1. INTRODUCTION

1.1 PROBLEM STATEMENT

The purpose of this project is to identify the effect that surface modifications have on the urban heat island phenomenon and related ozone problem in the metropolitan area of Chicago, IL. The basic hypothesis is that urban, summertime temperatures can be significantly lowered by increasing the vegetative landscape cover and enhancing the solar reflectivity of paved and roofed surfaces within an urban area. It is proposed that in addition to a decrease in temperature, the modification of an urban surface to include more vegetative cover and lighter, lower albedo surfaces will also reduce energy consumption, ozone exceedances, and detrimental environmental and human health effects associated with high levels of ozone.

The analysis is divided into three main parts. The first section of this report introduces the causes of ground level ozone and its effects in urban areas. It explains both the chemistry and transport associated with ozone exceedances. The second section is a compilation of the most viable mitigation strategies of urban heat islands: increasing vegetative cover and increasing proportions of light to dark surfaces. The effects, implementation strategies, and specific strengths and weaknesses associated with each approach are described, including a comparison of asphalt and concrete pavements systems using a life cycle analysis approach. The final section provides a case study of the Chicago area. This study entailed an examination of the land use, development of an urban fabric analysis in which total vegetative, paved, and roofed surfaces are investigated and quantified, and discussion on the effectiveness of possible mitigation strategies in the Chicago area. In general, the associated findings of my research are located within this final section.

1.2 OBJECTIVES

The overall goal of this project is to investigate the relationship between the urban heat island phenomenon, the ozone problem, and the effect of urban surface cover and color modifications in the metropolitan area of Chicago, IL.

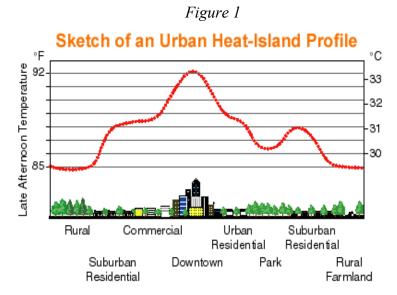The specific objectives of this work are to:

- Review the detrimental effects of the urban heat island phenomenon, particularly as a causative factor in promoting exceedances of air quality ozone standards, and identify mitigation alternatives that may reduce the effects of the urban heat island.

- Illustrate the differences in temperature between the urbanized center of Chicago and the surrounding areas in order to identify the heat island in the Chicago region.

- Examine the spatial distribution of ozone levels in the Chicago area and consider probable sources.

- Evaluate of the relationship between temperature and ozone.

- Develop a method to analyze the urban fabric of the Chicago area from aerial photographs, thus allowing the determination of the proportion of vegetative, roofed, and paved surfaces as a function of land use.

- Evaluate of the effectiveness of possible mitigation strategies as applied to the Chicago area, with special focus on vegetation and paving materials.

2. BACKGROUND

2.1 THE URBAN HEAT ISLAND

Over the past century, there has been an increasing trend towards urbanization. In 1900, approximately 150 million people lived in urban areas with populations of 20,000 or more. This was less than 10% of the world's population. Today this population has grown to approximately 2.2 billion, which constitutes close to 50% of the world's population.(1) In the United States today, roughly 80% of the people reside in metropolitan areas.(2)

High rates of urbanization have resulted in drastic demographic, economic, land use, and climate changes. The growth and expansion of our urban centers entail the construction of new roads, buildings, and other various human made structures to accommodate the growing population, and in turn, the destruction of the natural ground cover and landscape. This urbanization of the natural landscape can have profound meteorological impacts causing urban microclimates, referred to as **urban heat islands**, with elevated air temperatures of 2-8°F, increased energy demands, and elevated pollution concentrations compared to rural surrounding areas.(3) *Figure 1* provides an illustration of a typical heat island profile for a metropolitan area.

Figure 1

Source: Cooling Our Communities, USEPA (3)

While, most cities today exhibit heat island effects relative to predevelopment conditions, their individual intensities depend on a number of factors: geography, topography, land use, population density, and physical layout.

Urban heat islands are exacerbated by the loss of vegetation combined with the large quantities of low albedo surfaces, such as dark paving and roofing materials in urban areas. Vegetative cover, which includes trees, shrubs, and other plants, not only provides shade for buildings by intercepting solar radiation, but can cool the air by the evapotranspiration of absorbed ground water through its leaves. When this vegetative cover is destroyed, it is usually replaced by either pavement or buildings, which results in not only the loss of beneficial cooling mechanisms but the addition of detrimental heating effects. These detrimental heating effects are related to the albedo and emissivity of the paving and roofing materials utilized in the construction.

