values for each time of day for a 22 day period. The maximum ozone concentration appears at about 15:00. The sum of NO_2 and O_3 concentration peaks at 15:00 also.

Compared to the LV community in summer, NB has lower NO_2 concentration and lower O_3 concentration in winter. However, the NB community has similar tendency between the 24-hr variation of NO_2 and O_3 concentration to LV. The change of O_3 concentration is influenced by NO_2.

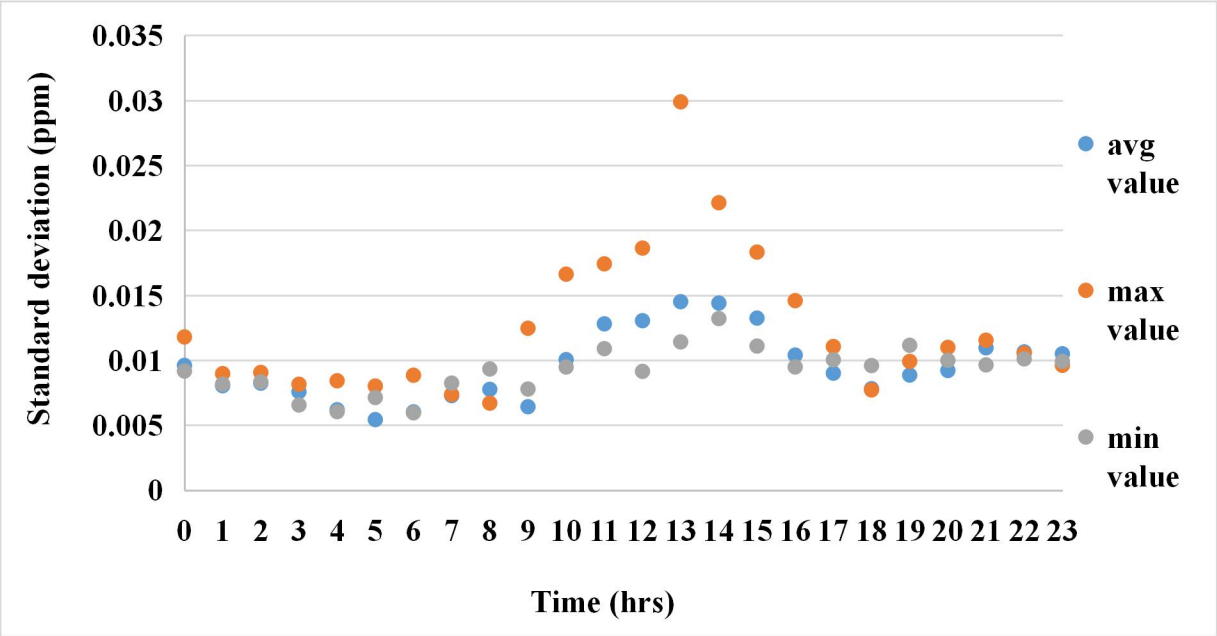

Figure 26. Comparison of the standard deviation of 1-hr average, maximum, and minimum of NO_2 concentrations for the NB community. The period is from 13:00 October 6, 2017 to 13:00 October 27, 2017.

The maximum, minimum and 1-hr average of NO_2 concentrations were all collected. The standard deviation of them for each hour in a day are shown in Figure 26. Figure 26 shows that the average value and the minimum value are more stable for data analysis. The standard deviation of max value is larger than the standard deviation of average value and minimum value. In statistics, the standard deviation, not only is used to express the variability of a population, but also is commonly used to measure confidence in statistical conclusions. The standard deviation is often called the "standard error" of the estimate or "standard error of the mean" when referring to a mean. It is computed as the standard deviation of all the means that would be computed from

that population if an infinite number of samples were drawn and a mean for each sample were computed ("Standard deviation," 2020).

In addition, the standard deviation of the average value is very close to the standard deviation of the minimum value. However, the minimum in each hour cannot exactly present the reasonable value for all data. 1-hr average value of NO_2 is preferred to use because of its stability and representativeness for all data in the hour.

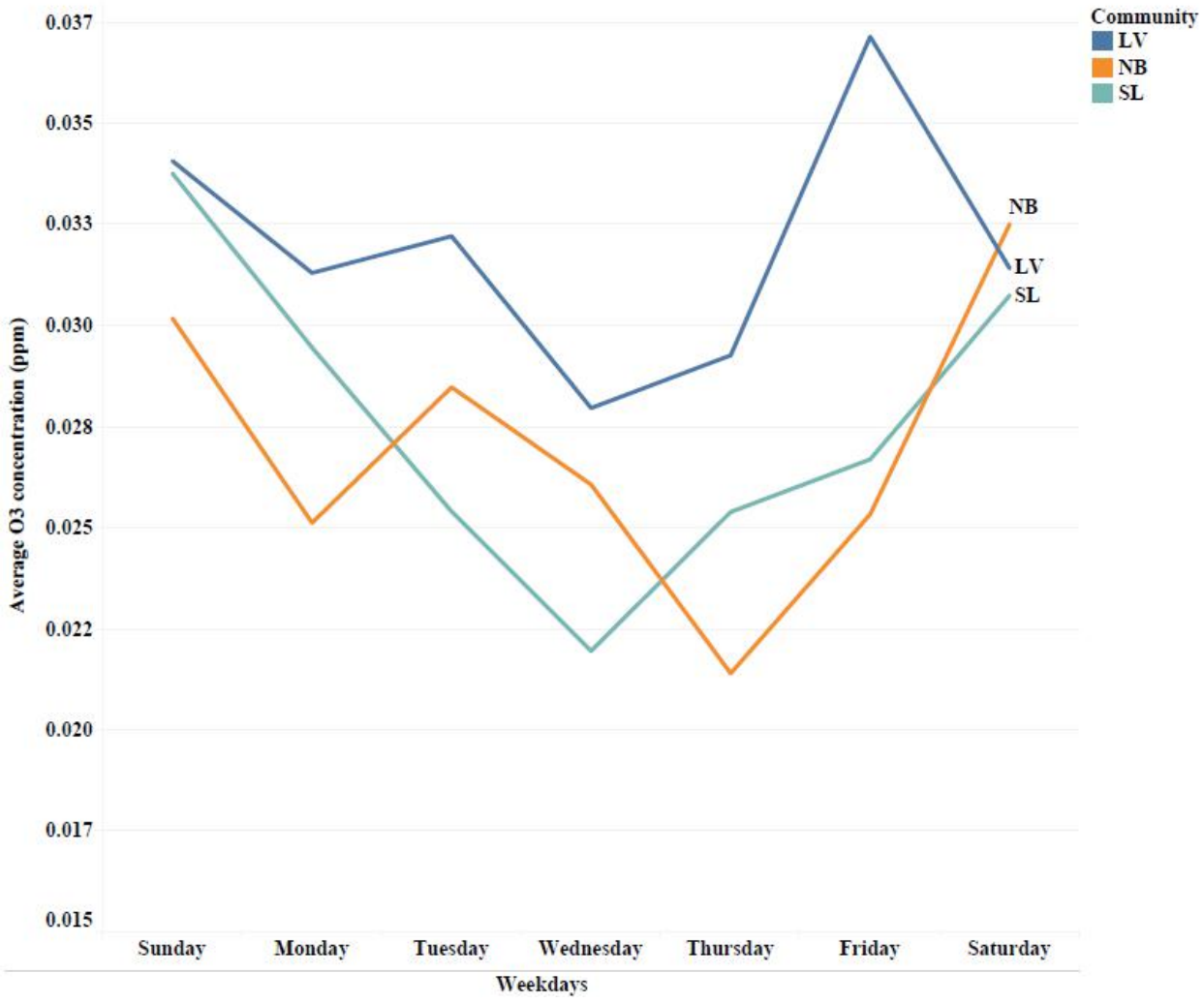

Figure 27. Weekday variation of average O_3 concentrations in LV, NB, and SL.

The LV, NB, and SL communities all have the lowest concentrations on Wednesdays and Thursdays. Also, they have comparatively higher concentrations on the weekends except for the

LV community which has the highest ozone concentration on Friday. In Cook County, Illinois, there were 36 days when the ozone concentration exceeded 70 ppb and was in the orange range from 71-85 ppb during 2015-2017 and 4 days when the ozone concentration was in the red range from 86-105 ppb.(American Lung Association, 2019) The SASA data reported in this chapter is within air quality standards. This indicates that ozone concentrations are influenced by NO_2 concentrations because NO_2 can produce ozone via chemical reactions. More traffic produces more NO*x* from vehicle exhaust, which then produces more ozone.

Chapter 5 - Other Data Analysis

In Chapter 5, the involved data were collected by the EPA regulatory monitors. The data could be found at http://fingolfin.kdd.cs.ksu.edu:8080/airquality/download/.

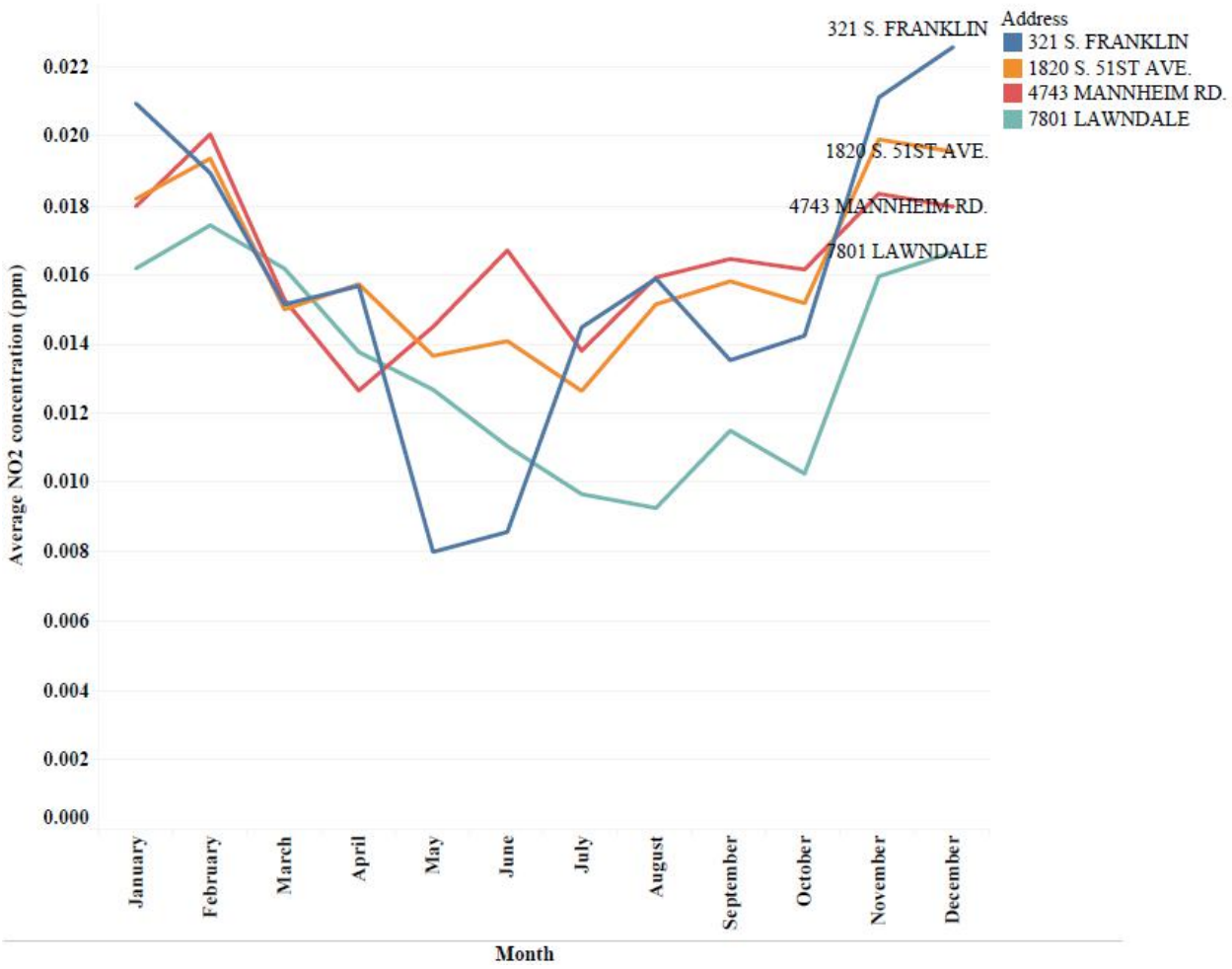

Figure 28. Monthly variation of 24-hr average NO_2 concentration at 4 addresses in Chicago from EPA monitoring in 2017.

Higher concentrations of nitrogen dioxide were measured at all measuring points in the urban setting during the winter than during the summer since the winter weather conditions reduce the self-cleaning capacity of the air in the city and increase the use of energy for heating; fuel consumption by vehicles is also higher. Air pollution greatly exceeds the measured value of

annual average, especially during the winter, due to the stable, calm, and cold anti-cyclone weather. (Mally & Ogrin, 2015)

In Figure 28, the NO_2 concentrations are lower during the summer than in the winter. The peak times are during November, December, and February, though the locations show differences in NO_2 concentrations. The different locations had the lowest concentration in April, May, July, and August. Winters have obviously higher NO_2 concentrations than in the summer.

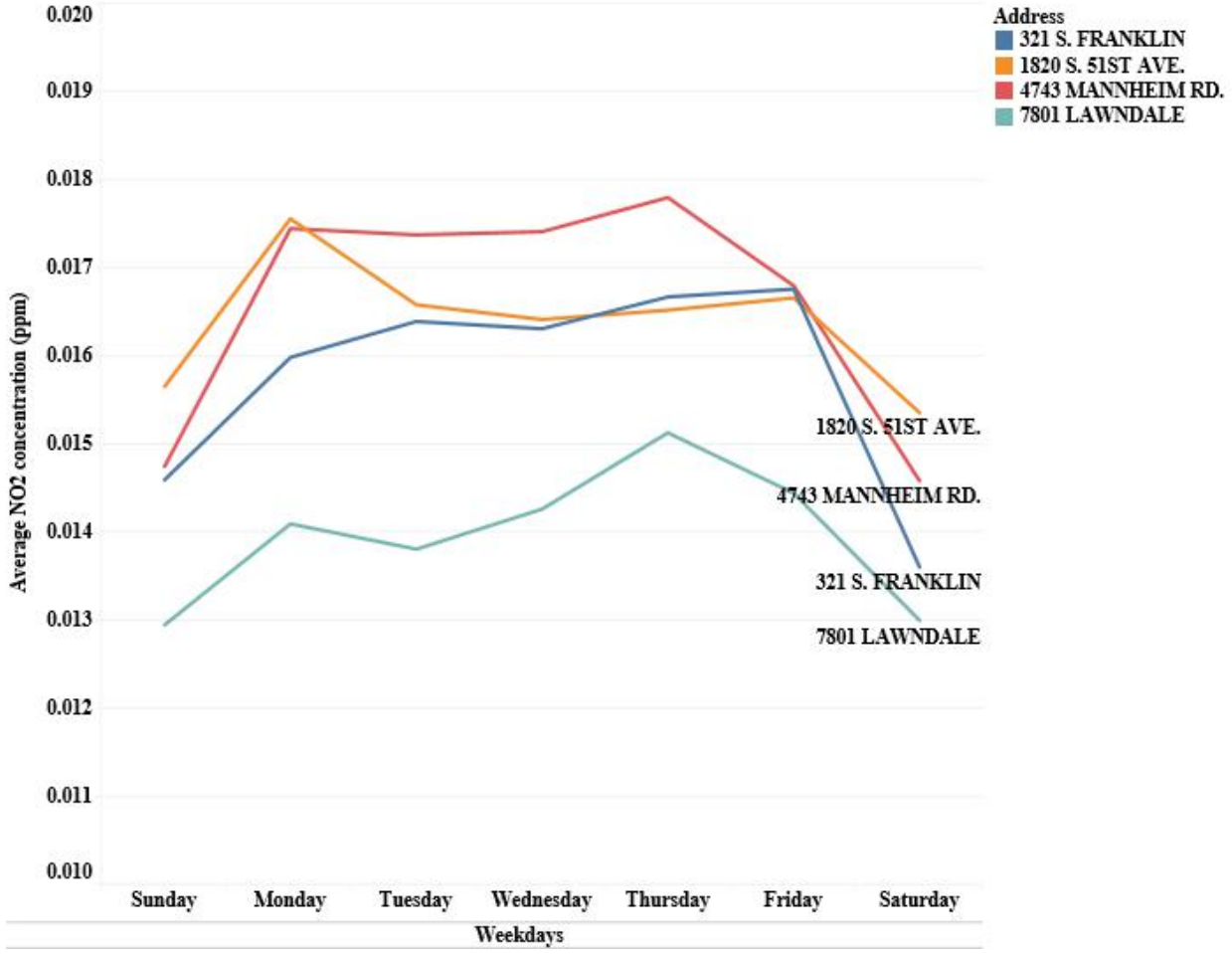

Figure 29. Weekday variation of 24-hr average NO_2 concentration at 4 addresses in Chicago from EPA monitoring in 2017.

Figure 29 shows that higher NO_2 concentrations exist in workdays than weekends. Saturday and Sunday have lower NO_2 emissions because some industrial plants stop operations and people don't need to use transportation as much.

In Figures 28 and 29, although the four locations are all in Chicago, they have obvious differences for monthly variation and weekday variation. The locations of monitors usually influence the results of measurement for concentration.

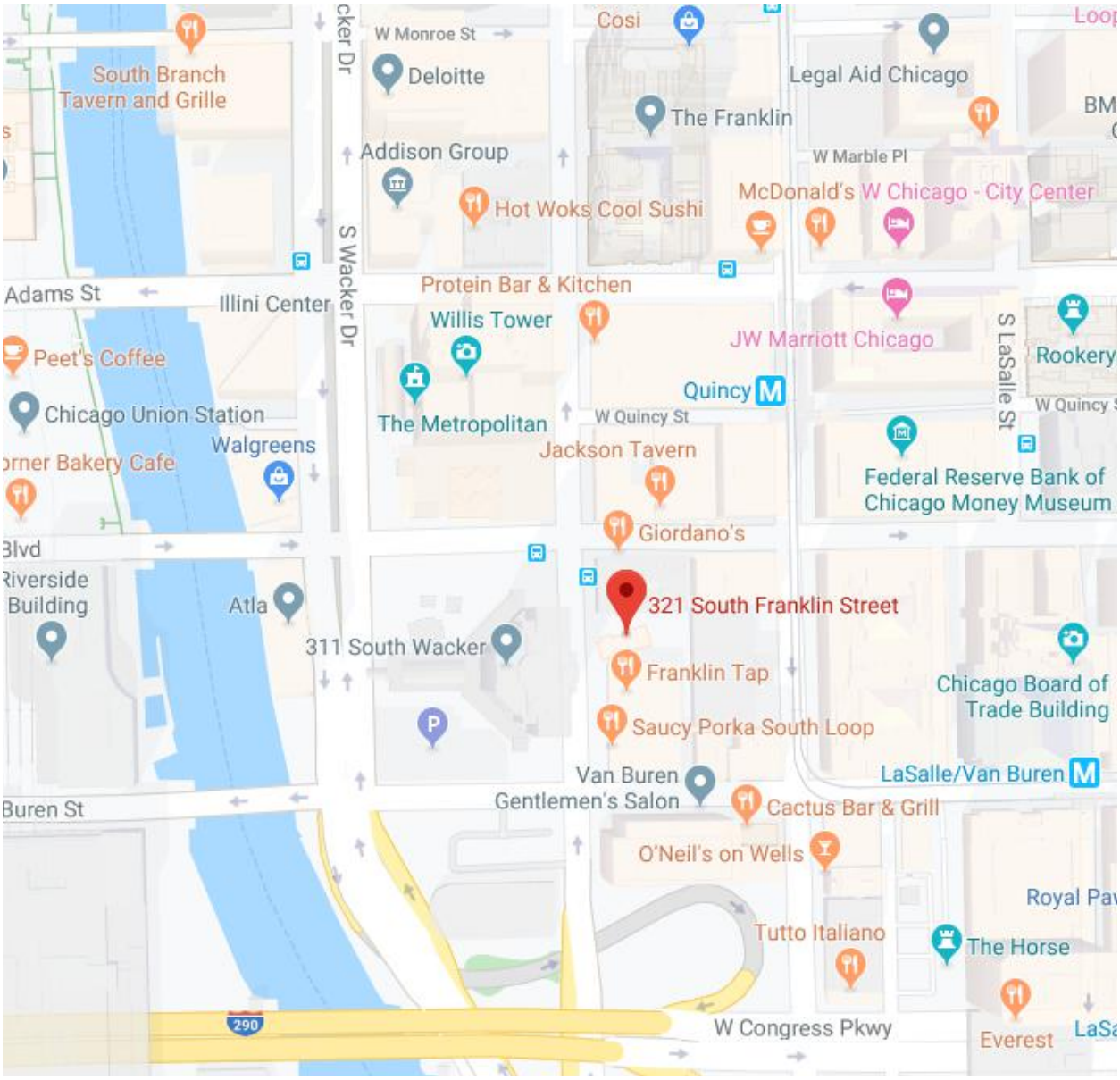

Figure 30. The map of 321 S Franklin St., Chicago, IL.

In Figure 30, the location of 321 S Franklin St., Chicago, IL is shown. There are many restaurants such as Giordano's, Franklin Tap, and Saucy Porka in the South Loop. In addition, it is a busy commercial district. Willis Tower, The Metropolitan, and the Chicago Board of Trade Building are tourist spots. They would lead to higher traffic intensity. This site is only monitoring NO_2.

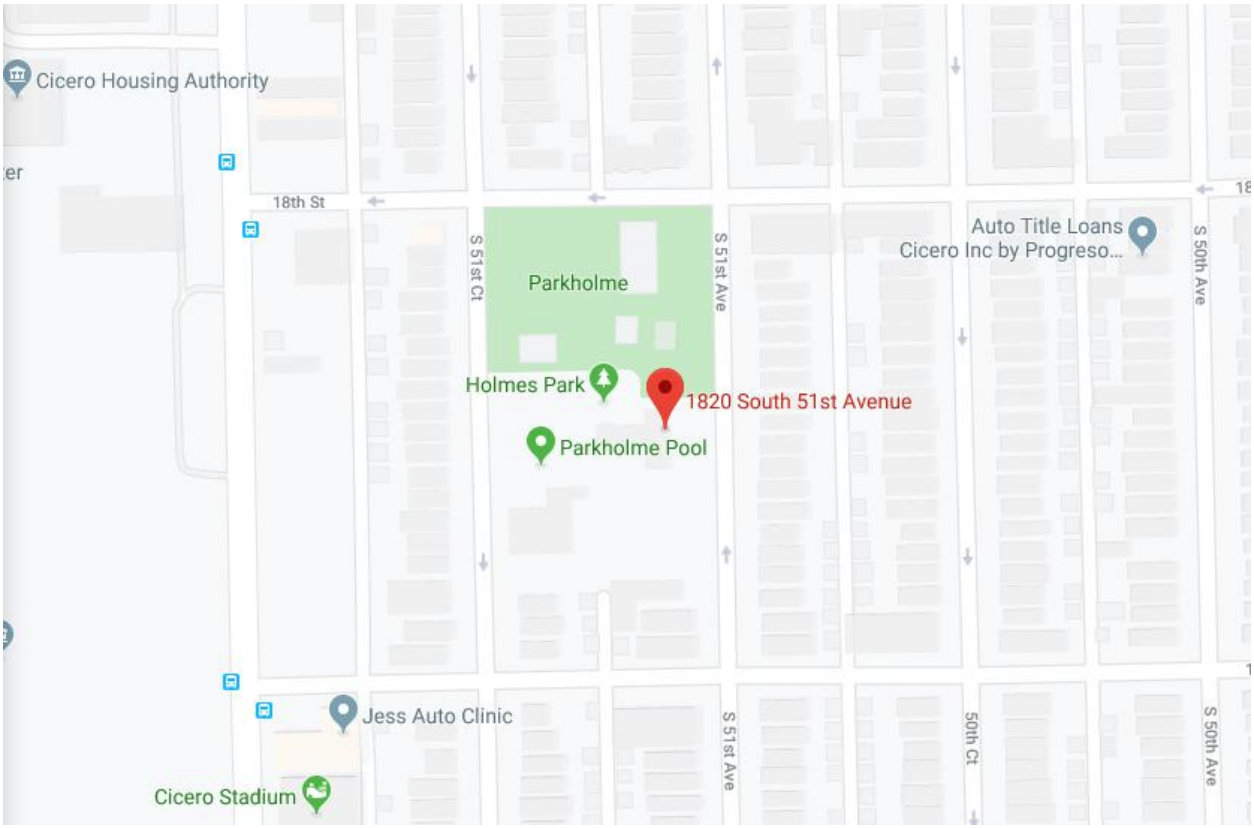

Figure 31. The map of 1820 South 51st Avenue, Cicero, IL.

In Figure 31, the neighborhood at 1820 South 51st Avenue is a large residential area. There are more parks and public infrastructures. The address of the monitor is near Holmes Park and Parkholme Pool, so higher impact from traffic on the NO_2 concentrations because people usually come here in their rest time. The location is also the address of EPA monitors for collecting data from Cicero in Figure 34-36.

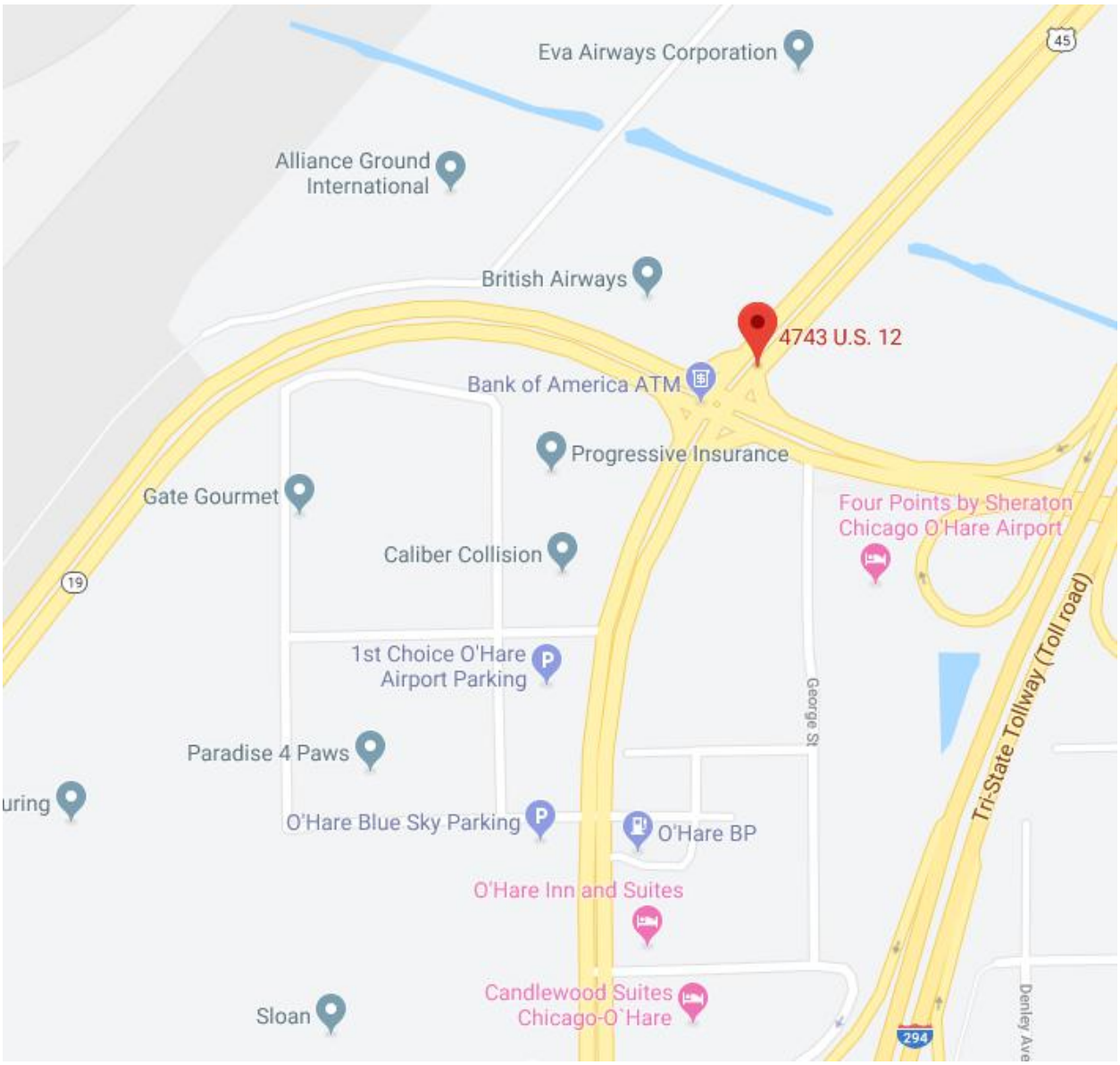

Figure 32. The map of 4743 Mannheim Road, Chicago, IL

In Figure 32, this area includes some of O'Hare Airport and several airways. Although not many commercial stores and restaurants are in this area, it is a place where traffic is concentrated because there are many vehicles in this area going to the airport. As the airport is the traffic hub connecting Chicago and other cities, there is heavy traffic around the airport. Vehicles and airplanes are the most ubiquitous mobile emitters. Additionally, the impact of traffic is the reason for NO_2 concentrations due to the location of the monitor at the main Toll Road.

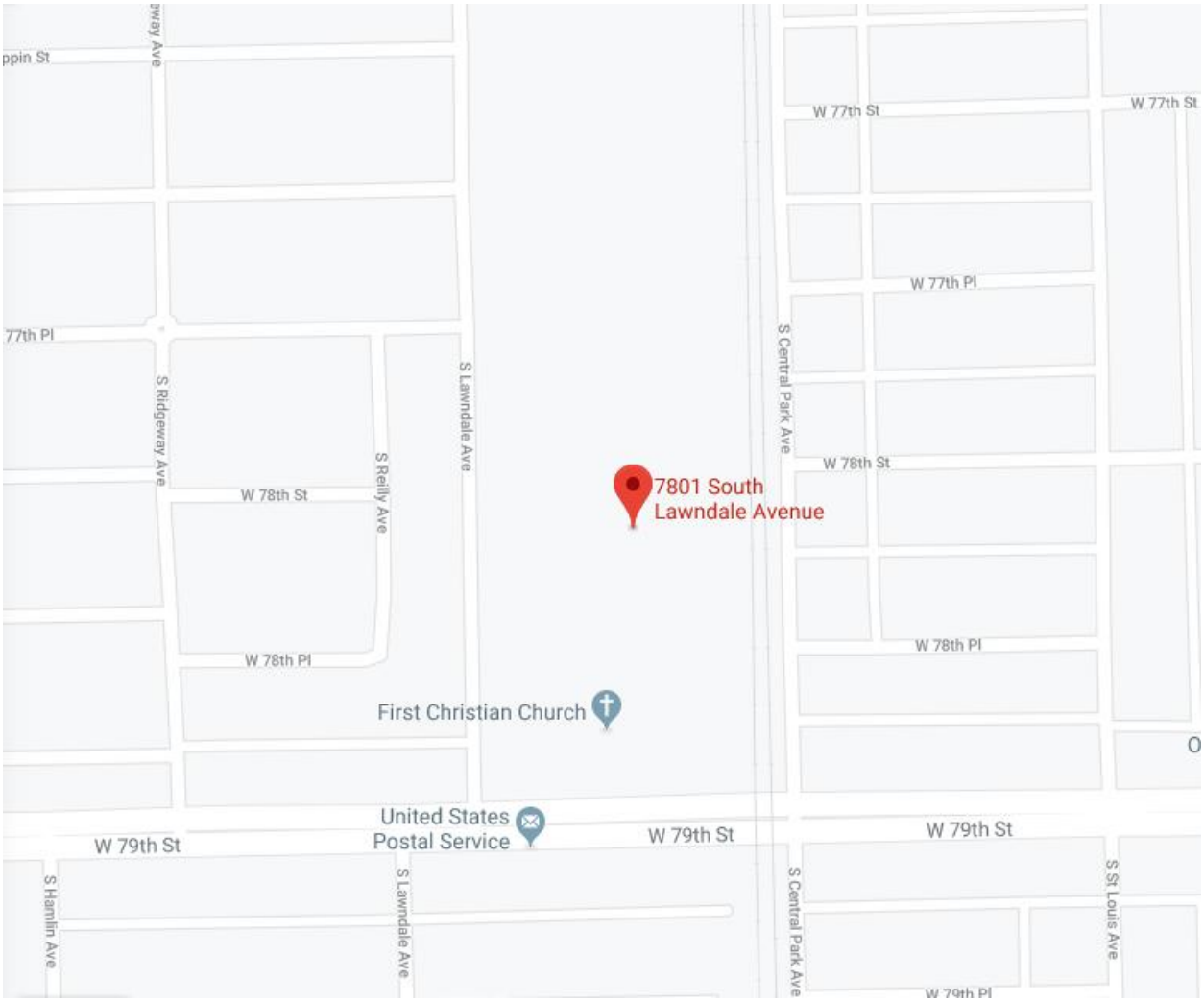

Figure 33. The map of 7801 South Lawndale Avenue, Chicago, IL.

In Figure 33, this EPA monitor "17-031-0063" at 7801 South Lawndale Avenue is located in a residential area and is a long distance from main roads such as W 79th St. The neighborhood does not have stores and restaurants. Only First Christian Church and the United States Postal Services would increase traffic intensity. The winter values may be lower because of lower emissions of NO*x* compared to greater emissions near 321 S. Franklin where there appears to be greater building density and activity.

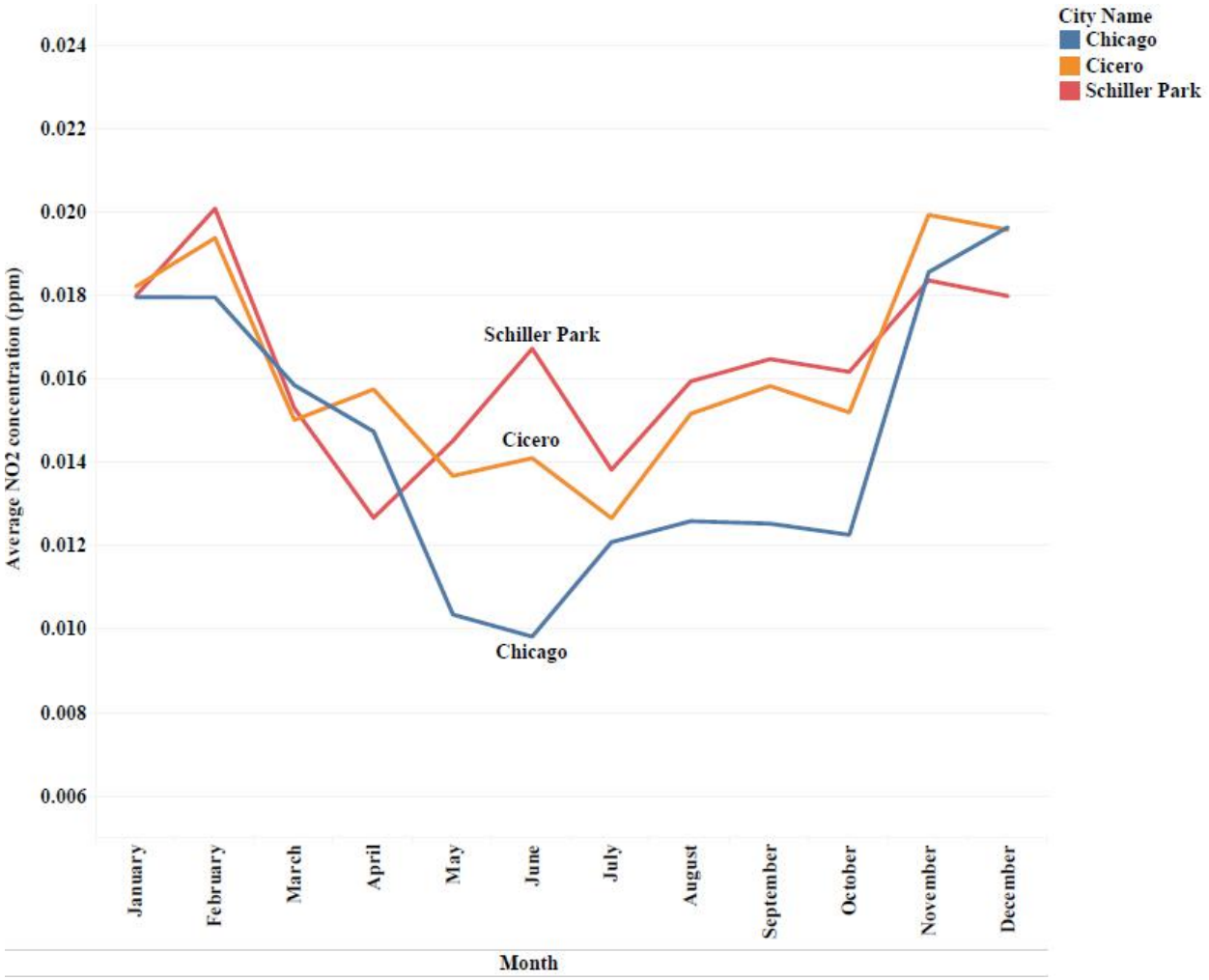

Figure 34. Monthly variation of 24-hr average NO_2 concentration at Chicago, Cicero, Schiller Park in Cook County from EPA monitoring in 2017.

For Figure 34, monthly variations in the NO_2 concentrations are lower during the summer than in winter. The peak times are during November - February, though the locations have differences in their NO_2 concentrations. The lowest concentrations are in April-July. Winters have obviously higher NO_2 concentrations than during the summer in this area, because of winter heating.

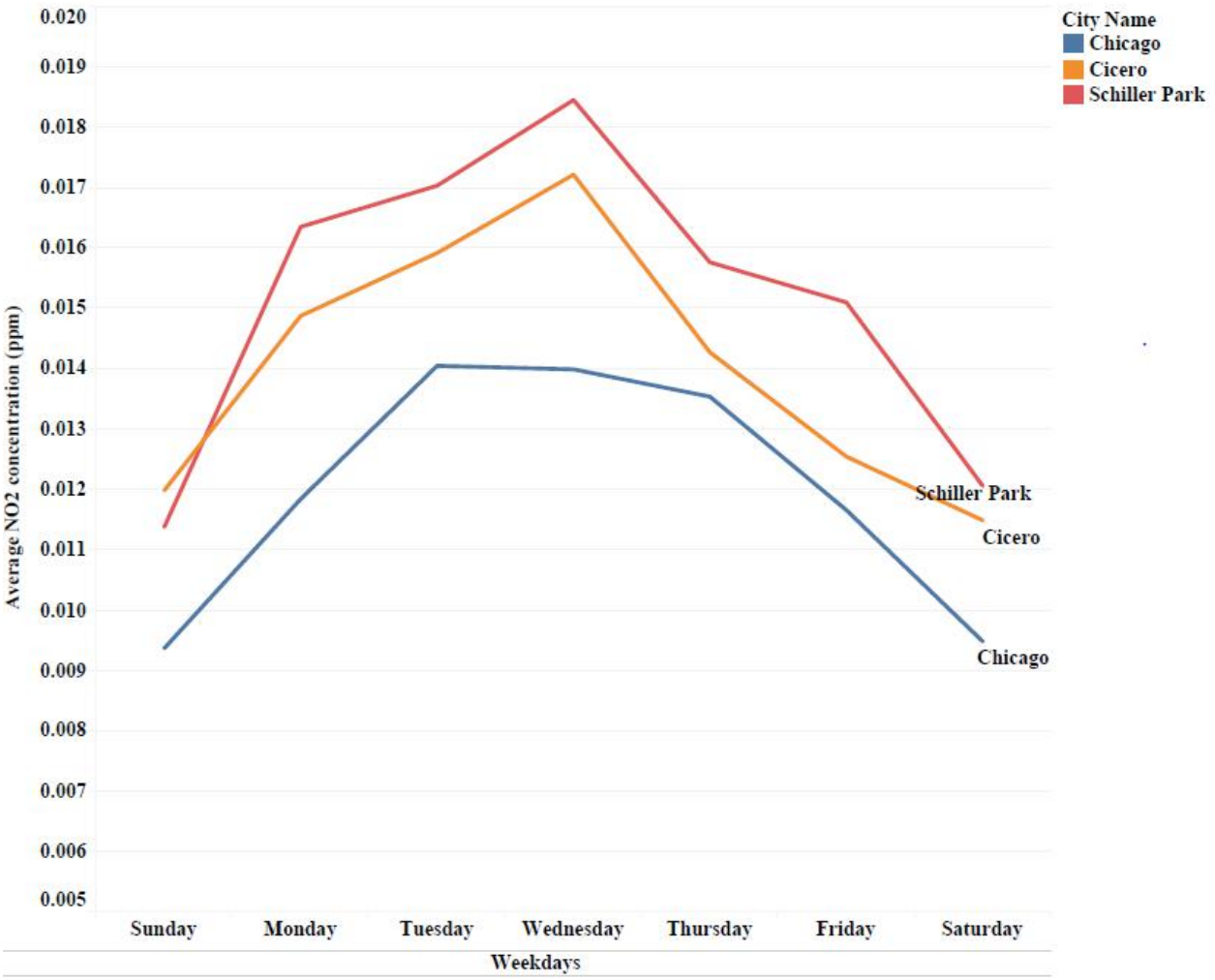

Figure 35. Weekday variation of 24-hr average NO_2 concentration at Chicago, Cicero, Schiller Park in Cook County from EPA monitoring in summer, 2017. Values are averages for each day of the week. The time period began on Tuesday, June 20 and ended on Friday, September 22 in 2017.

Figure 35 shows higher concentrations of NO_2 on workdays than on weekends in Schiller Park, Cicero, and Chicago in the summer. However, in Figure 36, there is less obvious difference between the workdays and weekends in the winter.