Most of materials used in construction produce low albedo and low emissive surfaces. Low albedo surfaces have low reflectivity, and consequently absorb solar radiation, instead of reflecting it back into space. Low emissive surfaces release this trapped heat energy slowly, thus causing the cooling process to progress at a slow rate also. These combined properties may result in an increase in the temperature of the surfaces, as much as 85°F above the ambient air temperature (4), which can sustain high temperatures into the night. For example, on a 90°F day, a dark asphalt parking lot surface can heat up to a temperature of 175°F. When the sun sets, the pavement surface will slowly begin to release the stored heat energy it accumulated throughout the day. However, as the pavement starts to cool off, the air around the surface begins to heat up, consequently maintaining elevated temperatures into the night. Thus, the thermal processes active in a heat island begin with the sunrise in the early morning, continue throughout the day, and often persist into the night.

The heating of urban areas has serious consequences that can effect both human health and the environment. Elevated temperatures can result in the degradation of urban air quality due to an increase in the rate of the formation of ground level ozone, which is the principal component of photochemical smog and the primary component of concern related to the heat island effect. The higher temperatures also create increased energy use, which is primarily due to a greater demand for air conditioning, for prolonged periods of time. It is estimated that for U.S. cities with populations larger than 100,000 people, peak utility loads will increase 1.5 to 2% for every 1°F increase in temperature.(3) Thus, as power plants burn more fossil fuels to meet the increase in energy demand, they also drive up both energy costs and pollution levels which may eventually lead to increased ozone production. In fact, one sixth of the electricity currently consumed in the United States goes to cool buildings, at an annual power cost of $40 billion.(4)

There are various ways of combating the urban heat island effect. One strategy is to increase the vegetative cover in urban areas so as to reestablish the beneficial cooling effects associated with it. Another strategy is to implement the use of lighter, high albedo materials for pavement and roofs. More reflective, cooler pavements have benefits in addition to reduced energy and photochemical smog. The use of cooler pavements can lead to longer pavement lifetimes, for high albedo pavement is less likely to be softened and damaged at high temperatures. In addition, at night, lighter pavements will reflect more light onto pedestrians and signs, helping to avoid accidents.

2.2. AIR QUALITY IN URBAN AREAS – GROUND LEVEL OZONE

Ozone (O_3) is a reactive oxidant gas produced naturally in trace amounts in the earth's atmosphere, and, depending upon its location in the atmosphere, ozone can be good or bad. The majority of the earth's atmospheric ozone, approximately 90%, is found in the stratosphere,

where it acts as a protective layer absorbing harmful ultraviolet radiation emitted by the sun and preventing it from reaching the earth's surface. The remaining 10% of the earth's ozone is located in the troposphere and is often referred to as ground level ozone. Here ozone exists as the primary ingredient in photochemical smog and has detrimental effects on human health and the environment.

Smog, traditionally defined as the combination of smoke and fog, is produced when both primary and secondary gaseous, aerosol, and particulate pollutants get trapped in the air. Primary air pollutants, such as carbon monoxide (CO), carbon dioxide (CO_2), sulfuric dioxide (SO_2), nitrous oxide (NO), suspended particulate matter, and hydrocarbons (volatile organic compounds), are substances released directly into the atmosphere. Secondary air pollutants, such as nitrogen dioxide (NO_2) and ozone (O_3), are formed as a result of reactions between primary pollutants and other naturally occurring constituents present in air.

The primary active pollutants in the creation of photochemical smog are nitrogen oxides (NO_x) and volatile organic compounds (VOCs). In the presence of sunlight, these reactants are rapidly converted to secondary pollutants, most of which is ozone, but organic nitrates, oxidized hydrocarbons, and photochemical aerosols are also part of the mix. Understanding the atmospheric chemistry and meteorological parameters and processes responsible for the formation of an occurrence of elevated concentrations of ozone in the ambient air is basic to the formation of strategies and techniques for its abatement. Such an understanding is required for representing those parameters and processes adequately in predictive models used to determine the emission reductions needed for complying with the National Ambient Air Quality Standards (NAAQS). In addition, the identification and quantification of ozone precursors in the ambient air are essential, along with emission inventories or emission models, for the development, verification, and refinement of photochemical air quality mechanisms and models, quantifying

emission rates, and adequately characterizing exposure-response factors for both biological and non-biological receptors.(5)

2.2.1. Effects

Over the last several decades, as a result of expanding population and industrial growth, air pollution, specifically ozone, has had increasing serious and wide spread impacts on the natural environment and human society. Ozone is the prime ingredient of photochemical smog in our cities and other areas of the country. Though it occurs naturally in the stratosphere to provide a protective layer high above the earth, at ground level, high concentrations of ozone can be harmful to people, animals, crops, and other materials.