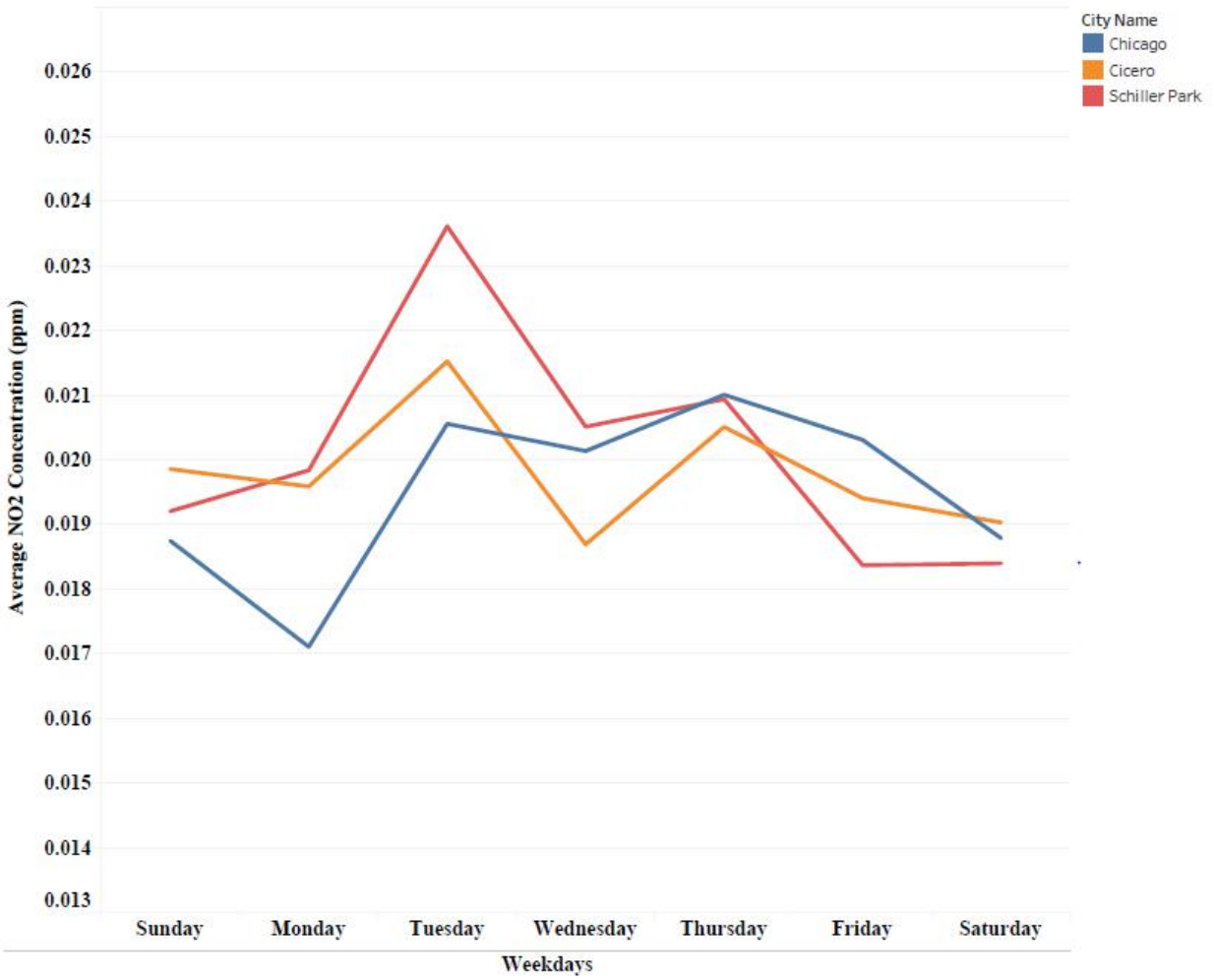

Figure 36. Weekday variation of 24-hr average NO_2 concentration at Chicago, Cicero, Schiller Park in Cook County from EPA monitoring in winter, 2017. Values are averages for each day of the week. The time period began on Thursday, December 21, 2017 and ended on Tuesday, March 20, 2018.

In Figure 34-36, the address of EPA monitor "17-031-0076" in Chicago is 7801 Lawndale; the site description in there is Com Ed Maintenance Bldg. Trailer (ComEd) as shown in Figure 37. The address of EPA monitor in Cicero is 1820 S. 51st Ave; the address of monitors in Schiller Park is 4743 Mannheim RD.

Figure 37. Ozone Sites – Illinois Chicago Area (Illinois Ambient Air Monitoring 2017 Network Plan, 2017)

Figure 37 shows the distribution of EPA ozone monitors in the Chicago area.

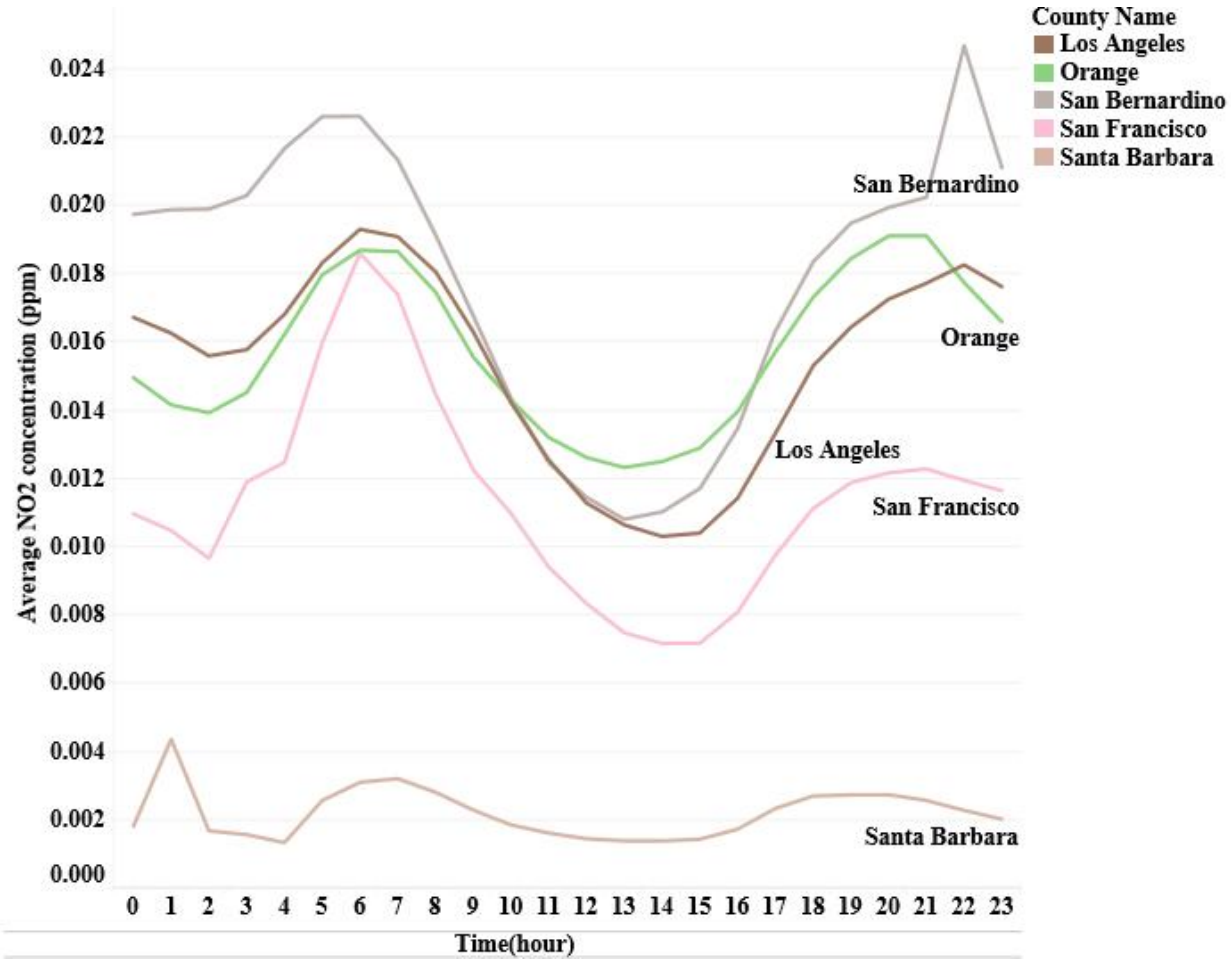

Figure 38. Hourly change of 1-hr average NO_2 concentration in different counties in California from EPA. The data of these cities are from 8:00 January 1, 2017 to 5:00 January 1, 2018.

Figure 38 shows hourly change of 1-hr average NO_2 concentration in different counties in California from EPA regulatory monitors. Figure h in Appendix A shows the geographic distribution of all data from hourly NO_2 concentration records by EPA monitors.

In Figure 38, Los Angeles, Orange, and San Francisco are large cities. They have higher traffic intensity during rush hour; thus, they have obvious peaks in NO_2 concentration around 6:00 and around 20:00. The lower concentrations are at night and in the afternoon, because these time periods have fewer NO_2 emissions from vehicles.

The lowest concentrations are for Santa Barbara, which may be due to dispersion and site of the

community. The largest concentrations are for San Bernardino which is inland away from the coast. The next highest concentrations are for Los Angeles which has a large area and large population.

For Santa Barbara, the change in NO_2 concentration within a day is lower than in many cities in California because marine pollution factors dominate the NO_2 emissions.

Ocean-going marine vessels represent a major source of uncontrolled air pollution that contribute to both local and worldwide emissions of nitrogen oxides, particulate matter, sulfur, air toxins, and greenhouse gases. Marine vessels emit a significant percentage of toxic airborne pollution worldwide.

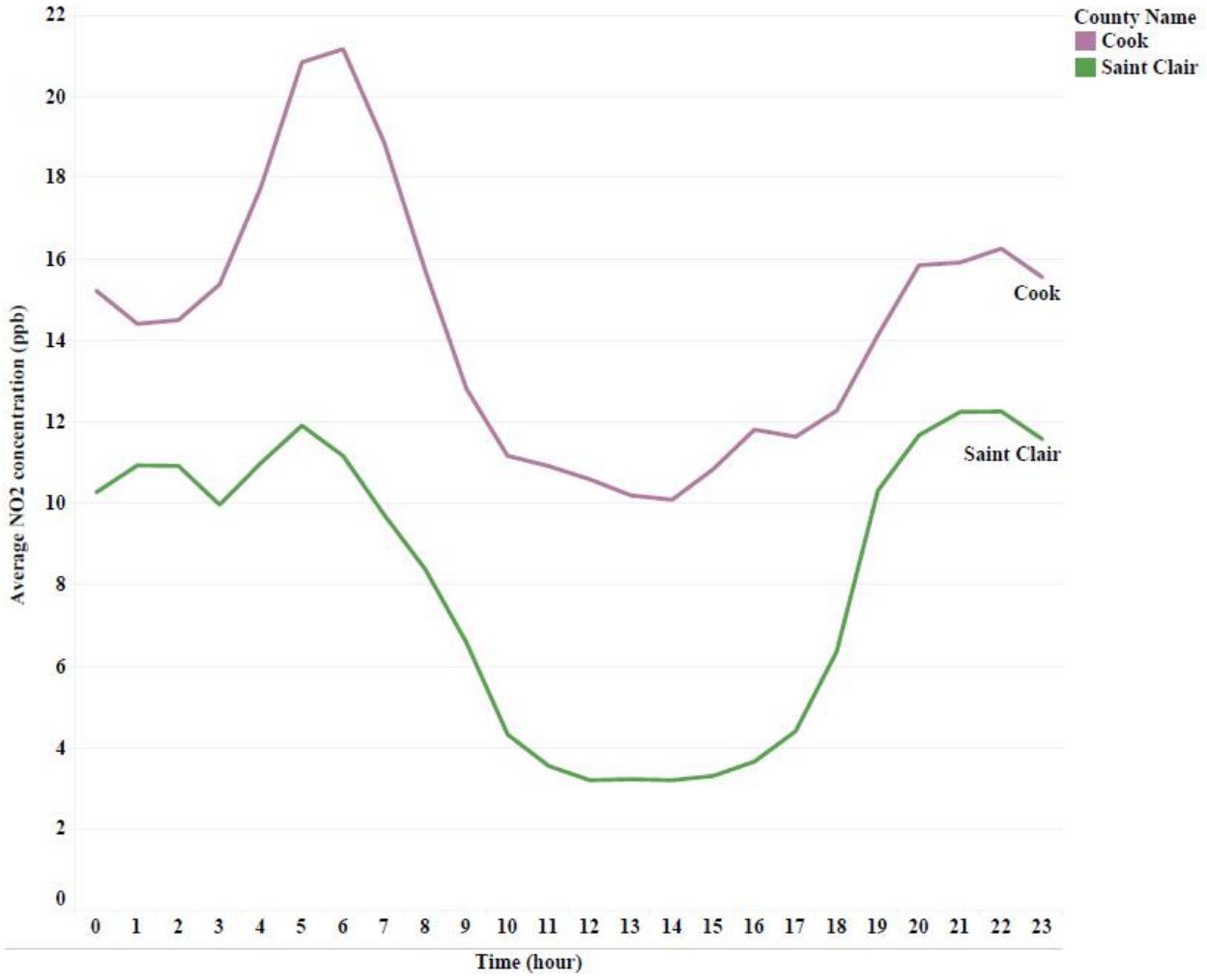

Figure 39. Hourly change of 1-hr average NO_2 concentration in different cities in Illinois on workdays in summer, 2017. The time period is from June 20, 2017 to September 22, 2017

As a local example, in 2005, ocean-going marine vessels made 7,086 trips along the 130 miles coastline of Santa Barbara County, producing 14,918 tons of NO, or 45 percent of the total NO*x* emission that year. Analysis of this activity reveals that ten percent of the vessels produced 50 percent of the emissions and 92 percent of the emissions came from foreign flagged ships. The Santa Barbara County Air Pollution Control District (District) has estimated that by 2020, ocean-going marine vessel traffic in the Santa Barbara Channel will produce nearly 75 percent of the NO*x* emissions that affect the county. The increase in vessels traveling the Southern California coast is a result of the state's role as a major point of entry and departure for trade between the US and Asia. ("*Resolution on Air Quality Ocean-Going Marine Vessel Emissions*," n.d.)

Figure 39 shows the hourly change of 1-hr average NO_2 concentration for Cook County, and Chicago is in Cook County. Compared to Chicago's data in Figure 10 in Chapter 4, the NO_2 trend by EPA monitors is not the same as by SASA "Aeroqual" sensors. The NO_2 concentration reached the maximum around 6:00 in EPA data, but it has been increasing until 10:00 in SASA data. The EPA data shows NO_2 concentration increases in the afternoon with a peak at about 20:00, but SASA data is different. The values are larger in Figure 10. The differences between them are caused by many reasons. One of direct reasons is SASA sensors are closer to a main road. Traffic influenced NO_2 trends more deeply.

The address of EPA monitor "17-031-0076" in Cook County is 7801 Lawndale, Chicago. The address of EPA monitor "17-163-0010" in St. Clair is 13th & Tutor, East St. Louis.

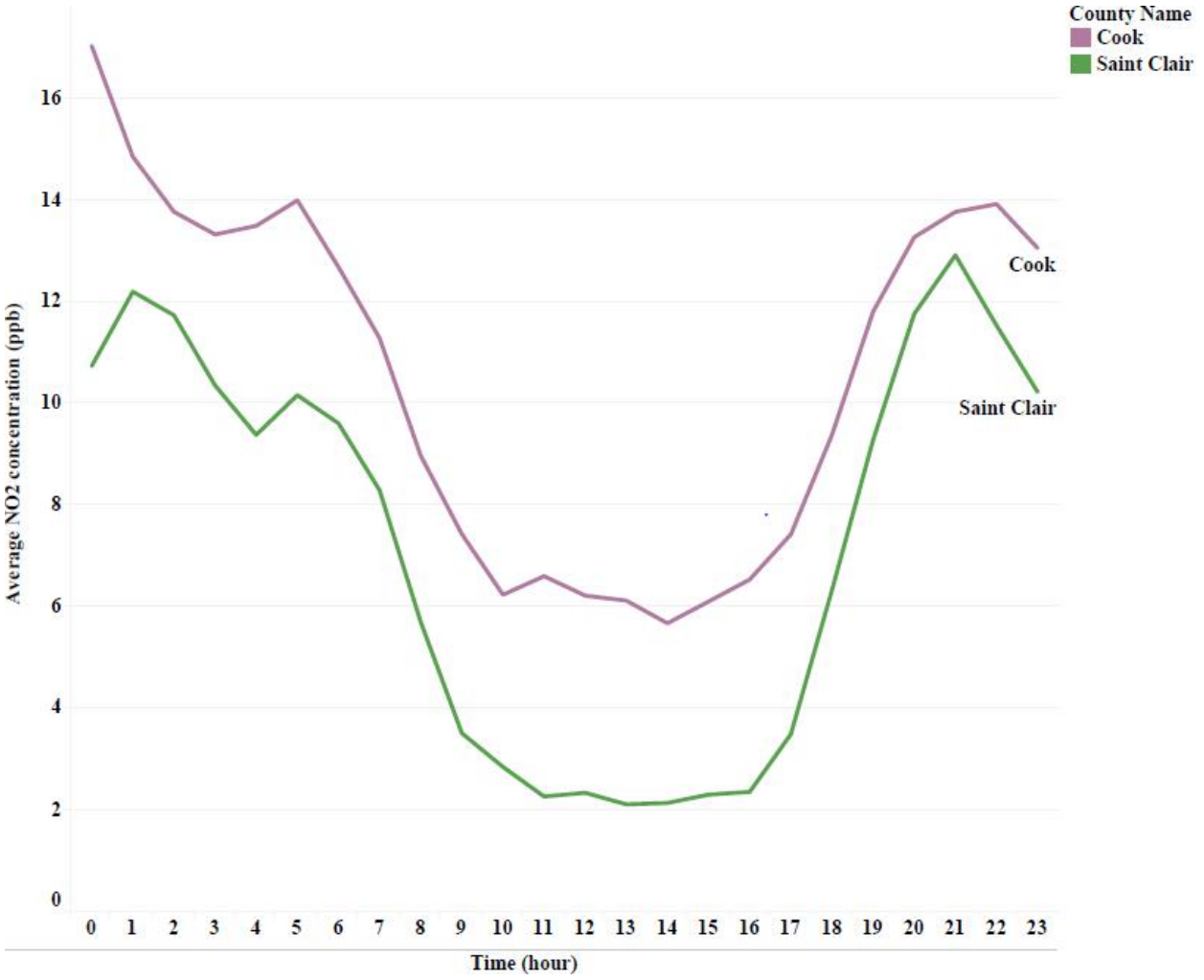

Figure 40. Hourly change of 1-hr average NO_2 concentration in different counties in Illinois on Sundays in summer 2017. The time period is from June 20, 2017 to September 22, 2017

When comparing Figure 39 and Figure 40, Cook County has a significant difference on the workdays from the weekends. In Cook County, there is a steep increase from 3:00, which peeks at 6:00 on the weekday. Although there is also a small peak around 5:00 on Sunday, it's much lower than on workdays. This phenomenon shows the impact of transportation on NO_2 concentrations. On workdays, people go out earlier. Thus, there is a peak in traffic intensity around 5:00. NO_2 concentrations also have a peak around 5:00, and 6:00.

Saint Clair County does not have any obvious differences between workdays and Sundays. Saint Clair has lower concentrations than Cook whether in the winter or summer. Comparing Figure 38 and Figure 39 shows that values are larger on workdays.

Cook County is a county in the U.S. state of Illinois. It is the second most populous county in the United States after Los Angeles County, California, and it contains the city of Chicago. As of 2017, the population was 5,211,263 people. ("Cook County, Illinois," 2019) St. Clair County, IL is a county located near St. Louis, MO bordering the east bank of the Mississippi River. As of the 2010 census, the population was 262,417 people.

St. Clair County has fewer people than Cook County. It might have fewer vehicles also. As a result, the lower NO_2 concentrations are reasonable for St. Clair County. The satellite maps of Cook and St. Clair counties are shown in Figure b and f in Appendix A.

Figure 41. Hourly change of 1-hr average NO_2 concentration in different counties in Illinois on Sundays in winter 2017. The time period is from 0:00 December 21, 2017 to 0:00 March 21, 2018

Comparing Figure 40 and Figure 41, the average level of NO_2 concentrations for Cook County in the winter are higher than in the summer, because of more heating use in the winter. Cook and Saint Clair both have obvious variations in concentrations due to traffic intensity. For example, In Figure 40, Cook and Saint Clair counties both have a peak at 6:00 because many people need to go to work or to other destinations at that time. On the other hand, Figure 41 shows that NO_2 concentration is high at 3 am, which is due to winter heating. The high NO_2 concentration might relate to no sunlight in the nighttime. As shown in Equation 2, NO_2 can react with sunlight to

produce NO. However, at 3:00, because there is no sunlight, the reaction cannot happen. It results in NO_2 accumulation.

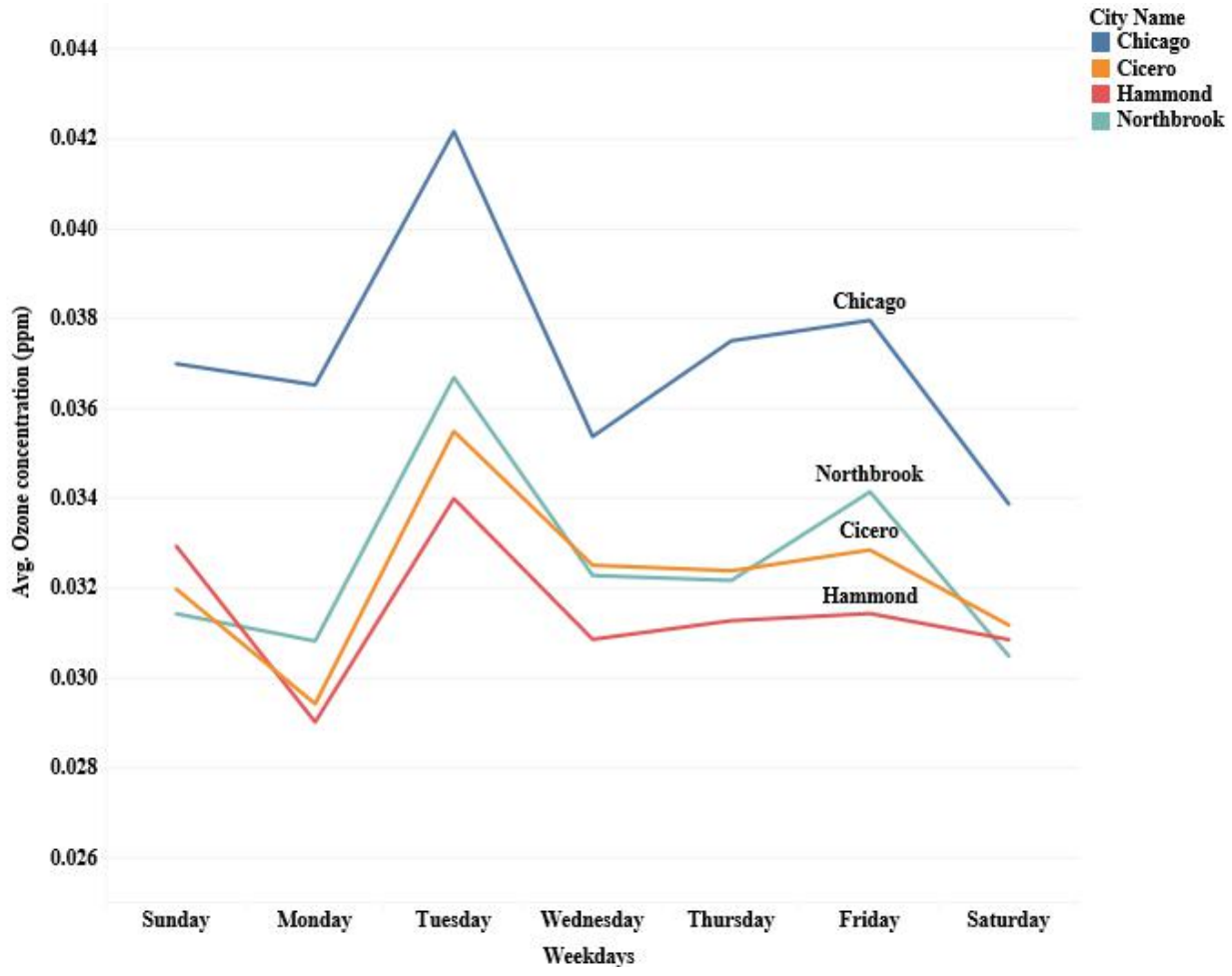

Figure 42. Weekday variation of 24-hr average O_3 concentration in Chicago, Cicero, Hammond, and Northbrook in summer 2017.