Human Health Effects

Scientists have been studying the effects of ozone on human health for many years and have found that about one out of every three people in the United States is at a higher risk of experiencing ozone related health effects.(6) So far, several types of ozone related short-term health effects have been detected, but the specific mechanism associated with these effects are not known. When inhaled, even at very low levels, ozone can:(6,7,8)

- irritate the respiratory system and cause acute respiratory problems;
- reduce lung function and temporarily decreasing lung capacity approximately 15 to 20 percent in healthy adults;
- aggravate asthma increasing the seriousness and frequency of attacks that require medical attention or the use of additional asthma medication;
- inflame and temporarily damage lung tissue;

- may aggravate chronic lung diseases, such as emphysema, bronchitis, and pneumonia;

- impair the body's immune system defenses, making people more susceptible to respiratory illnesses, including emphysema, bronchitis, and pneumonia; and

- lead to increase hospital admissions and emergency room visits for 10 to 20 percent of all summertime respiratory-related hospital visits in the northeastern U.S. are associated with ozone pollution.

All these effects are considered to be short-term effects because they disappear once exposure has ended. Scientists, however, are concerned that long-term, or repeated short-term, exposures to ozone may irreversible changes in lung. For example, there is concern that repeated ozone impacts on the developing lungs of children may lead to reduced lung function as adults. Also, there is concern that ozone exposure may worsen the decline in lung function that occurs as a natural result of the aging process. Research is ongoing to help better understand the possible long-term effects of ozone exposure.(6)

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. For example, summer camp studies in the eastern U.S. and southeastern Canada have reported significant reductions in lung function in children active outdoors.(7)

Asthmatics are also at high risk for ozone related problems, and fourteen Americans die every day from asthma, a rate three times greater than just 20 years ago.(7) 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. Children, in particular, make up 25 percent of the population and comprise 40 percent of the asthma cases.(7)

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.

Scientists have studied other groups to find out whether they are at increased risk from ozone. So far there is no evidence to suggest that either the elderly or people with heart disease have heightened sensitivity to ozone. However, like other adults, elderly people will be at higher risk from ozone exposure if they suffer from respiratory disease, are active outdoors, or are unusually susceptible to ozone as described above.(6)

Environmental Effects

Review of the scientific literature also highlights a wide range of biological, physical, and chemical factors associated with ozone's effects in the environment. The effects of ozone on terrestrial ecosystems begin with the responses of individual biotic organisms, which vary among species and depend upon pollutant concentration, exposure period, development stage, nutrition, climate, insects, and disease. The effects are initiated by reactions between ozone and the cellular constituents that influence biochemical and physiological plant processes.(9)

Most plants require a balance of resources to maintain optimal growth, and when injured or stressed, plants compensate by allocating their available resources to the point of detriment to

minimize stress effects. 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: (7,9)

- 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;

- reduce growth and decrease survivability of plant and tree seedlings;

- increase susceptibility to disease, insects, and environmental stresses;

- kill or damage leaves so that they become spotted or brown or fall off the plants too soon which significantly decrease the natural beauty of an area, such as in national parks and recreation areas; and

- reduce the yield of economically important agricultural crops, such as soybeans, kidney beans, cotton, and wheat, and commercial forests.

The effects of ground-level ozone on long-lived species such as trees are believed to add up over many years so that whole forests or ecosystems can be affected. For example, ozone can adversely impact ecological functions such as water movement, mineral and nutrient cycling, energy flow, and habitat conditions for various animal and plant species. However, a significant level of uncertainty encompasses the effects of O_3 at the population and community levels within an ecosystem. This is because very few studies have been conducted on multi-species systems, for the majority of the documented studies report the response of organisms, not ecosystems, to ozone. Thus, further research is necessary to fill in the knowledge gap.(9)

2.2.2. Regulations and Standards

The predominant part of the United States' population is located in its rapidly expanding metropolitan and other urban areas, which generally cross the boundary lines of local jurisdictions and often extend into two or more States. The growth in the amount and complexity of air pollution associated with urbanization, industrial development, and the increasing use of motor vehicles, has resulted in mounting dangers to the public and environmental health and welfare.(10)

Air pollution comes from many different sources and is a result of a wide variety of pollutants. There are six major pollutants, including ozone, are found all over the United States. These pollutants, known as criteria air pollutants, can injure health, harm the environment and cause property damage.

The Clean Air Act (CAA), established in 1970, was established for multiple purposes. First, it served as a principal technical and financial framework for national, state, and local efforts to protect air quality, develop air pollution prevention, and implement control programs. Second, it worked to protect and enhance the quality of the Nation's air resources as to promote the public health, welfare and the productive capacity of its population. Third, it initiated and accelerates a national research and development program to achieve the prevention and control of air pollution.(10,11)

In 1971, under Clean Air Act, the United States Environmental Protection Agency (USEPA) established the National Ambient Air Quality Standards (NAAQS) for the six criteria pollutants in an attempt to protect public health, the environment, and the quality of life from the adverse effects of air pollution. *Table 1* summarizes the current National Ambient Air Quality Standards.(12)

Table 1: National Ambient Air Quality Standards

POLLUTANT	STANDARD VALUE [†]		STANDARD TYPE
Carbon Monoxide (CO)			
8-hour Average	9,000 ppb	(10 mg/m^3)**	Primary
1-hour Average	35,000 ppb	(40 mg/m^3)**	Primary
Nitrogen Dioxide (NO$_2$)			
Annual Arithmetic Mean	53 ppb	(100 μg/m^3)**	Primary & Secondary
Ozone (O$_3$)			
1-hour Average*	120 ppb	(235 μg/m^3)**	Primary & Secondary
8-hour Average	80 ppb	(157 μg/m^3)**	Primary & Secondary
Lead (Pb)			
Quarterly Average		1.5 μg/m^3	Primary & Secondary
Particulate < 10 micrometers (PM-10)			
Annual Arithmetic Mean		50 μg/m^3	Primary & Secondary
24-hour Average		150 μg/m^3	Primary & Secondary
Particulate < 2.5 micrometers (PM-2.5)			
Annual Arithmetic Mean		15 μg/m^3	Primary & Secondary
24-hour Average		65 μg/m^3	Primary & Secondary
Sulfur Dioxide (SO$_2$)			
Annual Arithmetic Mean	30 ppb	(80 μg/m^3)**	Primary
24-hour Average	140 ppb	(365 μg/m^3)**	Primary
3-hour Average	500 ppb	(1300 μg/m^3)**	Secondary

† Units of measure for the standards are parts per billion (ppb) by volume, milligrams per cubic meter of air (mg/m^3), and micrograms per cubic meter of air at 25 C(μg/m^3)

* The ozone 1-hour standard applies only to areas that were designated nonattainment when the ozone 8-hour standard was adopted in July 1997. An area will attain the standard when the 3-year average of the annual 4th-highest daily maximum 8-hour concentrations is less than or equal to 80 ppb. This provision allows a smooth, legal, and practical transition to the 8-hour standard.

** Parenthetical value is an approximately equivalent concentration.

Source: http://ftp.epa.gov/airs/criteria.html (12)

For each pollutant, two limits were established. The first set of limits, referred to as the primary standard, protects public health and is based entirely on health-related information, without considering the costs of attaining the standard. The second set of limits, or secondary standard, is intended to protect public welfare and prevent environmental and property damage. This includes effects on soils, water, crops, vegetation, buildings, property, animals, wildlife, weather, visibility, transportation, and other economic values, as well as personal comfort and well being.(11,12)

Since the USEPA first established the ozone standards in 1971 it has been known that ozone has clear, documented impacts on human health and environmental ecosystems. In 1993, the USEPA reaffirmed the existing standard based on scientific information obtained from ozone studies published through the late 1980s. Since the early 1970's, however, over 3,000 new studies have been published on the health and ecological effects of ozone, as well as on ozone monitoring and ambient air quality levels.(7,11) Many of these new studies indicate that the health effects associated with ozone occur at exposure levels below the current primary standard. In addition, they showed that exposure times longer than one hour may increase human health risks.(7)