In Figures 42-43, the address of EPA monitor "17-031-0076" in Chicago is 7801 Lawndale. The address of EPA monitor "17-031-4002" in Cicero is 1820 S. 51st Ave. The address of EPA monitor "17-031-4201" in Northbrook is 750 Dundee Rd.

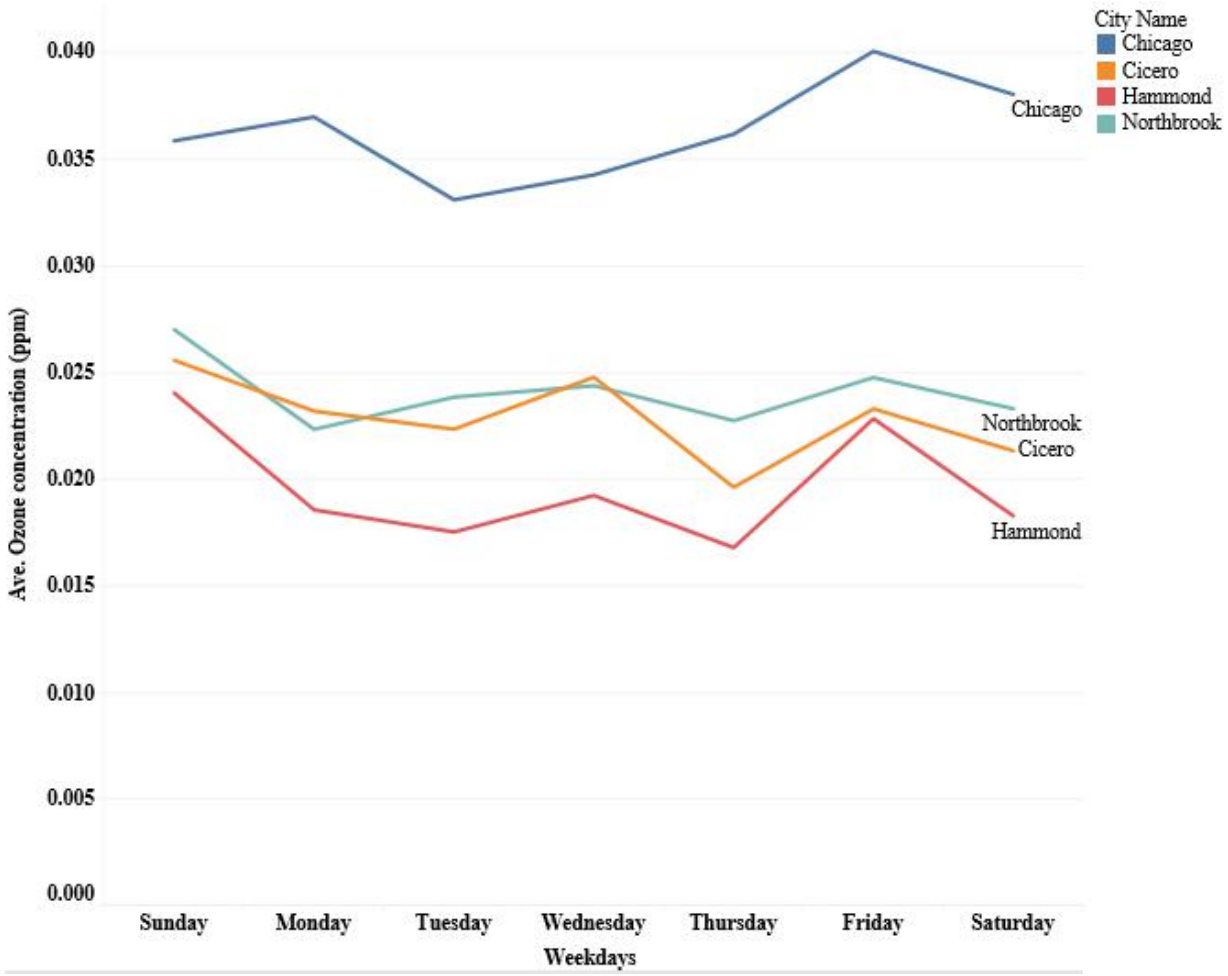

Figure 43. Weekday variation of 24-hr average O_3 concentration in 4 cities in winter 2017.

In Figure 42 and Figure 43, the daily average ozone concentrations are displayed for a week. No obvious regular variations were found on workdays. Chicago has high average ozone concentrations in the summer, but it has lower ozone concentrations in the winter.

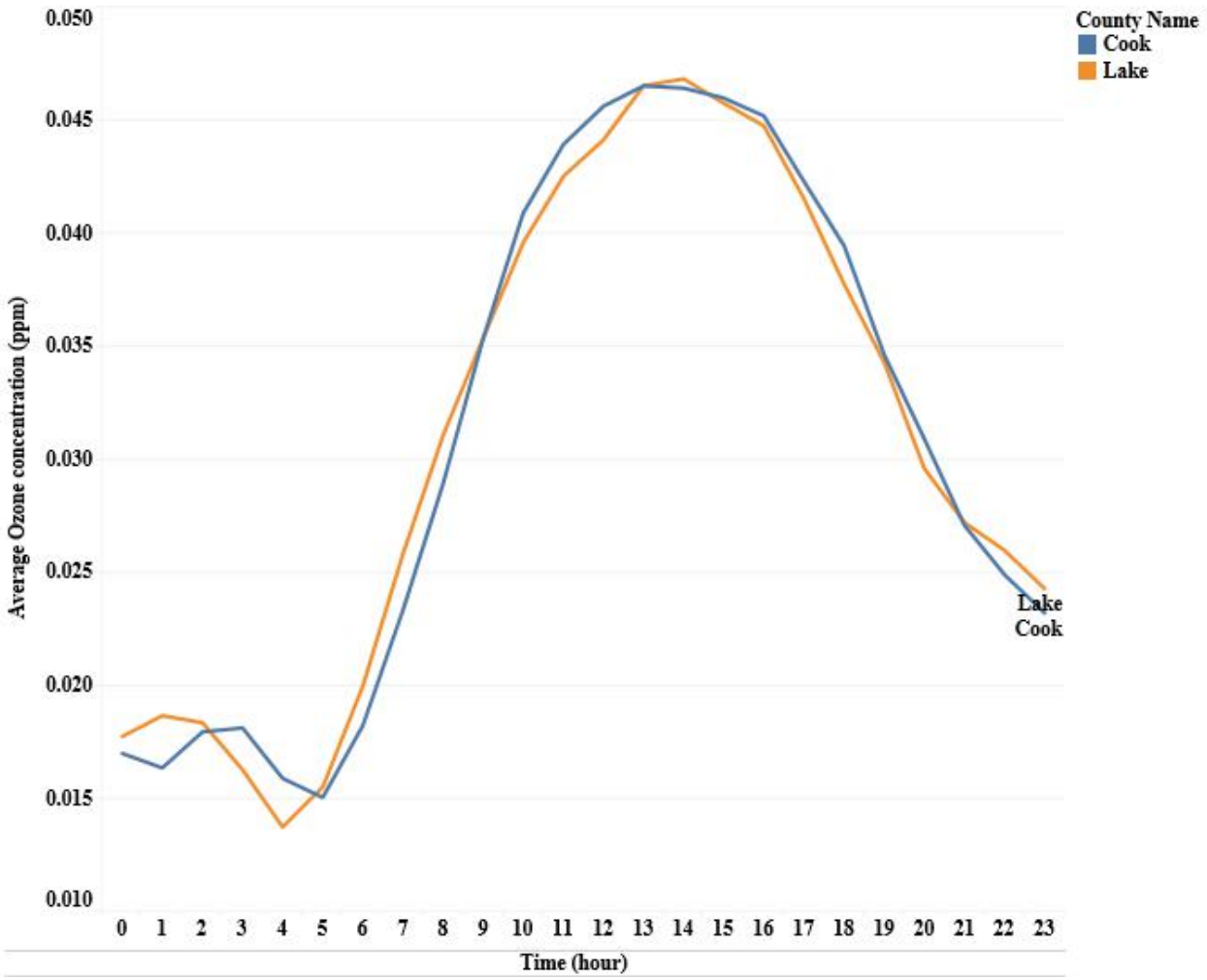

Figure 44. Hourly variation of 1-hr average O_3 concentration in Lake County, , Illinois, and Cook County, Illinois from EPA monitoring in summer 2017 on Sundays.

Comparing Figures 44-47, Lake County and Cook County have larger differences in the winter than in the summer. In Figures 44 and 45, there are more similar change patterns for ozone concentrations with time of day. The peak ozone concentrations are larger in the summer.

All detailed addresses of EPA monitors for the counties in Chapter 5 are found from Illinois Ambient Air Monitoring 2017 Network Plan (*Illinois Ambient Air Monitoring 2017 Network Plan*, 2017).

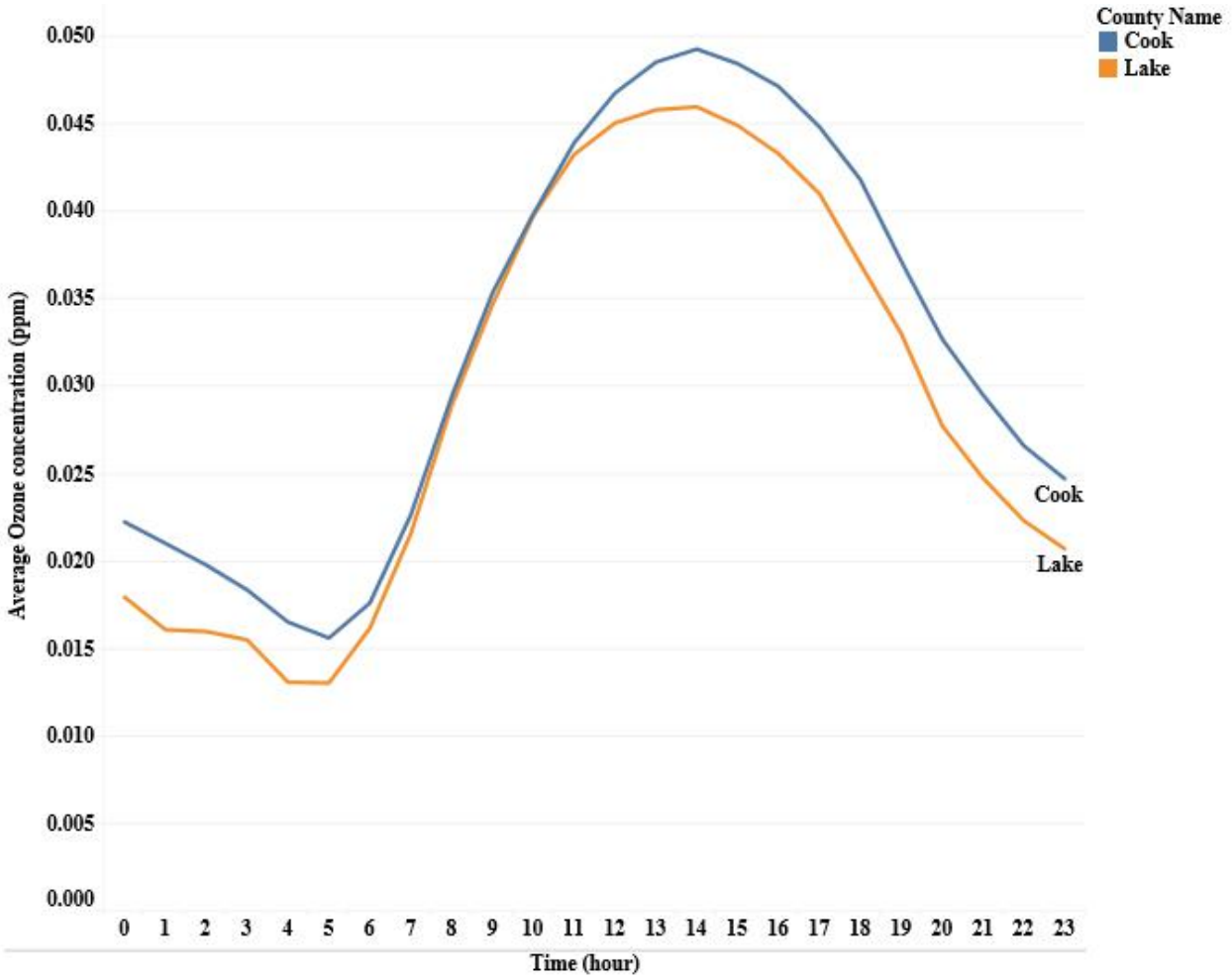

Figure 45. Hourly variation of 1-hr average O_3 concentration in Lake County, Illinois, and Cook County, Illinois from EPA monitoring in summer 2017 On workdays.

In Figures 44-47, the address of EPA monitor "17-031-0076" in Cook County is 7801 Lawndale, Chicago. The address of EPA monitor "17-097-1007" in Lake County is Illinois Beach State Park, Zion.

Comparing Figure 44 to Figure 45, Lake County and Cook County have closer ozone concentration on Sundays than on workdays. The monitor in Cook County is closer to main roads, so traffic causes more emission on workdays. The results of their differences are reasonable.

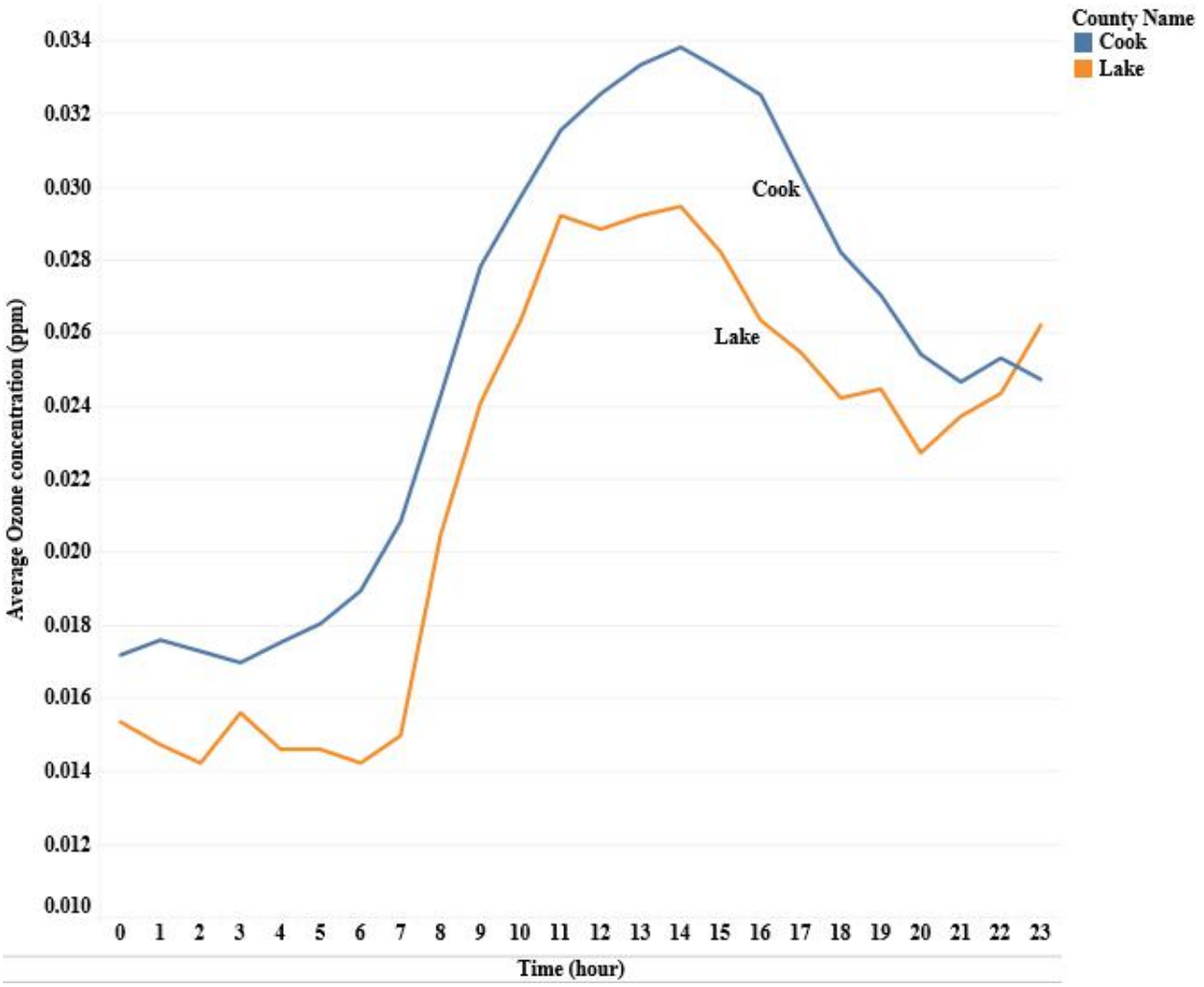

Figure 46. Hourly variation of 1-hr average O_3 concentration in Lake County, Illinois, and Cook County, Illinois from EPA monitoring in winter 2017 On Sundays.

In Figure 46 and Figure 47, on workdays, for Cook County, it can be noted that from 12:00 to14:00, the ozone concentrations have peaked. The concentrations at Lake County reached the maximum around 13:00. However, on Sundays, there are two peaks in ozone concentrations for Lake County at 11:00 and 14:00. Rush hours are more dispersive on Sundays because people can choose to go out more freely on Sundays. The differences between workdays and Sundays in people's behavior influence traffic. Traffic influences NO_2 concentrations in the atmosphere. The series of reactions related to NO_2 produce ozone; thus, changes in ozone concentrations are influenced by changes in NO_2 concentration.

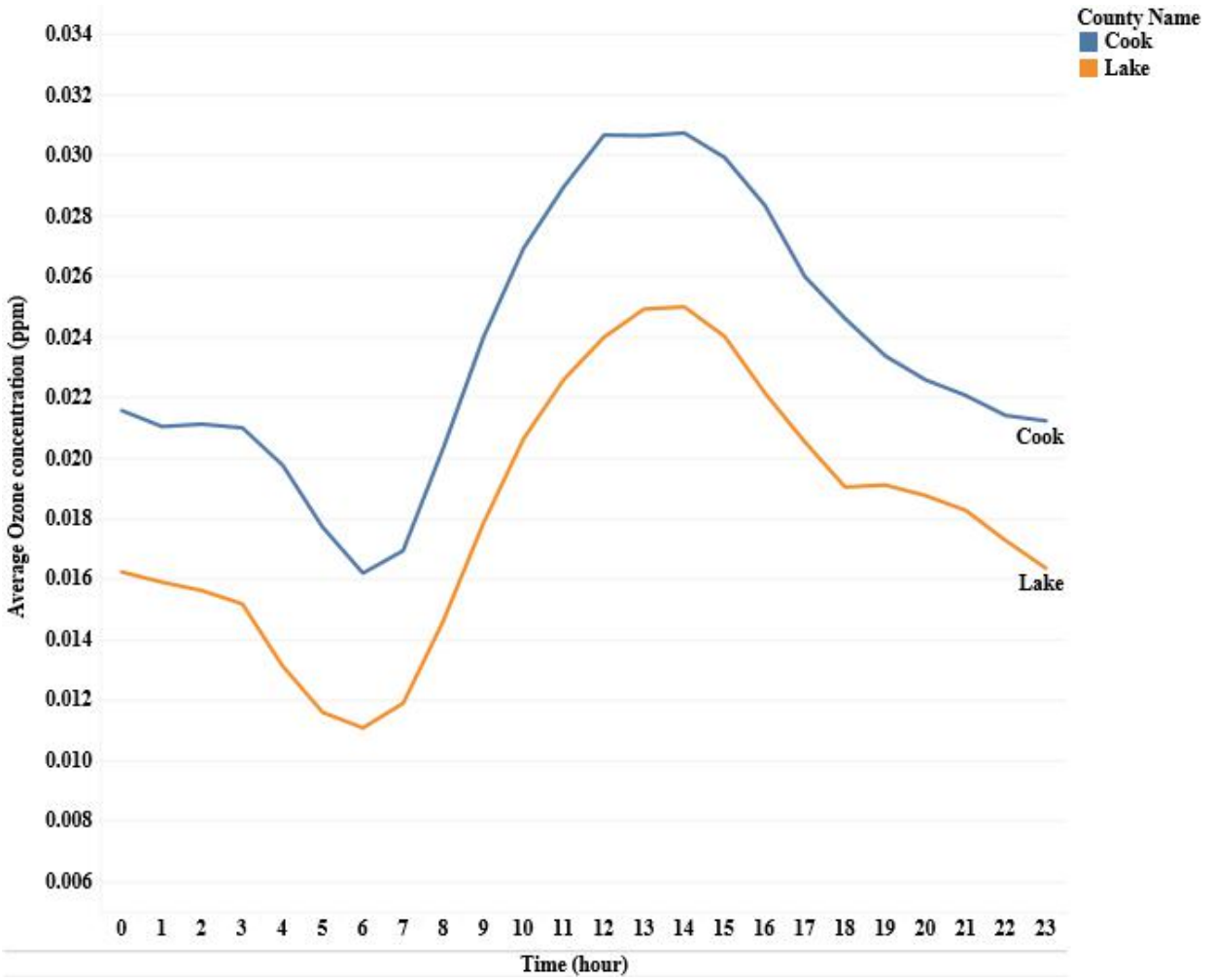

Figure 47. Hourly variation of 1-hr average O_3 concentration in Lake County, Illinois, and Cook County, Illinois from EPA monitoring in winter 2017 on workdays.

During the winter, there is more industrial pollution and NO*x* pollutants from heating use in Cook County; Lake County is a county located in Indiana. In 2010, its population was 496,005, making it Indiana's second-most populous county. (*Lake County QuickFacts from the US Census Bureau*, 2011) Cook County has a much greater population than Lake County. The figures show that most of the time, ozone concentrations in Cook County are higher than Lake County. However, Lake County also has busy urban areas. So, in these areas, NO*x* concentrations are deeply influenced by transportation, while ozone concentrations are influenced by NO*x* concentrations and solar radiation.

Chapter 6 - Air Quality Improvement

6.1 Greening and Planting

For street canyons in urban areas, urban greening could be an effective tool to reduce street-level concentrations. Concentrations can be reduced by controlling emissions, increasing dispersion, or increasing deposition rates (Pugh et al., 2012).

Compared to controlling emissions or enhancing dispersion, less attention has been paid to increasing deposition rates as a pollution control method. Increasing deposition surfaces is one of the most effective ways to substantially reduce pollutant concentrations in the atmosphere where people are likely to be exposed. Another effective method for pollution control is to enhance deposition velocities to in-canyon surfaces. There are two detailed methods to enhancing deposition velocities to surfaces, such as, Green walls and street trees. Many researchers have focused on canyon residence time and wind speed, because they are determining factors for pollutant concentration reductions. Increased residence time within the canyon acts to increase street-level pollutant concentrations. For green walls, in an idealized city of uniform street canyons with h/w=1, annual average concentrations of in-canyon NO_2 were reduced by 9% by greening of canyon walls across large areas of street canyons. In the other hand, street trees have the potential to substantially lengthen canyon air residence times and so increase street-level pollution concentrations. Although vehicular pollutants are reduced by dispersion, this is limited at the street-level by in-canyon air recirculation and low wind speeds. Pollutant concentrations can also be reduced by increasing dry deposition to surfaces.(Pugh et al., 2012; Solmon et al., 2004)

Urban tree planting is a cost-effective means to improve air quality. Vegetation plays a vital role in urban environments. Trees help reduce the potential adverse health and environmental effects of NO_2 by removing it from the air. Gaseous air pollutants are taken in primarily through the leaf stomata (pores). The removal of gaseous pollutants is more permanent than the removal of particulates because the gases are often absorbed and converted within the leaf interior (US EPA, 2015). O_3 can be fully detoxified within the plant's leaf structure. O_3 can be removed after entering the stomata and undergoing subsequent reactions within the intercellular region. At high O_3 levels, O_3 accumulates within the intercellular spaces and decreases the total O_3 flux (Fares et

al., 2010). Some O_3 can be permanently removed due to plants' metabolic pathways (Mikkelsen et al., 2004; Nowak et al., 2006) Healthy trees can remove significant amounts of air pollution in cities, where it is often concentrated (US EPA, 2015). In addition, vegetated roofs and facades can help to reduce the cooling demand in summer and also contribute to insulation in winter, leading to less heat loss into the atmosphere and savings in energy consumption for the immediate environment (Simon et al., 2019). If baseline shrubs on the ground were supplemented with 20% intensive green roofs, these structures could remove 1.74 and 1.24 metric tons/year of O_3 and NO_2. In contrast, if baseline trees and shrubs on the ground were supplemented with 20% extensive green roofs only, 1.27 and 0.65 metric tons/year of O_3 and NO_2 would be removed. Although trees were not investigated as part of green roof structures, they were found to reduce air pollutants to the greatest degree due to their high surface area (Gourdji, 2018). In the other hand, to increase the vegetative cover in urban areas so as to reestablish the beneficial cooling effects associated with it is an effective way of combating the urban heat island effect (Gray & Finster, 1999).

However, in the presence of nitrogen oxides (NO*x*), produced mainly in vehicle emissions, some gaseous emissions from vegetation can in fact contribute to decreased air quality (Churkina et al., 2017) In addition, there are large inputs of energy from fossil fuels to maintain vegetation structure. For example, the equipment includes that for transport or maintenance, chain saws, back hoes, leaf blowers, chippers, and shredders which are utilized and cause emissions of VOCs and nitrogen oxides. And then VOCs and nitrogen oxides also might lead to ozone pollution by photochemical reactions (Churkina et al., 2017). While lower pollutant emissions generally improve air quality, lower nitrogen oxide emissions, particularly ground-level emissions, may lead to a local increase in ozone concentrations under certain conditions due to nitrogen oxide scavenging of ozone (Simon et al., 2019). In urban and suburban areas with substantial levels of NO*x*, isoprene contributes to the formation of ground-level ozone (Simon et al., 2019). Designing an effective way of tree planting is important because biogenic volatile organic compound (BVOC) emissions of various tree species are different. Planting some common types of trees will increase the pollution, because they release significant amounts of biogenic volatile organic compounds into the atmosphere, including isoprene, monoterpenes (MT) and sesquiterpenes (SQT). For example, oak and pine emit large quantities of BVOC into the

atmosphere; consequently, planting such tree species in large numbers could potentially worsen inner city air quality (Pugh et al., 2012). Drought tolerant, deciduous broad-leaved trees with low biogenic volatile organic compound emissions including Japanese Maple or Acerpalmatum 'Shaina' and 'Mikawa-Yatsubusa' are options to reduce O_3 levels. Magnolias are tolerant to NO_2 and it is important in their metabolic pathways (Gourdji, 2018).

Targeting the problem of planting in urban areas, the effective ways are always explored which can improve air quality and cause less NO*x* emission and ozone pollution at the same time. There are some suggestions for efficient pollution controls. First, finding suitable types of trees is the most important. For example, sustaining existing tree cover could maintain pollution removal levels. Developing vegetated roofs and facades, and increasing surface area of green roofs are good ways. Maximize use of low VOC emitting trees could reduce ozone formation. Utilizing or planting low maintenance trees to reduce pollutants emissions from maintenance activities is also a feasible way. Second, more reasonable design or plans of planting is necessary. For the consideration of reducing pollutant emissions from power plants, selecting energy conserving locations to plant trees is better. Additionally, planting trees in the side of roads could shade parked cars. It can reduce vehicular VOC emissions (Nowak, 2002). Plant trees in polluted areas or heavily populated areas could maximize tree air quality benefits. Third, select environmental-friendly methods to maintain vegetation. Supplying ample water to vegetation enhances pollution removal and temperature reduction. Reducing fossil fuel use in maintaining vegetation can reduce NO*x* pollutant emissions.

6.2 Urea for Diesel Vehicle

Wang et al. (2008) found that diesel taxis have high NO*x* emissions. Diesel taxis with NO*x* emissions are almost three times that of gasoline taxis. Although light diesel engines have the advantages of energy saving and reduced carbon dioxide emissions, light gasoline vehicles are superior to light diesel vehicles in terms of NO*x* control. Diesel engines can be run with a lean burn air-to-fuel ratio (overstoichiometric ratio), to ensure the full combustion of soot and to prevent their exhausting unburnt fuel. The excess air necessarily leads to generation of nitrogen oxides (NO*x*), which are harmful pollutants, from the nitrogen in the air (*Urea tanks on diesel trucks—That's the law in the United States starting in 2010*, 2008). The high compression ratios

of diesel engines create high combustion temperatures in combustion chamber. Therefore, diesel engines offer a very effective infrastructure for the formation of NO*x* emissions. Compression ratio and air excess coefficient values of diesel engines are considerably higher than those of gasoline engines. In this case, when compared with gasoline engines, diesel engines cause the generation of NO*x* emissions at much higher rates. When cylinder temperature exceeds about 1500°C, N_2 gas in the air taken into the cylinder reacts with oxygen to form NO*x*. (Reşitoğlu, 2018) Depending on the increase in temperature, NO*x* also increases. Each increase of 1% in temperature over 1700°C causes 20% increase in NO*x*.

The technology of Selective catalytic reduction (SCR) is used to reduce the amount of NO*x* released into the atmosphere. An SCR technology has been used in industrial stationary applications, and then was introduced to the NO*x* emissions of mobile diesel engines. 'urea SCR or "urea-based SCR,' is the only technology available that can remove enough NO*x* from diesel exhaust to comply with strict new limits imposed by the U.S. Environmental Protection Agency (EPA), says Glenn Kedzie, Environmental Counsel for the American Trucking Associations ("Urea tanks on diesel trucks—that's the law in the United States starting in 2010," 2008).

Urea tanks have been standard equipment for most new diesel trucks, buses, cars, and sport utility vehicles (SUVs) manufactured in the United States after Jan. 1, 2010. An automotive grade of urea was injected into the vehicles' exhaust stream to "scrub" nitrogen oxide (NO*x*) from the diesel exhaust. The automotive urea, called "diesel exhaust fluid" (DEF) in the United States and AdBlue, a trademarked name in Europe, reduces NO*x* by as much as 90% alone, and can take NO*x* to near-zero levels when used in combination with diesel particulate filter technology, says Kim Doran, spokesperson of the newly formed North American SCR Stakeholders Group and editor of FactsAboutSCR.com, a Web site dedicated to SCR news. DEF and AdBlue are an aqueous urea solution 32 (AUS 32), a clear 32.5% nitrogen solution of high-purity urea in demineralized water. The urea solutions are safe to handle, manufacturers claim. AdBlue can be bought in bulk in Europe or by the liter at some service stations ("Urea tanks on diesel trucks—that's the law in the United States starting in 2010," 2008). Urea SCR cleans the exhaust after combustion. The urea solution is held in a separate storage tank and injected as a fine mist into the hot exhaust gases. The heat breaks the urea down into ammonia-the actual NO*x*-reducing agent. Through a catalytic converter, the ammonia breaks the NO*x* down to

harmless nitrogen (N) gas and water vapor. The exhaust is no longer a pollutant; the atmosphere is about 80% nitrogen gas. The advent of DEF and AdBlue is creating a new demand for urea, the world's most widely used nitrogen fertilizer. Some are concerned that the new use will drive fertilizer prices higher. Others think it will be an incentive for manufacturers to increase production and thus, lower prices.

Doran says, 'Because SCR technologies reduce NO*x* exhaust to almost zero, engines can be tuned to maximize fuel efficiency. The exhaust coming from the tailpipe of an SCR-equipped vehicle may actually be cleaner than the air around it.' In fact, according to Daimler Trucks, the engine efficiency achieved by using SCR technology in Europe has saved customers more than 280 million liters of diesel and nearly half a billion dollars in fuel spending. At the same time, the environment was spared about 800,000 metric tons of carbon dioxide ("Urea tanks on diesel trucks-That's the law in the United States starting in 2010," 2008). SCR technologies are worthy to promote the use of the application due to their advantages.

AdBlue is the fluid used in most vehicles is known as, a registered trademark owned by the German Association of the Automobile Industry (VDA), which ensures standards are maintained. The fluid is stored in a tank in the car, but unlike petrol or diesel it is not injected into the engine; instead it is fed into part of the vehicle's exhaust. A chemical reaction converts the harmful NO*x* exhaust gases into harmless nitrogen and water (*What is AdBlue, how is it refilled and why do diesel cars use it?*, n.d.).

Diesel exhaust fluid (DEF) from a separate tank is injected into the exhaust pipeline, where the aqueous urea vaporizes and decomposes to form ammonia and carbon dioxide. Within the SCR catalyst, the NO*x* is catalytically reduced by the ammonia (NH_3) into water (H_2O) and nitrogen (N_2), which are both harmless; and these are then released through the exhaust. DEF is a 32.5% urea solution, CO $(NH_2)_2$. When it is injected into the hot exhaust gas stream, the water evaporates and the urea thermally decomposes to form ammonia and isocyanic acid under high temperature conditions:

$$CO(NH_2)_2 \rightarrow NH_3\,(g) + HNCO \qquad \text{Equation 12}$$

The isocyanic acid hydrolyses to carbon dioxide and ammonia:

$HNCO + H_2O \rightarrow CO_2 + NH_3$ Equation 13

Overall, this is $CO(NH_2)_2 + H_2O \rightarrow 2\ NH_3 + CO_2$ Equation 14

From this point, ammonia is used as a reducing agent in the SCR system to reduce NO*x* emissions.

$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O$ Equation 15

$6\ NO_2 + 8\ NH_3 \rightarrow 7\ N_2 + 12\ H_2O$ Equation 16

The overall reduction of NO*x* by urea is:

$2CO(NH_2)_2 + 4\ NO + O_2 \rightarrow 4\ N_2 + 4\ H_2O + 2\ CO_2$ Equation 17

$4CO(NH_2)_2 + 6\ NO_2 \rightarrow 7\ N_2 + 8\ H_2O + 4\ CO_2$ Equation 18

("Diesel exhaust fluid," 2019)

Besides, there are other main reactions that happen without oxygen,

$4\ NH_3 + 6NO \rightarrow 5\ N_2 + 6\ H_2O$ Equation 19

$2\ NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O$ Equation 20

6.3 The Development of Electric Vehicles

Compared with traditional cars, for NO*x*, although the emissions of coal-fired power plants, which may provide electricity to all-electric cars, is higher than the emissions of traditional vehicles, many coal-fired power plants have used the related technology of denitrification for the disposal of waste which avoided the direct discharge of much polluted gas and dust particles into the air.

When considering air quality, the advantages of all-electric vehicles are obvious. However, emissions may exist in the upstream enterprises. For example, the electricity generation process

in coal-fired power plants result in air pollution, though all-electric vehicles do not directly discharge any air pollutants.

For effective and recommended solutions, in China, coal-fired power plants carried out the relative approaches for the discharge of the pollutants. On the other hand, the Chinese government has promoted the development of clean energy power plants, such as nuclear power, solar power, and wind power, which can reduce the environmental stresses ("Comparative Analysis on Emission between Electric and Conventional Vehicles" 2012.).

As a country with a heavy air pollution problem due to its rapid industrialization and population growth for the past 30 years, China has been concerned with environmental protection and pollution regulation in recent years. Many prevention and control measures provide some important referential value. China's government and people have increasingly been concerned over the development of electric vehicles (Poon, 2018). Currently, all-electric vehicles and plug-in hybrid electric vehicles (PHEVs) are the main electric vehicles (EVs) produced in domestic factories. EVs have a huge advantage in terms of the environment, air quality, and energy, over traditional automobile vehicles. China has focused on increasing the efficiency of its energy consumption, improving the energy structure, and looking for new sustainable technologies for the environment. For the production of EVs, China's producers are focusing on researching batteries (Moss, 2019). The lithium-ion battery is the most ideal battery in current technology. Compared with past EVs, their battery sizes and all-electric range have increased, but they are still lower than some advanced U.S. EVs. In addition, the demand for electric public transportation is extremely high because of China's large population. Improving the charging net is important to the development of EVs. At the same time, solar power can also be considered a sustainable way to improve air quality and conserve energy. China's companies have their own technologies for the solar highway. The solar highway is suited to travel by electrical vehicles.

When considering the necessity of EVs in China, EVs' efficiency of energy conversion is useful for evaluating EV's economic efficiency and their value in environmental protection.

From 2008 to 2016, the standard coal consumption of thermal power generation has gradually decreased, and thermal power efficiency has increased. After 2008, the line loss rate of China's domestic electric grid has decreased, meaning power transmission efficiency has increased.

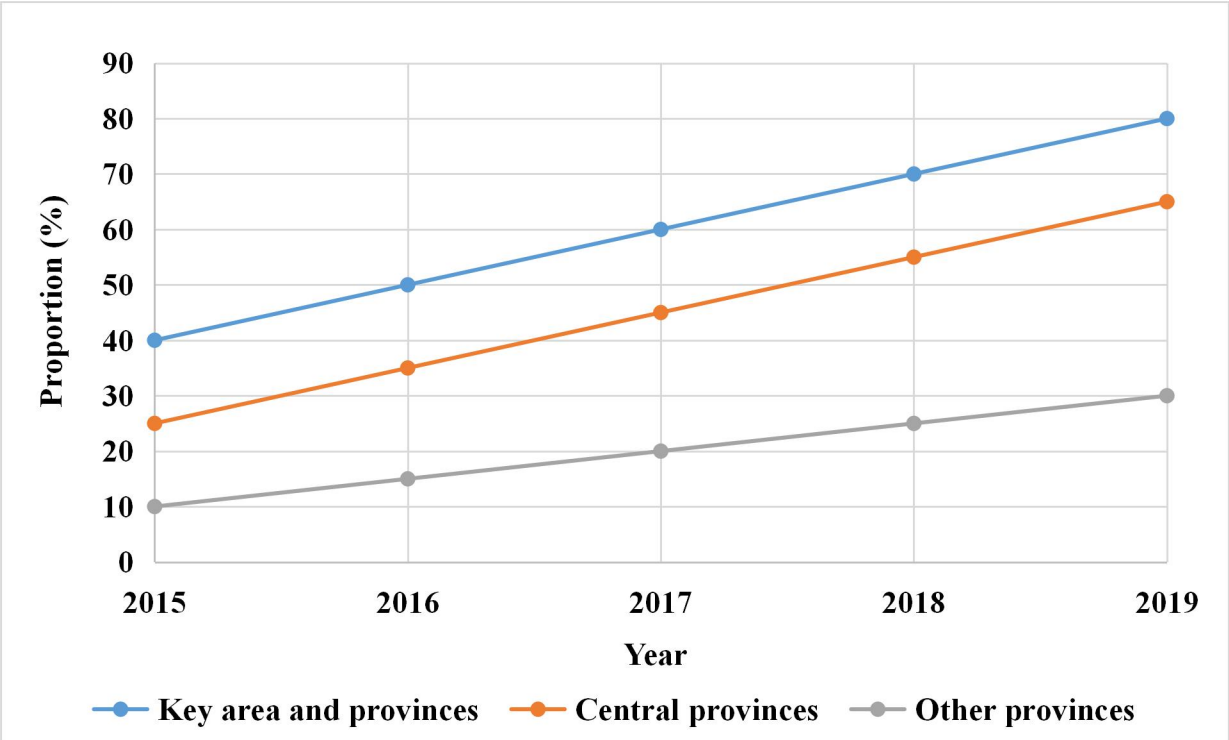

Figure 48. The proportion of electric buses increased and replaced diesel buses of different area in China from 2015 to 2019. (chinabaogao, 2018)

Figure 48 shows the proportion of electric buses in total increased and replaced diesel buses in different areas of China. The key areas and provinces curbing atmospheric pollution includes Beijing, Shanghai, Tianjin, Hebei, Shanxi, Jiangsu, Zhejiang, Shandong, Guangdong, Hainan. They were higher than in the central provinces and other provinces, but they all have been linearly increasing from 2015 to 2019. Central provinces include Anhui, Jiangxi, Hebei, Hunan.

Figure 49 shows ten cities and provinces of the most Powered Charging Stations in China in April 2018. The most number is in Beijing, which has 40,184 powered charging stations for EVs. These powered charging stations provide electric energy to EVs. Due to the current battery technologies available in China, there are fewer all-Electric Ranges than foreign cars. Thus, the construction of powered charging stations has become more important. However, there are many

problems in the development of EV charging stations. Data from the China Electric Vehicle Charging Infrastructure Promotion Alliance before April 2019 show the utilization rate for charging stations was lower than 15 percent on average across the country. Many EV charging stations, because they are not busy, have even been treated as free parking lots by car owners (Liu, 2019).