In the mid-1990's, another lengthy scientific review process, which included an extensive external scientific review, was initiated. As a result, the USEPA determined that changes in the regulations were necessary to protect public health and the environment. Thus, the Clean Air Act was amended in 1997 to provide a higher level of protection than the current standard. This was accomplished by lowering and changing the form of the standard from an expected exceedance form to a concentration-based form so that it more directly relates to ozone concentrations associated with health effects. This new form also avoids exceedances, regardless of size, from being counted equally in the attainment tests.(7)
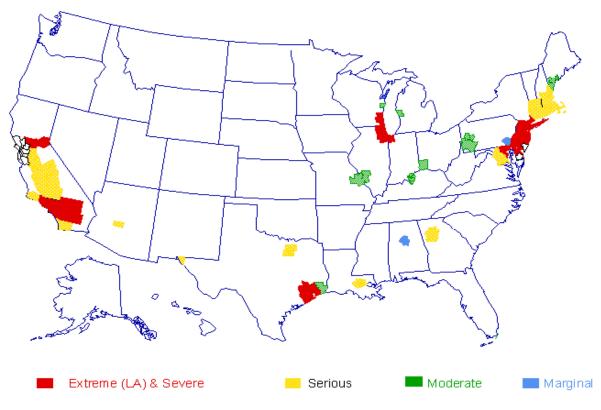
The USEPA sets air quality standards that, above all, protect the public health. The revised standards will provide additional protection to nearly 125 million Americans, including 35 million children by reducing the risk associated with ozone exposure and thus diminishing its damaging effects and prevent approximately 15,000 premature deaths, 350,000 cases of aggravated asthma, and 1 million cases of significantly decreased lung function in children each year.(7,11) However, along with standards for ozone, USEPA will issue an implementation package designed to give states, local governments and business the flexibility they will need to meet protective public health standards in a reasonable, cost-effective way, thus providing for both cleaner air and the nation's continued economic progress.(7)
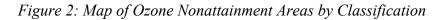
It is interesting to note that on May 14, 1999, the U.S. Court of Appeals ruled this new standard unconstitutional.(13) Although the USEPA has the authority under the Clean Air Act Amendments of 1990, to set a standard for ozone levels, it does not have the authority to make a stricter standard without conclusive scientific evidence the new standard will improve health. As a result, because ozone does not have a known threshold exposure level, it is difficult to show definitively that a stricter standard of 80 ppb provides better health protection.

A geographic area that meets or surpasses the primary standard is called an attainment area; areas that don't meet the primary standard are called nonattainment areas. Although USEPA has been regulating criteria air pollutants since the 1970 CAA was passed, many urban areas are classified as nonattainment for at least one criteria air pollutant. It has been estimated that about 90 million Americans live in nonattainment areas.(11) The USEPA works with state governors to identify nonattainment areas for each criteria air pollutant, and then classifies these areas according to how badly they are polluted.

There are currently five classes of nonattainment areas for ozone, based on the severity of

the pollution problem. These include: marginal, moderate, serious, severe, and extreme. *Figure 2* and *Table 2* provides a map and list, respectively, of the current ozone nonattainment areas for the 1-hour ozone standard, as of July 1998. The results presented with in this table are based on air quality data from 1995-1997. According to these classifications, Chicago is categorized as a severe zone for ozone pollution.(14)

Figure 2: Map of Ozone Nonattainment Areas by Classification

Source: http://www.epa.gov/airprogm/oar/oaqps/ (14)

Table 2: Ozone Nonattainment Areas by Classification

Extreme: 280 ppb and above
• Los Angeles South Coast Air Basin, CA
Severe: 180 up to 280 ppb
• Baltimore, MD • Chicago-Gary-Lake County, IL-IN • Houston-Galveston-Brazoria, TX • Milwaukee-Racine, WI • New York-N. New Jersey-Long Island, NY-NJ-CT • Southeast Desert Modified AQMA, CA • Philadelphia-Wilmington-Trenton, PA-NJ-DE-MD • Sacramento Metro, CA • Ventura Co, CA
Serious: 160 up to 180 ppb
• Atlanta, GA • Baton Rouge, LA • Boston-Lawrence-Worcester (E. MA), MA-NH • Dallas-Fort Worth, TX • El Paso, TX • Greater Connecticut • Phoenix, AZ (Serious as of 12/12/97) • Portsmouth-Dover-Rochester, NH • Providence (All RI), RI • San Diego, CA • San Joaquin Valley, CA • Santa Barbara-Santa Maria-Lompoc, CA (Serious as of 1/9/98) • Springfield (Western MA), MA • Washington, DC-MD-VA
Moderate: 138 up to 160 ppb
• Beaumont-Port Arthur, TX • Cincinnati-Hamilton, OH-KY • Louisville, KY-IN • Manitowoc Co, WI • Muskegon, MI • Pittsburgh-Beaver Valley, PA • Portland, ME • St Louis, MO-IL
Marginal: 121 up to 138 ppb
• Birmingham, AL • Door Co, WI • Kent & Queen Anne's Cos, MD (clean 94-96) • Lancaster, PA (clean 94-96) • Sunland Park, NM (New Area 1995)

Source: http://www.epa.gov/airprogm/oar/oaqps/ (14)

2.3 THE OZONE PROBLEM

2.3.1 Chemistry

The gas phase chemistry of the troposphere involves the oxidation of organic molecules in the presence of nitrogen oxides via free radical chain reactions. Because atmospheric oxidation incorporates very low concentrations of reactants, an external source of energy, in the form of solar radiation, is required to drive the reactions.

Ozone can be considered as the principal product of tropospheric chemistry. The only ozone forming reaction that occurs in the atmosphere is that between atomic and molecular oxygen. The sunlight that reaches the troposphere exhibits wavelengths exceeding only approximately 290 nm. As a result, the source of the atomic oxygen in the troposphere cannot be O_2, for it only absorbs radiation of shorter wavelengths.(15) Instead, the source of atomic oxygen is the photolysis of nitrogen dioxide (NO_2) in the presence of sunlight at wavelengths < 420nm.(15,16)   Thus, tropospheric chemistry can be considered to start as a result of the photolysis of NO_2,

$$NO_2 + h\nu \rightarrow NO + O \tag{E1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{E2}$$

where M represents N_2, O_2, or another third molecule that can absorb excess vibrational energy thus stabilizing the O_3 molecule formed. Relatively little ozone is formed as a result of reactions (E1) and (E2) alone since O_3, once formed, reacts rapidly with NO to regenerate NO_2,

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{E3}$$

Consider for a moment the dynamics of a system in which only reactions (E1), (E2), and (E3) are taking place, assuming that known initial concentrations of NO and NO_2, $[NO]_0$ and $[NO_2]_0$, in the air are placed and irradiated in a reactor of constant volume at constant

temperature. The rate of change for the concentration of NO_2 after the irradiation begins is given by,

$$\frac{d[NO_2]}{dt} = -k_{(1)}[NO_2] + k_{(3)}[O_3][NO] \qquad \text{(E4)}$$

Treating $[O_2]$ as constant, there are four species in the system: NO_2, NO, O, and O_3. The dynamic equation could also be written for NO, O, and O_3, just as was done for NO_2 in equation (E4). For example, the equation for $[O]$ is given by,

$$\frac{d[O]}{dt} = k_{(1)}[NO_2] - k_{(2)}[O][O_2][M] \qquad \text{(E5)}$$

If the right hand side of equation (E5) was evaluated numerically, the result would be very close to zero. Physically, this indicates that the oxygen atom is so reactive that it disappears by reaction (E2) virtually as fast as it is formed by reaction (E1). In dealing with highly reactive species such as the oxygen atom, it is customary to invoke the pseudo-steady-state approximation (PSSA) and thereby assume that the rate of formation is exactly equal to the rate of disappearance, for example,

$$k_{(1)}[NO_2] = k_{(2)}[O][O_2][M] \qquad \text{(E6)}$$

The steady state oxygen atom concentration in this system is then given by,

$$[O]_{ss} = \frac{k_{(1)}[NO_2]}{k_2[O_2][M]} \qquad \text{(E7)}$$

Note that $[O]_{ss}$ is not constant; rather it varies with $[NO_2]$ in such a way that at any instant a balance is achieved between its rate of production and loss. This approximation illustrates that the oxygen atom concentration adjusts to changes in the NO_2 at a rate many orders of magnitude faster than the rate at which NO_2 concentration changes. As a result, on the time scale of the

NO_2 dynamics concentration, which is dependent on light intensity, the ozone steady state equation (E7) should always be satisfied.(15)

In reality however, the troposphere is not a steady state reactor. Thus, the rate of ozone formation is not simply proportional to the concentration of NO_2. Instead, the rate of O_3 formation is a non-linear function of many factors including temperature, intensity and spectral distribution of sunlight, tropospheric ratios and concentrations of the hydroxyl radical (HO•), nitrogen oxides (NO_x), and volatile organic compounds (VOCs), and their corresponding chemical compositions.