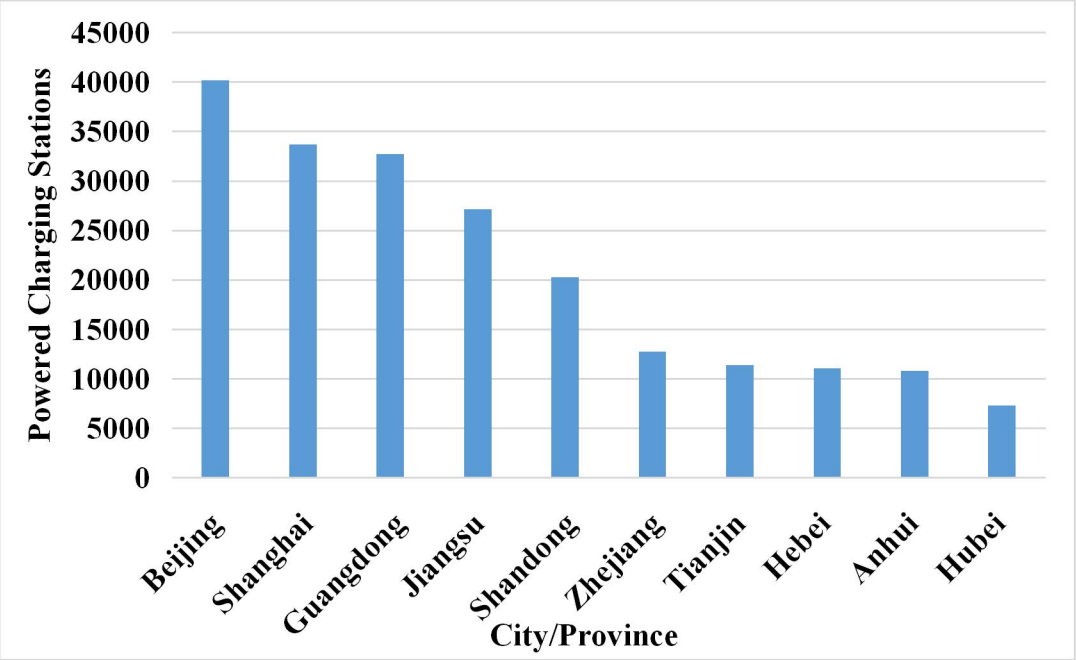

Figure 49. Top 10 cities/provinces of Powered Charging stations in China in April 2018 (*Statistical Analysis of China's Electric Vehicle Charging Station Industry in 2018 and Analysis of the Number of Charging Stations in Various Provinces and Cities*, 2018)

In addition to traditional powered charging stations, China also has developed solar powered charging stations. China is building roadways with solar panels underneath that may soon be able to wirelessly charge cars and digitally assist automated vehicles. On December 28, 2017, the first photovoltaic freeway in the world was opened to traffic at Jinan, Shandong, China ("Jinan is building the world's first photovoltaic highway." 2017). The Jinan solar highway, part of the Jinan City Expressway, is a 1.2 mile stretch. The building technique involves installing transparent concrete over a layer of solar panels. It was the second solar roadway in the city, with the first opened in September 2017 using a different technology. The Jinan solar photovoltaic

highway is constructed with three layers. The top layer is a transparent concrete layer that directly touches the vehicles. It has structural properties similar to standard asphalt. The central layer consists of the solar panels, which can be used to generate solar energy. The bottom layer is an insulating layer, used to separate the solar panels from the damp earth underneath.

Zhang Hongchao, a professor in Transportation Engineering at Tongji University, which provided the core technology, said, the photovoltaic road surface is used to transform the solar energy to electric energy. It realizes solar power generation. The technology of this highway is called weight bearing photovoltaic pavement technology. It uses photovoltaic power components that fit the traffic conditions of the road that is directly installed in the road's surface. The surface of the pavement is called "transparent concrete." The technical index and traffic safety properties of transparent concrete have both surpassed common asphalt and concrete pavement (*Incredible! The world's first high-speed photovoltaic road appeared in Jinan*, 2017).

China's government and people have been increasingly concerned with the development of electric vehicles. Currently, all-electric vehicles and PHEVs are main EVs for the production of domestic factories and the demand for transportation. EVs have a huge advantage in the aspect of the environment, air quality, and energy, instead of traditional automobile vehicles. China has focused on increasing the efficiency of energy consumption, improving the energy structure and looking for new sustainable technologies for environment. For EVs' production, China's producers focus on improving the battery. The lithium-ion battery is the most ideal battery for the current technology. In addition, the demand of electrical public transportation is extremely high because of the large population. Improving the charging net is the important way for the development of EVs. At the same time, solar powered systems are a sustainable way for better air quality and energy conservation. China's companies have their own technologies for the solar highway. The solar highway is suited to the travel by electrical vehicles. The development of electrical vehicles and their infrastructure in China has reference value for other countries' developing similar systems.

Chapter 7 - Summary and Conclusions

Available studies on the air quality impacts of nitrogen oxides and ozone were reviewed. The whole process of assessments has focused on understanding how air quality is affected by these pollutants in specific urban environments. This review analyzed and listed factors affecting NO*x* concentration in air such as emissions from transportation, and emissions from industrial production due to rapid industrialization and urbanization. The details of transportation influencing air quality of NO*x* and Ozone were discussed. Methods of air quality monitoring were categorized. The impacts of several types of vehicles and vehicle technologies for NO*x* emissions were reviewed. The study focused on changes in pollutant concentrations made by urban transportation. In Chapter 4, there is data analysis on NO_2 concentration and O_3 concentration in several communities in Chicago. In Chapter 5, additional data analysis shows NO_2 concentration and O_3 concentration in other areas in U.S. The data visualization and analysis focus on the variation of 24-hr concentration, the seasonal variation of concentration, differences between workdays and weekends on NO_2 and O_3 concentrations in these two chapters. In addition, suggestions for improving air quality are provided.

The key summary and conclusions are as follows:

- NO*x* is considered a better indicator of traffic pollution than is NO_2 alone, because NO_2 is a secondary oxidation product of atmospheric reactions involving NO, the latter of which is directly emitted in combustion,
- NO_2 may cause many serious environmental problems including ozone formation and aggravate illnesses for the human body.
- Photochemical smog is formed by solar radiation on air containing nitrogen oxides, volatile organic compounds, and particulates from combustion processes. Smog comes from combining the words smoke and fog, and it contains nitrogen oxides, organic compounds, ozone, and particulates.
- Exhaust from motor vehicles, chimneys, smoke stacks and other combustion systems produce nitrogen oxides.
- Air quality monitors have become significant because of reductions in cost and progress in the ability to measure values continuously and display and record the data.

Concentrations of NO_2 and ozone vary with time and position. Values measured along busy streets provide local data that can help people to understand their air quality.

- How to develop an effective air monitoring system with useful measured values and effective distribution of the data is important. There are two main types of models: top-down and bottom-up to model NO_2 and ozone in communities. Top-down approach is a Macro-approach. Bottom-up approach is a Micro-approach.
- Modern vehicles with diesel engines emit more NO*x* than cars with gasoline engines.
- In the SASA project, the community of Little Village has many restaurants and stores, including auto shops. The commercial activities tend to attract more vehicles in this area. Transportation can influence the NO_2 concentrations. Busy traffic means more NO_2 emissions because of automobile exhaust. In addition, the monitors are located near the main streets, which makes the NO_2 concentrations higher due to the emissions from transportation.
- Northbrook has more greenery than the LV community; the traffic intensity is less than in the LV community; fewer commercial activities exist in this area; the monitors are located far away from the main transportation roads, resulting in lower NO_2 concentrations in the NB community.
- Southeast has many houses and apartments but few shops, thus, the transportation activity is lower than in the LV community. However, many people who live in this area need to leave by vehicles, so the intensity of traffic in this area is not very low, and the monitors are close to the intersection of main streets. It makes the concentration higher due to the emissions from transportation.
- South Loop is an education zone because there are many schools. Thus, the transportation activities will be influenced by the students' traffic behavior and school hours. There will be more regular variations of NO_2 concentrations due to emissions from transportation. Additionally, there are also some shops. They also can bring much traffic to the area. Moreover, the monitoring sensors are close to schools, so the data collected on NO_2 concentrations has time disciplines, as they are influenced by school hours. More vehicles produce more NO_2 emissions. It makes the average NO_2 concentration in the SL community higher than in other communities.
- For the analysis of 24-hr variation of NO_2 concentration by SASA "Aeroqual" sensors, it

is noteworthy that in summer there are lower NO_2 concentrations in the nighttime than in the daytime. The change of NO_2 concentrations is influenced by people's behaviors. The concentrations have lower value in the nighttime due to there being less traffic at night, but it begins rapidly increasing from 5:00 to 10:00 because people are starting to go out early in the morning, using various transportation methods. The highest peak is around noon. The concentration dramatically decreases in the afternoon.

- The workdays and Sundays differ in terms of the highest value of the 1-hr average NO_2 concentrations.
- Higher concentrations of nitrogen dioxide were measured at all measuring points in the urban setting during the winter than during the summer, because of emissions associated with heating.
- In LV communities, with the increasing O_3 concentration in the afternoon, NO_2 concentration is decreasing due to most of NO_2 takes part in the reactions to form O_3. O_3 concentration has a negative relationship with NO_2 in the early afternoon.
- The change in ozone concentration is directly influenced by NO_2 concentrations because NO_2 can produce ozone after a series of reactions. Daily changes in NO_2 concentrations are obviously influenced by traffic.
- Large cities, such as Los Angeles and San Francisco, have higher traffic intensity during rush hour; thus, they have obvious peaks in NO_2 concentration influenced by people's traveling behavior. The large difference of NO_2 concentrations between daytime and nighttime are because of NO*x* emissions from vehicles. However, for the harbor city, such as Santa Barbara, the change in NO_2 concentrations within a day is lower because marine pollution factors dominate the NO_2 emissions.
- EPA monitors are providing more precise data, but additional money needs to be spent to monitor local air quality with EPA monitors. The low-cost air quality monitors have been developing rapidly due to low cost, and the importance of understanding local concentrations of pollutants.
- For street canyons in urban areas, in-canyon greening could be an effective tool to reduce street-level concentrations of NO_2. To increase the vegetative cover in urban areas so as to reestablish the beneficial cooling effects associated with it is an effective way of combating the urban heat island effect.

- Urban tree planting is a cost-effective way to improve air quality. However, some gaseous volatile organic hydrocarbon emissions from vegetation can in fact contribute to decreased air quality. Thus, finding suitable types of trees and reasonable design for controlling NO*x*, ozone and VOC emission is important.
- The technology of selective catalytic reduction (SCR) is used to reduce the amount of NO*x* released into the atmosphere. Urea tanks have become standard equipment for most new diesel trucks.
- When considering air quality, the advantages of all-electric vehicles are obvious. However, emissions may exist in the upstream generation of electricity with coal. The development of electrical vehicles is expected to be an important aspect in the future.

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Appendix A - Satellite Maps for SASA Project

Figure a. Satellite map for Northbrook, Illinois

All satellite maps are from Google Maps. The permission is provided at https://www.google.com/permissions/geoguidelines/.