The hydroxyl radical (HO•), in particular, is key with respect to ozone chemistry. Although it does not react with any of the major constituents of the atmosphere, such as N_2, O_2, CO_2, or H_2O, the OH radical is the most reactive species in the troposphere. This is because it reacts with most trace species in the atmosphere, is present in relatively high concentrations (on the order of 10^6 molecules cm^{-1} during daylight hours (15)), and is regenerated as a result of its atmospheric reactions. The OH radical is generated through the photolysis of ozone via the following atmospheric reaction pathway:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad \text{(E8)}$$

$$O(^1D) + H_2O \rightarrow 2\ HO• \qquad \text{(E9)}$$

where $O(^1D)$ is the exited singlet oxygen atom .

The reaction of OH with many hydrocarbons (RH) leads to alkyl peroxy radicals, and upsets the steady state equilibrium of ozone with respect to NO_x, (E1) through (E3),

$$RH + HO• \rightarrow R• + H_2O \qquad \text{(E10)}$$

$$R• + O_2 + M \rightarrow RO_2• + M \quad \textit{(fast)} \qquad \text{(E11)}$$

For a generalized example of the VOC reaction cycle, the reaction of HO• with aldehydes (RCHO) will be considered.(15) In reactions similar to those presented in (E10) and (E11), aldehydes react with OH radicals to form the acyl (RCO•) and acyl peroxy (RC(O)O$_2$•) radicals,

$$RCHO + HO• \rightarrow RCO• + H_2O \tag{E12}$$

$$RCO• + O_2 + M \rightarrow RC(O)O_2• + M \quad \textit{(fast)} \tag{E13}$$

The peroxy radicals react rapidly with the NO, thus competing with O$_3$ in reaction (E3), to form NO$_2$ and other free organic radicals,

$$RO_2• + NO \rightarrow RO• + NO_2 \tag{E14}$$

$$RO_2• + NO + M \rightarrow RONO_2 + M \tag{E15}$$

$$RC(O)O_2• + NO \rightarrow RC(O)O• + NO_2 \tag{E16}$$

The most common fate for the smaller alkoxy radicals is reaction with O$_2$, leading to HO$_2$ radicals and a carbonyl compound,

$$RO• + O_2 \rightarrow RCHO + HO_2• \tag{E17}$$

The RC(O)O• radicals are of short lifetime, decomposing to form an alkyl radical (R•) and CO$_2$, with the subsequent generation of another peroxyalkyl radical,

$$RC(O)O• \rightarrow R• + CO_2 \tag{E18}$$

$$R• + O_2 \rightarrow RO_2 \tag{E19}$$

Finally, the hydroperoxyl radicals can react with NO to regenerate OH and complete the cycle,

$$HO_2• + NO \rightarrow NO_2 + HO• \tag{E20}$$

Atmospheric propagation reactions involve hydrocarbon oxidation steps, illustrated in reactions (E12) to (E19), and NO to NO$_2$ conversion reactions, such as that found in (E20). The generalized mechanism is a propagation chain in which the hydrocarbon molecule RH is

converted into the carbonyl RCHO and two NO to NO_2 conversions occur, with the OH radical recreated at the end of the sequence of reactions. As primary hydrocarbons are oxidized to carbonyls, the carbonyls join the primary hydrocarbons in the suite of compounds that can be attacked by OH. Aldehydes formed as intermediate products can themselves photolyze to create fresh HO_x species; this is actually a branching step since more radicals are produced in the step than consumed. This type of branching is essential to sustain the photochemical cycle.

These propagation reactions affect ozone chemistry in two significant ways. First, NO_2, the major reactant in the formation of ozone (E1) & (E2), is produced as a product of this reaction series. Second, the primary component in the scavenging of ozone (E3), NO, is utilized as a reactant in these reactions. Consequently, as a result of the OH and VOC reactions (E8) through (E20), the overall ozone level may rise, for not only is the production of O_3 increased, but its destruction is decreased.

Key termination reactions in tropospheric chemistry include,

$$HO\bullet + NO_2 + M \rightarrow HNO_3 + M \tag{E21}$$

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2 \tag{E22}$$

$$RO_2\bullet + HO_2\bullet \leftrightarrow ROOH + O_2 \tag{E23}$$

$$RO_2\bullet + NO + M \rightarrow RONO_2 + M \tag{E24}$$

$$CH_3C(O)OO\bullet + NO_2 + M \leftrightarrow CH_3C(O)O_2NO_2 + M \tag{E25}$$

It should be noted that the nitric acid forming reaction (E21) is the predominant termination step under all but the most pristine (low NO_x) background tropospheric conditions; and, reactions (E23) and (E25) are reversible.