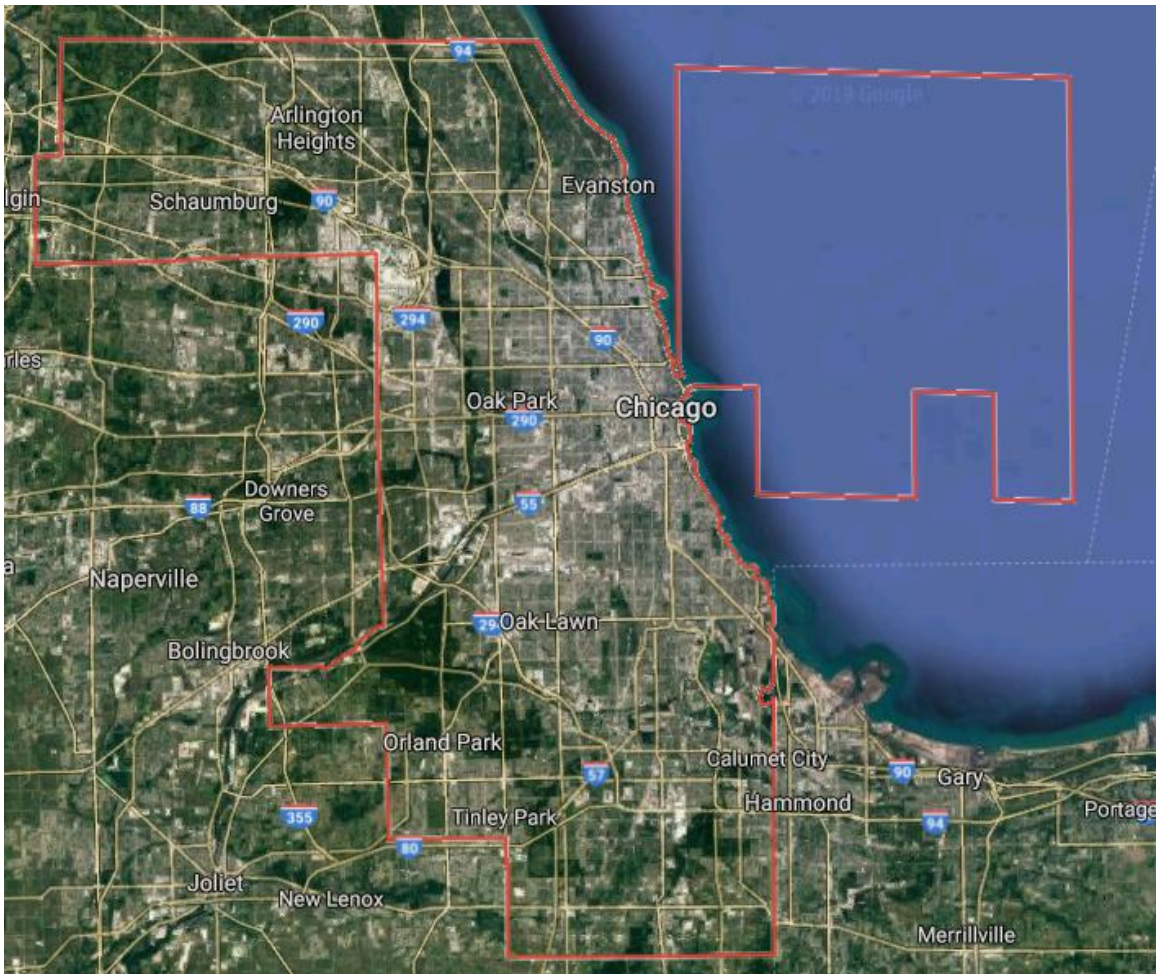

Figure b. Satellite map for Cook County, Illinois

Figure c. Satellite map for Hammond, Indiana

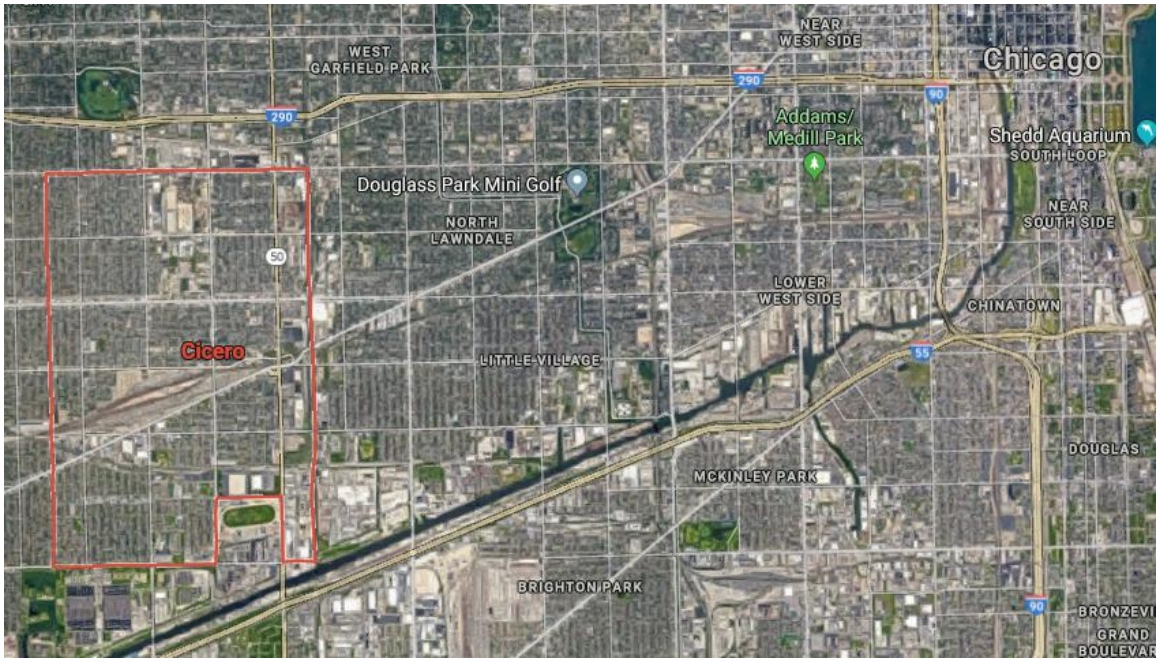

Figure d. Satellite map for Cicero, Illinois

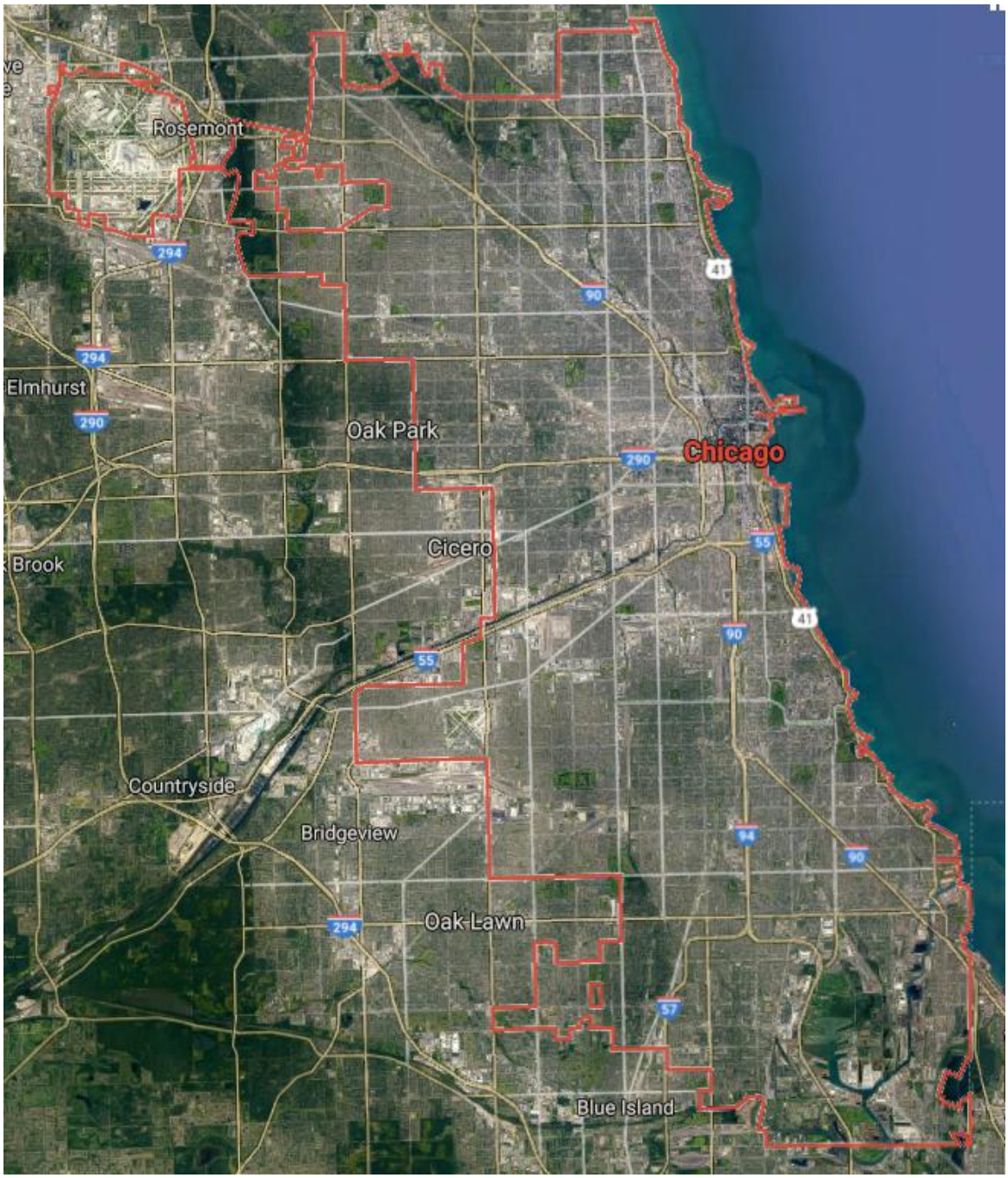

Figure e. Satellite map for Chicago, Illinois

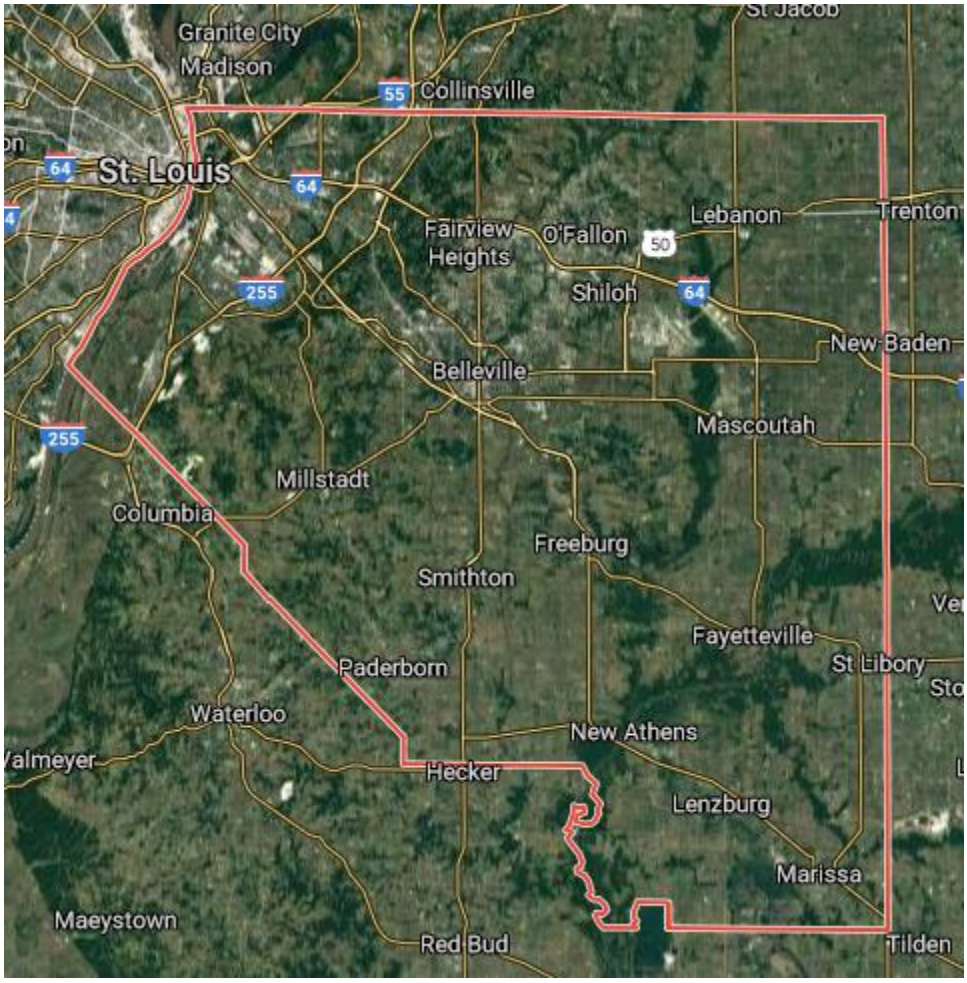

Figure f. Satellite map for St Clair, Illinois

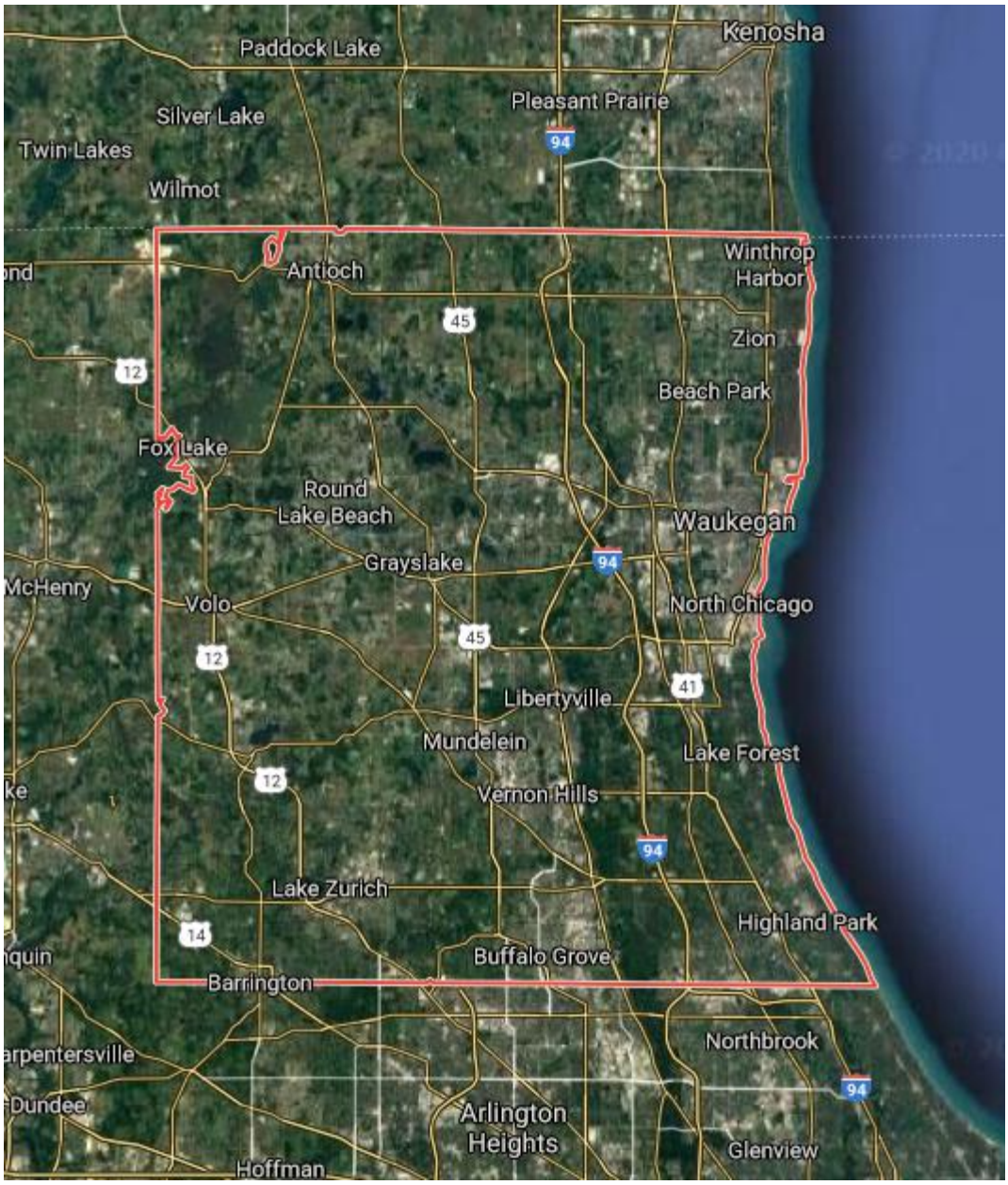

Figure g. Satellite map for Lake County, Illinois

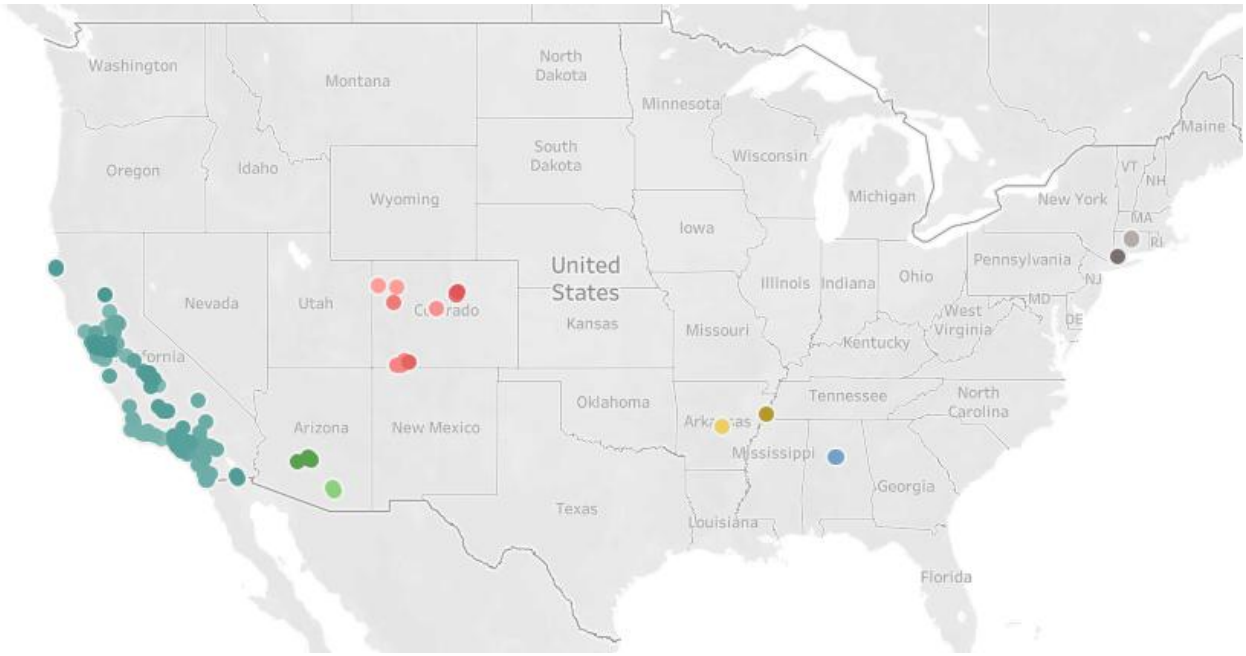

Figure h. Geographic distribution of the data from hourly NO_2 concentration records by EPA regulatory monitors for Figure 37.

The data of these cities in Figure 37 are provided by EPA regulatory monitors. They could be found at http://fingolfin.kdd.cs.ksu.edu:8080/airquality/download/. In Figure 31, the cities are selected as representative cities to analyze the hourly variation.

Appendix B - Other Data Visualization for Illinois and California

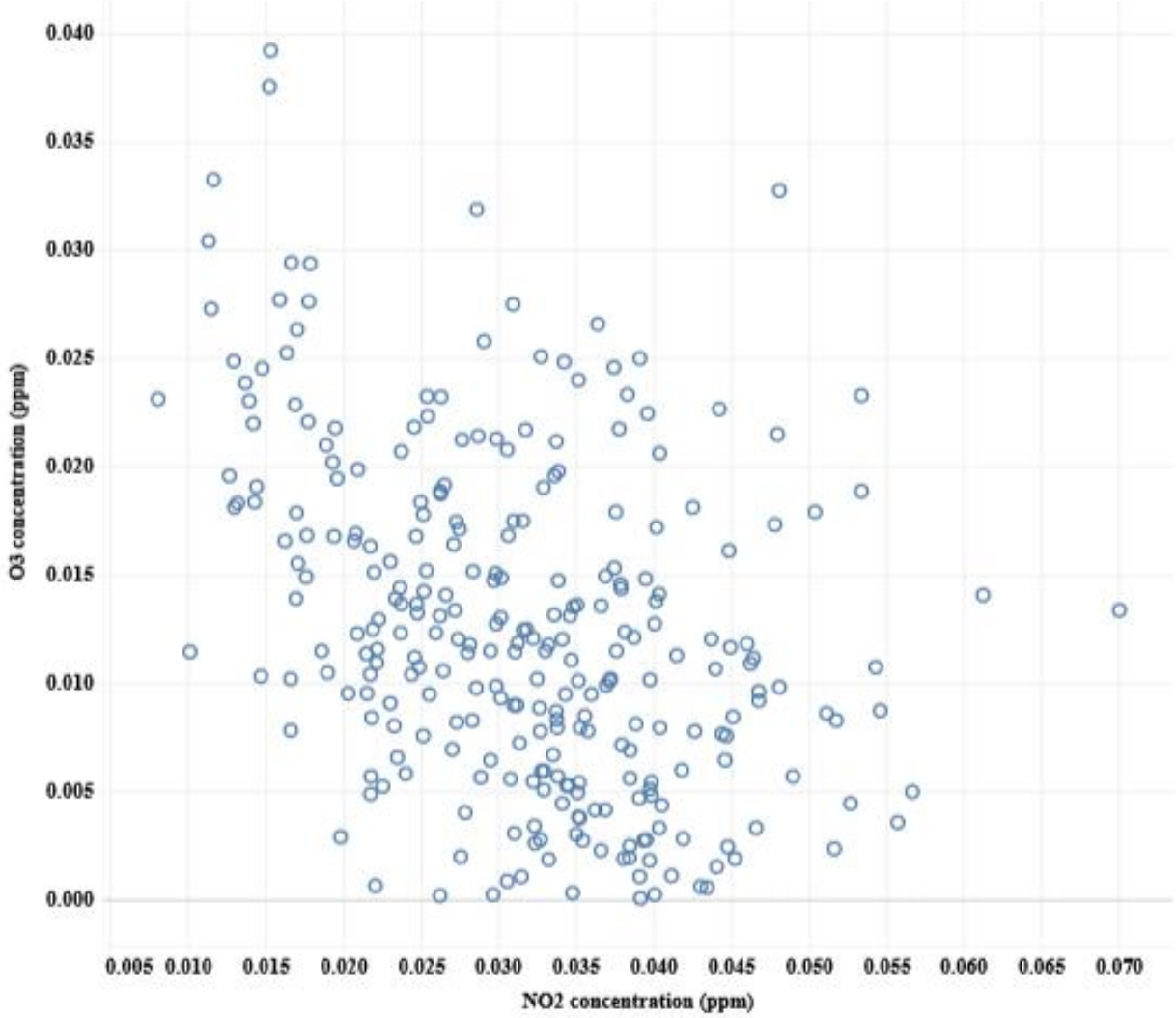

Figure h. Correlations between Ozone and NO2 in Chicago.

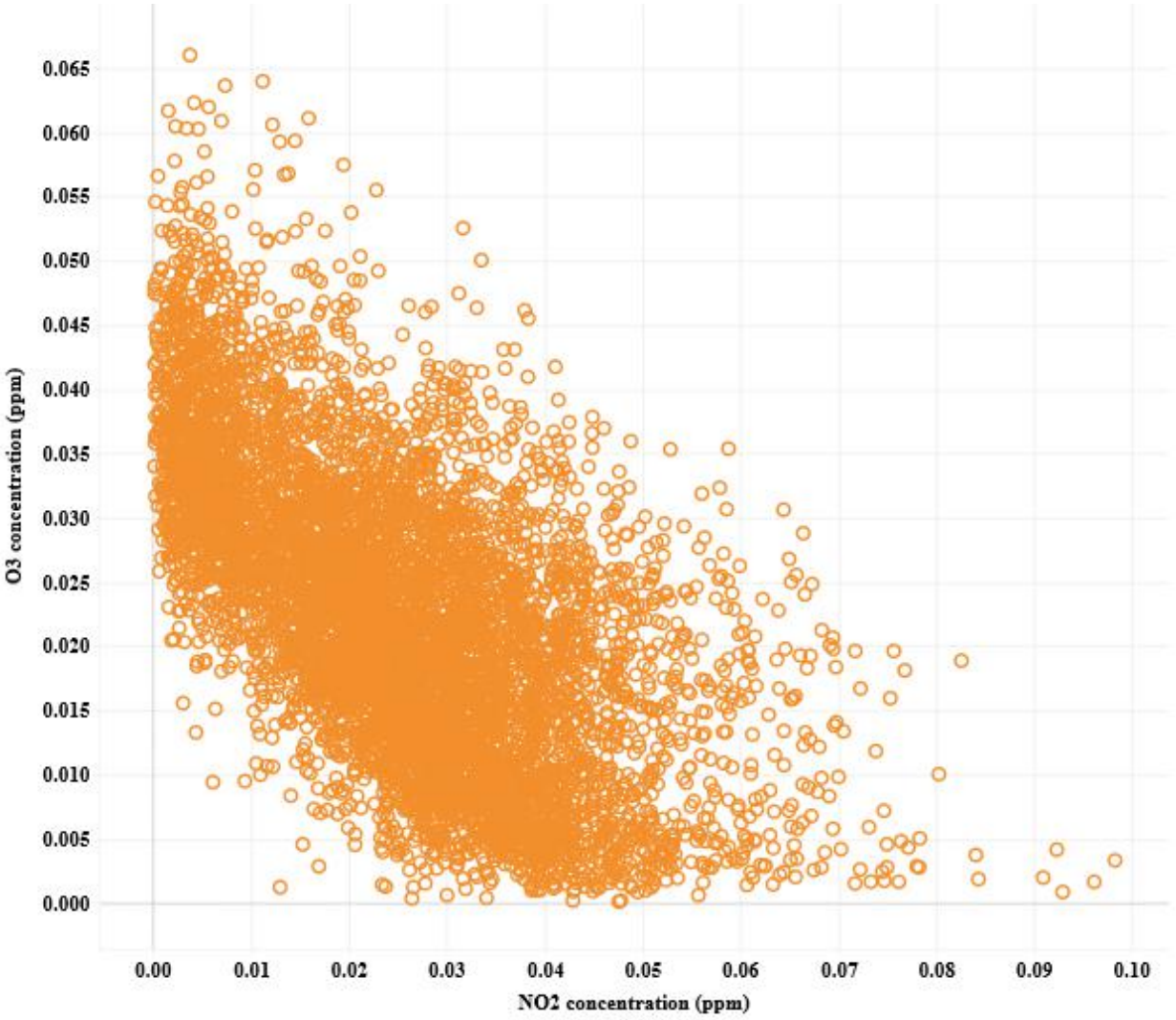

Figure i. Correlations between Ozone and NO_2 in Los Angeles.

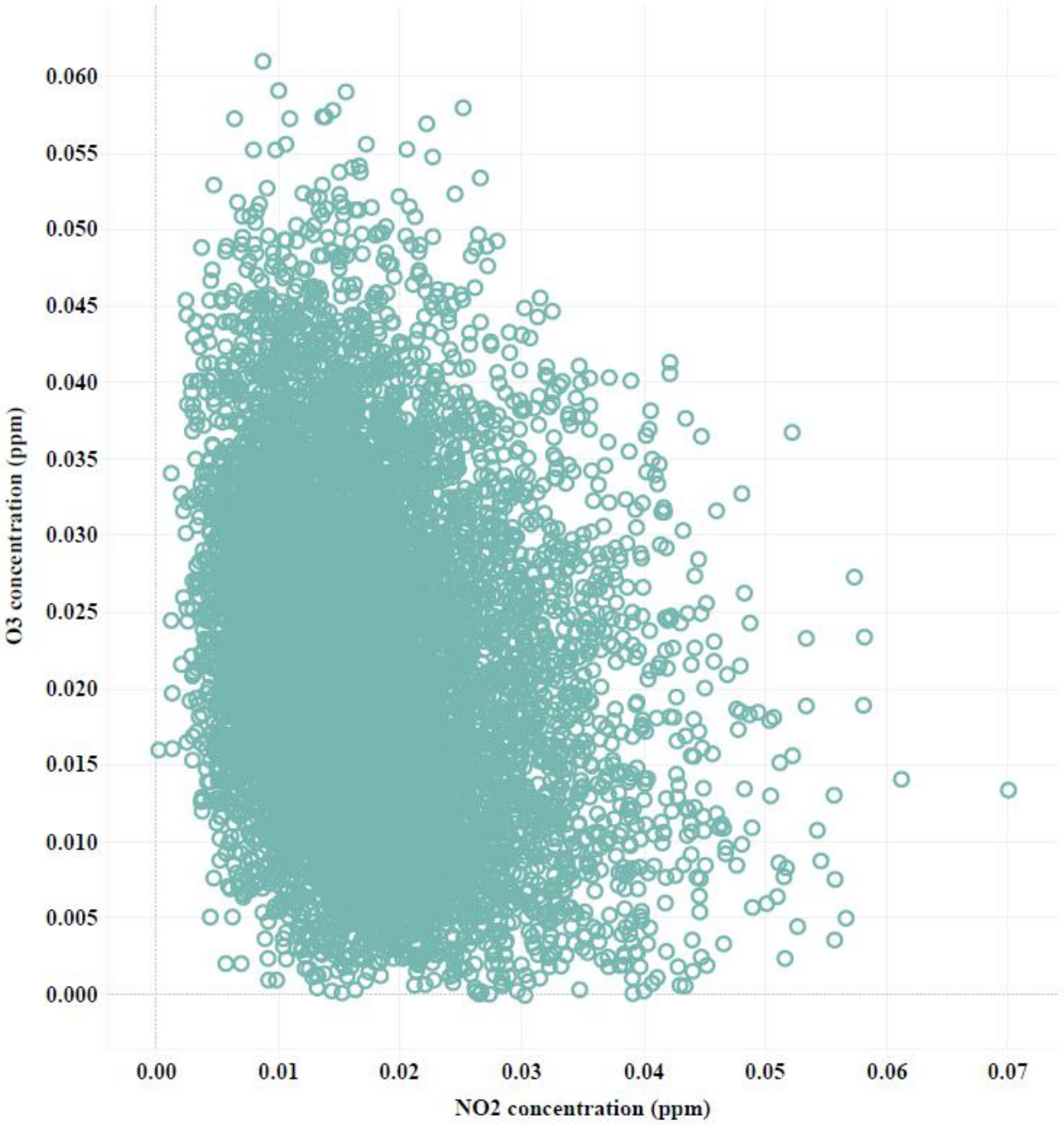

Figure j. Correlations between Ozone and NO_2 in Illinois.

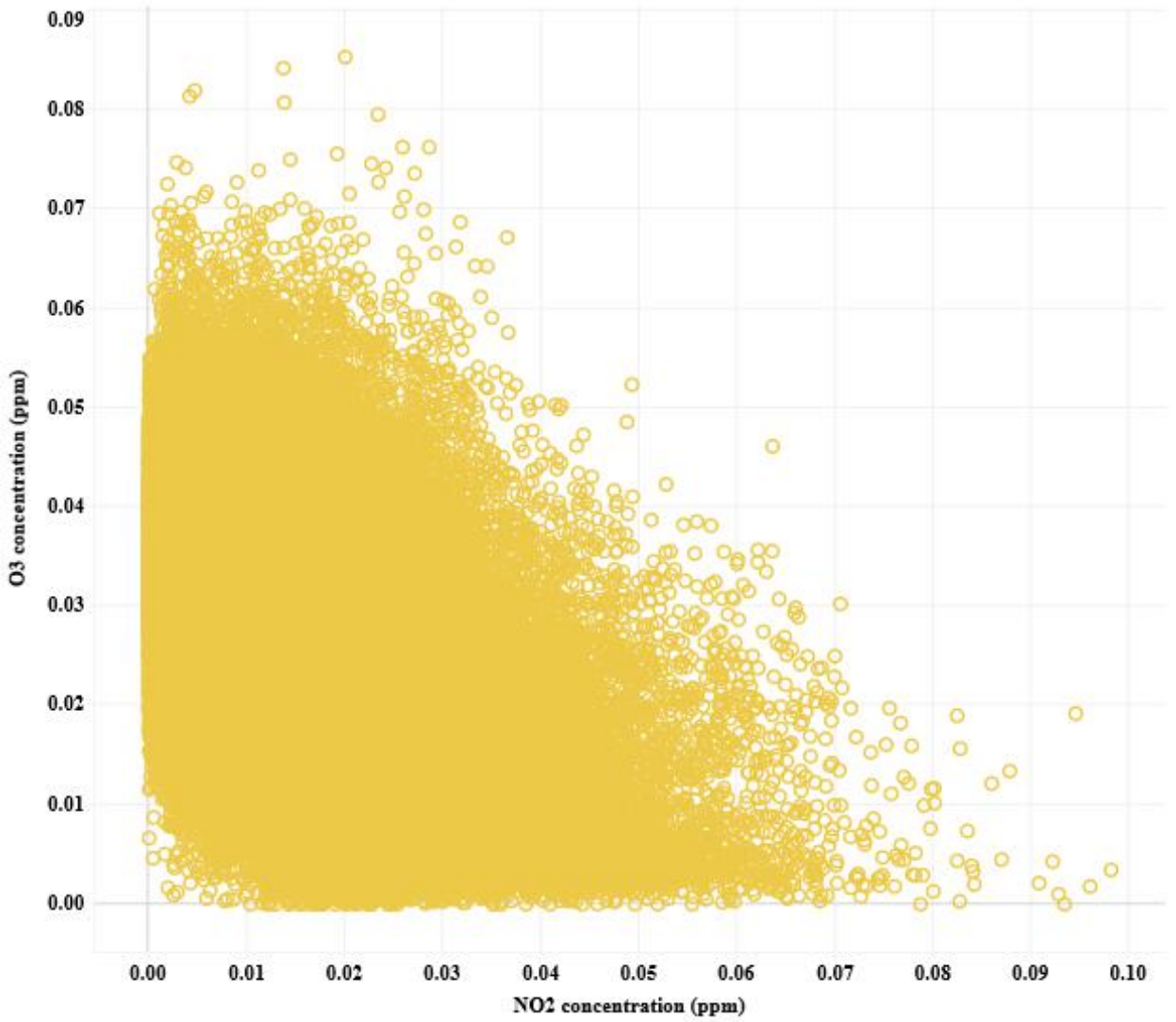

Figure k. Correlations between Ozone and NO_2 in California.

There are some relationships between ozone and nitrogen dioxide concentrations due to the chemical and photochemical reactions, Equation 1-4. When a higher NO_2 concentration results, there is a lower O_3 concentration at night.

In Figures j and k, the correlation between O_3 and NO_2 concentrations is presented; values for Illinois are smaller than for California. It was expected that the effect of photochemical reactions is more in California. The possible reasons for the production of ozone is related to photochemical reactions as shown in Equations 1-4. Two cities from these states, Chicago and

Los Angeles are compared. The values for Chicago are smaller than for Los Angeles. The figures illustrate that there are larger concentrations of NO_2 and O_3 in Los Angeles, California.

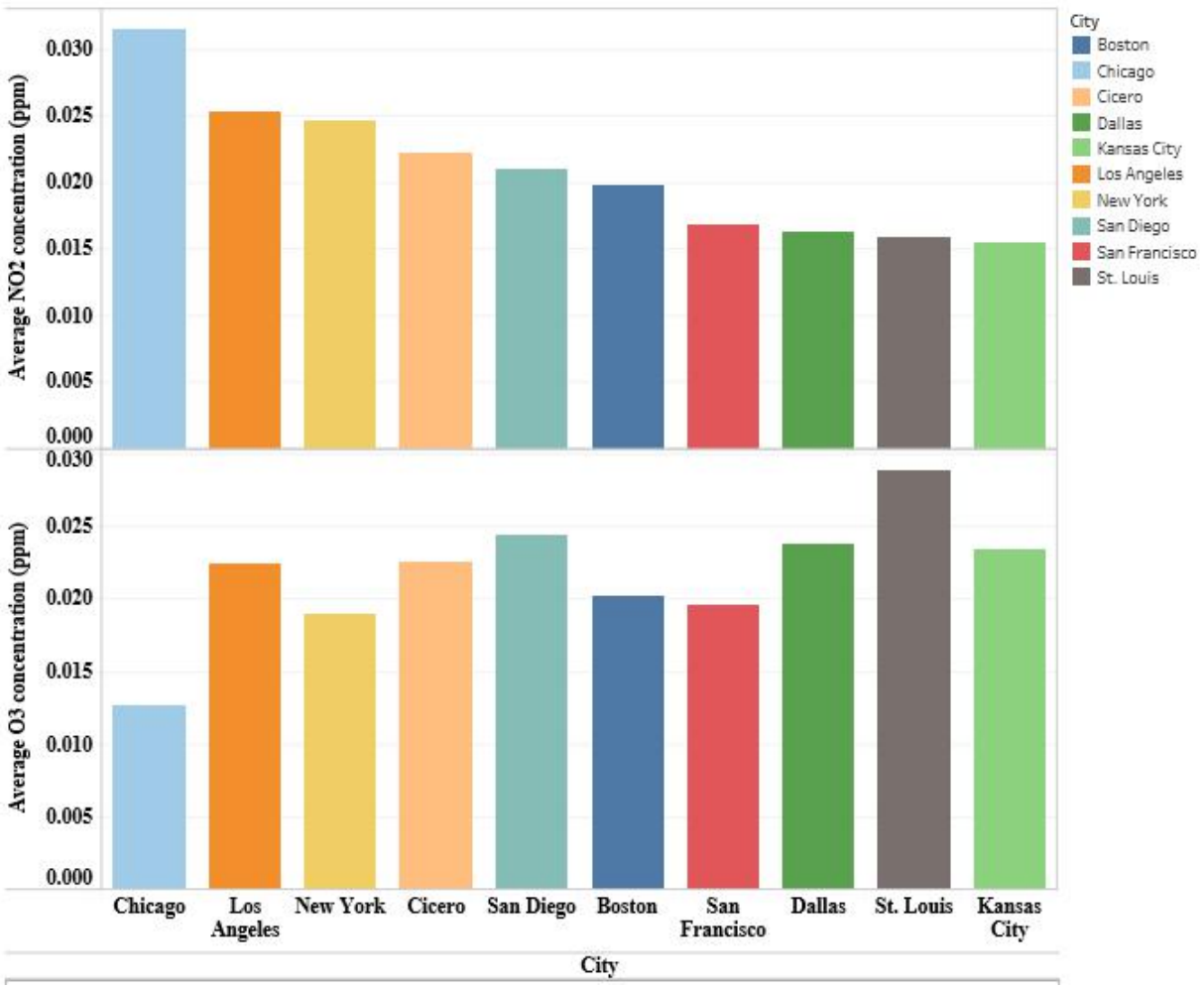

Figure l. Average NO_2& O_3 concentration in different cities.

Chicago has a higher concentration of NO_2 than other cities in Figure l, but lower concentration of O_3.

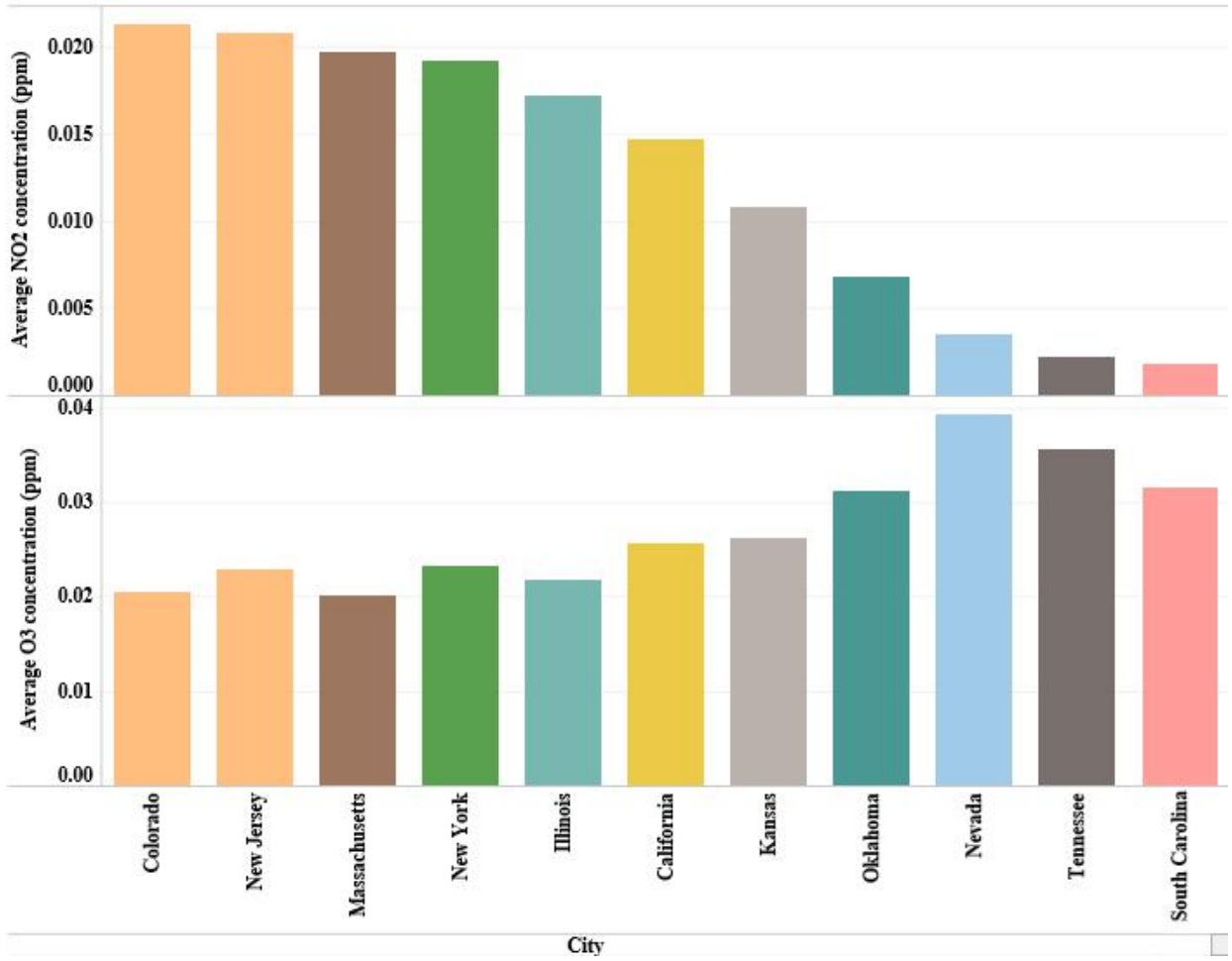

Figure m. 24-hr average NO_2& O_3 concentration in different states.

Average NO_2 concentration in Illinois is higher than California. However O_3 concentration in Illinois is lower than California.

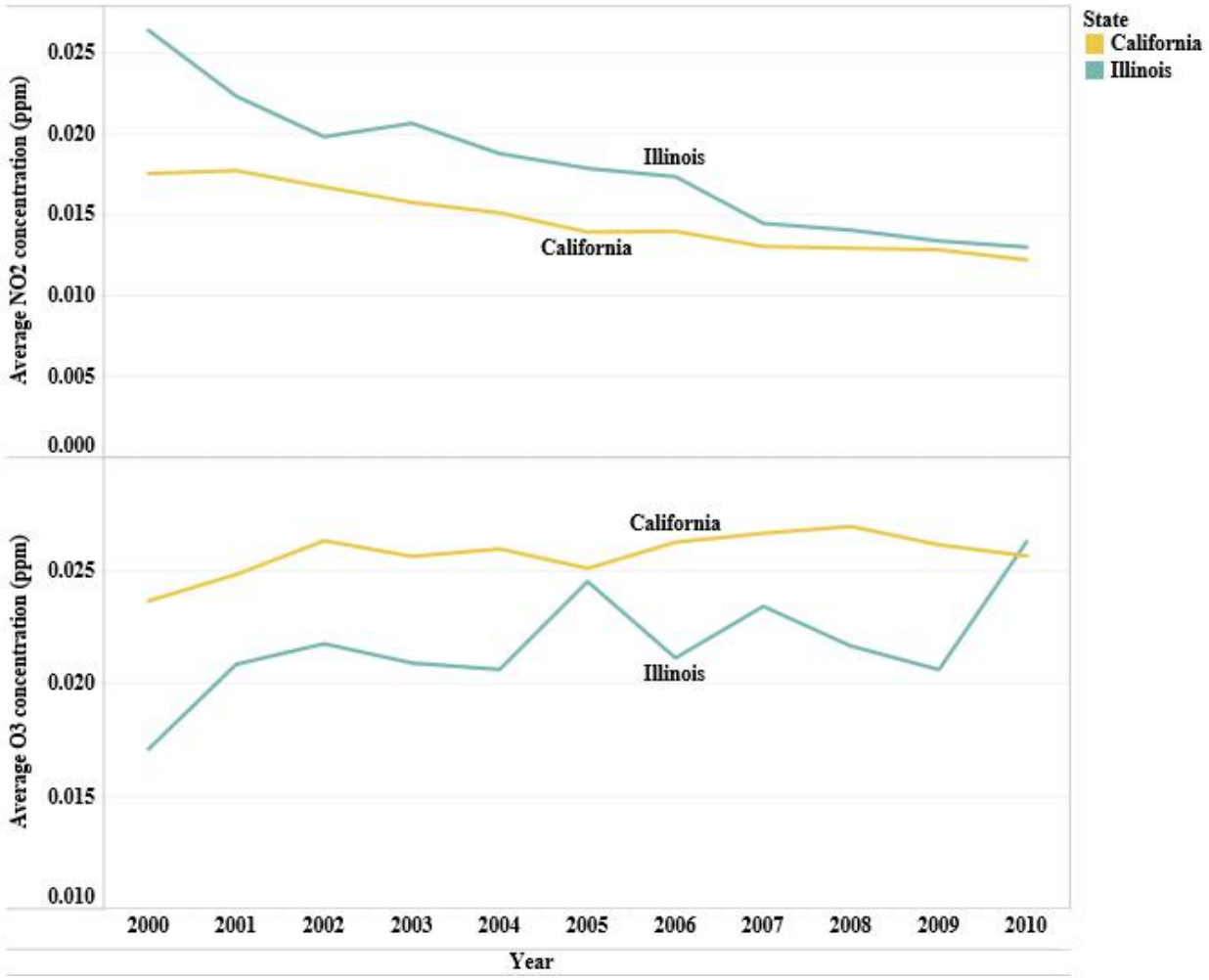

Figure n. Yearly variations of 24-hr average NO_2& O_3 concentration in Illinois and California.

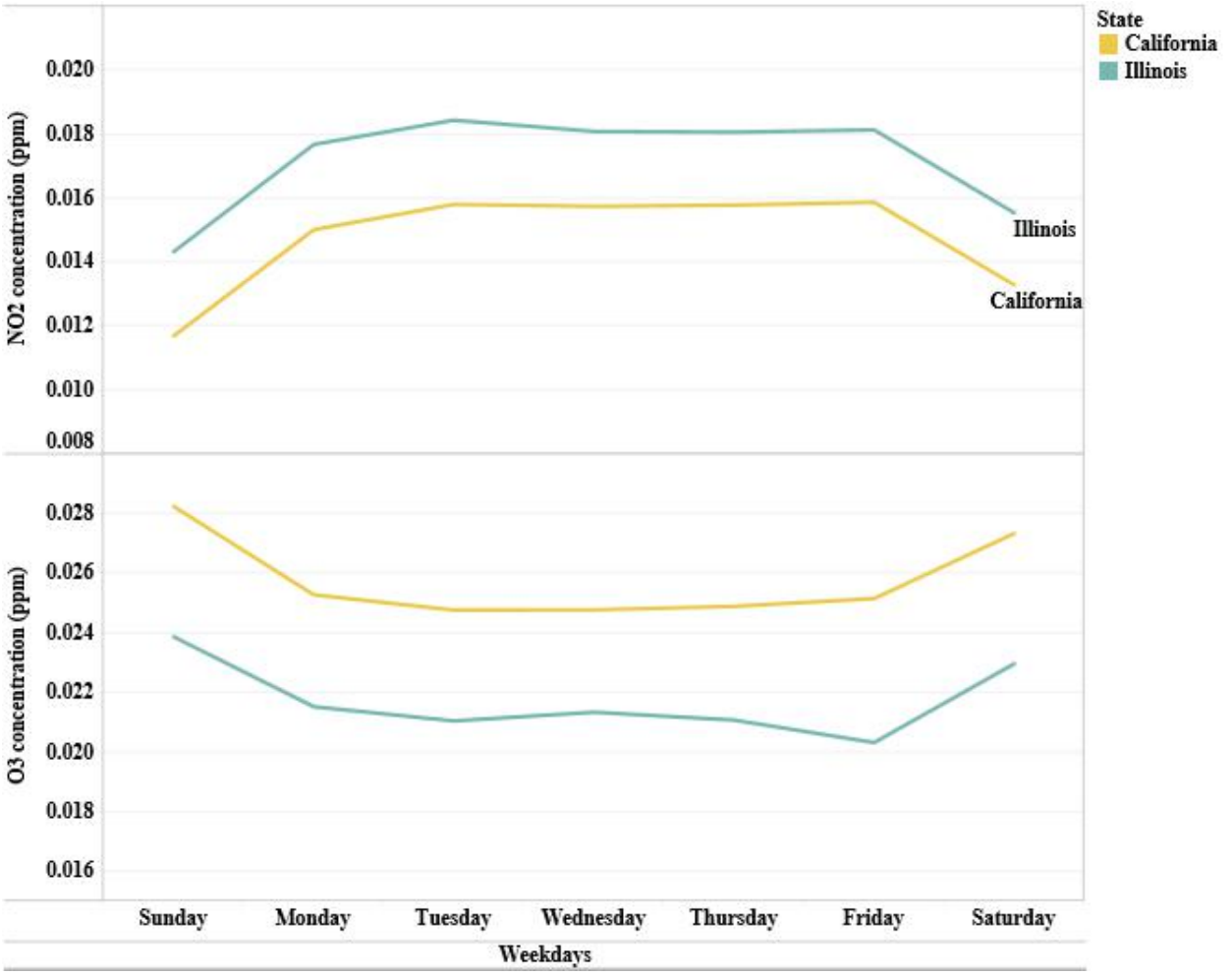

Figure o. Weekday variations of 24-hr average NO_2 & O_3 concentration in Illinois and California.

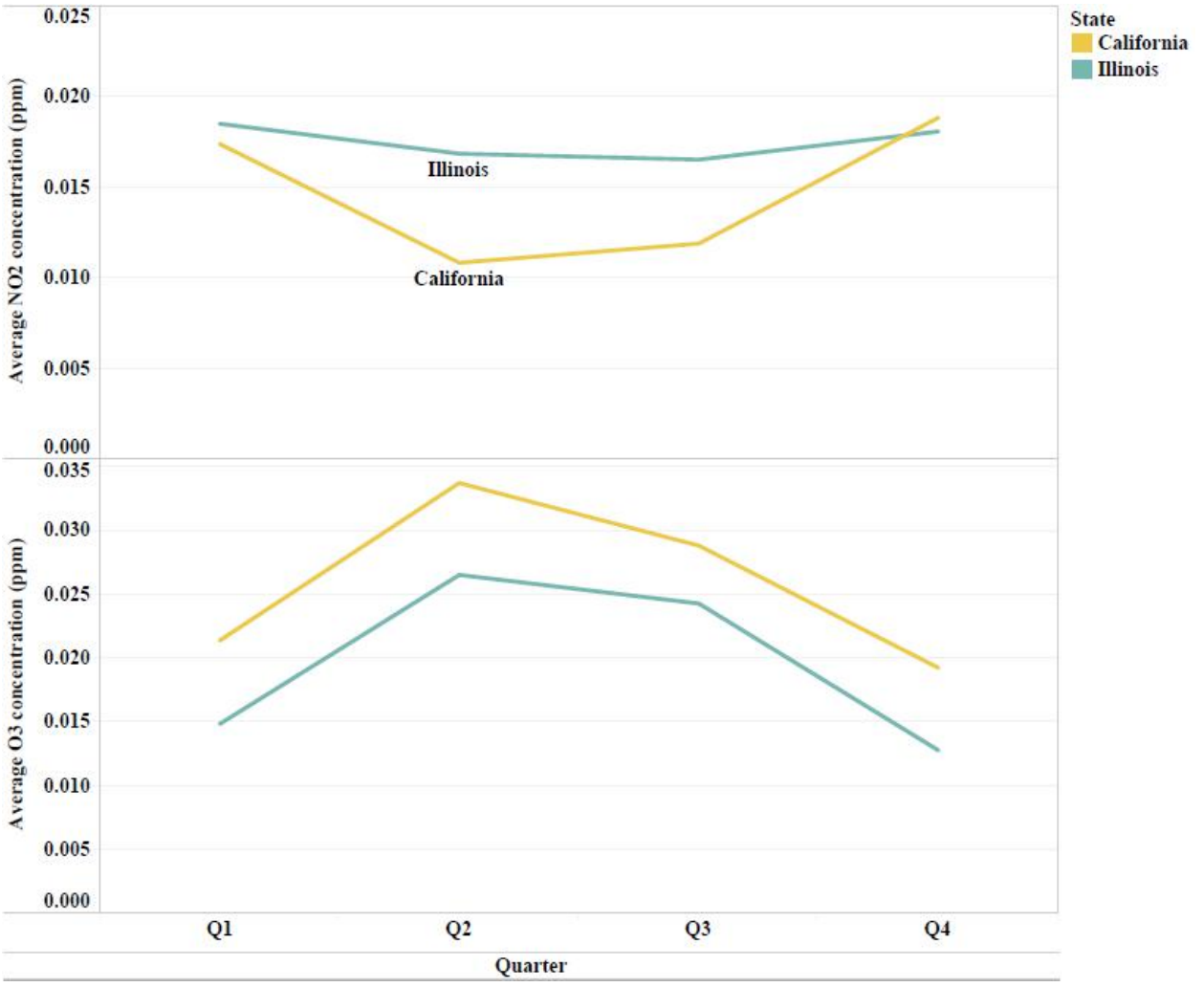

Figure p. Quarterly variations of 24-hr average NO_2& O_3 concentration in Illinois and California.

NO_2 concentration is decreasing in recent years due to environmental protection progress and energy transition. In general trend, less anthropogenic emission of NO_2 makes lower NO_2 concentration in air. In Illinois and in California, the average NO_2 concentration has decreased from 2000 to 2010, as shown in Figure n.

In addition, Figure o shows NO_2 concentration is higher from Mondays to Fridays, and lower on weekends. It might be influenced from transportation. Workdays have more vehicle emissions. Through the comparison between 4 quarters in each year, it is found the Second quarter and the third quarter have lower NO_2 concentrations. It shows the NO_2 concentration is lower in summer

than winter. The seasonal change of NO_2 in Illinois is smaller than California, even though Chicago has larger temperature differences in different seasons.

Figures h-p show corresponding values of ozone and NO_2. Data of Figures h-q is from U.S. pollution data since 2000. The data source is from the database of U.S. EPA: https://aqs.epa.gov/aqsweb/airdata/download_files.html.