The hydroxyl radical (HO•) is the key reactive species in the chemistry of ozone formation, since reaction with the OH radical determines the atmospheric lifetime of the VOCs

that participate in the photochemical production of ozone in the troposphere. The VOC-OH reaction, such as those illustrated in reactions (E10) and (E12), initiates the hydrocarbon oxidation sequence that will eventually accelerate the production of ozone through the generation of NO_2. In addition, the new organic radicals produced may also eventually lead to the additional production of both NO_2 and $HO\bullet$, as a result of reactions (E17) & (E20). The NO_x-OH reaction (E21) acts as a key termination step that removes OH radicals from the active VOC oxidation cycle, (E12) through (E19), retarding the further production of ozone via this reaction chain. Thus, the rate of ozone production is not simply proportional to the amount of NO_x present.

A competition exists between VOCs and NO_x for the OH radical. At ambient conditions, considering an average urban mix of VOCs, the ratio of the NO_2-OH to VOC-OH rate constants is about 5.5 ($1.7 * 10^{-4}$ ppm^{-1} min^{-1}: $3.1 * 10^{-3}$ ppmC^{-1} min^{-1}). Thus, when the VOC to NO_2 concentration ratio is approximately 5.5:1, the rates of reaction of VOC and NO_2 with OH would be equal. If the VOC to NO_2 ratio is less than 5.5:1, the reaction of OH with NO_2 predominates; whereas, when the ratio exceeds 5.5:1, the OH reacts preferentially with VOCs in a NO_x limited regime. In general, increasing VOC concentrations results in the production of more ozone; while, increasing NO_x concentrations may lead to either more or less ozone depending on the prevailing VOC to NO_x ratio.(15) Therefore, at a given level of VOC, there exists a NO_x concentration at which a minimum amount of ozone is produced. This means that there is an optimum VOC to NO_x ratio.(5,15) Indeed, in most of the troposphere, except in areas of strong NO_x sources, the availability of NO_x governs the rate of ozone production.

2.3.2. Sources

The distribution of ozone in the troposphere is maintained through combined radiative, chemical, and dynamical processes. There are three main sources of ozone in the troposphere: downward transport of stratospheric ozone into the troposphere, surface transport of ozone via meteorological processes, and in situ photochemical production of O_3 from reactions involving ground level emissions of NO_x and VOCs.

Ozone exhibits temporal variability over hourly, diurnal, synoptic (3-5 days), weekly, seasonal, and long-term (5-20 years) time scales. The ozone changes on weekly and long-term scales are caused primarily by anthropogenic emission changes, while changes at the hourly, diurnal, synoptic and seasonal scales are influenced by atmospheric processes and meteorology.(17)

Stratospheric-Tropospheric Transport

The mechanisms by which stratospheric ozone is transported downward and mixed into the troposphere are reasonably well understood. However, there are many different methods utilized to calculate exact concentrations. One approach, based on the 'downward control' principle, uses an average meridional circulation in the stratosphere that is derived from the continuity equation and stratospheric temperature derivations from radiative equilibrium, caused by energy dissipation due to large scale dynamic perturbations (18). Another approach, estimates the stratospheric to tropospheric transfer of ozone using measured distributions of stratospheric constituents, such as N_2O, NO_x, and O_3, along with knowledge of the stratospheric reaction chemistry.(19) In general, the portion of the O_3 near the surface of the earth which can be attributed to stratospheric-tropospheric transport falls in the 5-15 ppb range for a seasonal

average (5), and accounts for only approximately 0.1% of all the ozone produced in the

stratosphere (16). Thus, it is apparent that the contribution of stratospheric ozone can not alone

account for the elevated ground level ozone concentrations.

Surface Transport

Ozone levels result from a complex interaction of atmospheric chemical reactions,

atmospheric mixing processes, urban air masses, general meteorology, and distant and local

precursor sources. Thus, the identification and understanding of the transport of photochemical

O_3 and its precursors by atmospheric and meteorological processes are essential to

comprehending photochemical air pollution and the potential extent of its effects.(17)

The concentration of an air pollutant depends significantly on the degree of mixing that

occurs between the time a pollutant, or its precursors, is emitted and the time it arrives at the

receptor. Surface transport processes, in particular, can not only determine the movement of

ozone formation and destruction constituents, but can act on ozone itself determining its

distribution throughout much of the atmosphere. Thus, it is essential to examine the atmospheric

dynamics of the meteorological factors that are responsible for the transport mechanisms of

ozone.

The dominant meteorological factors that influence ground level O_3 concentrations and

distributions are atmospheric mixing and temperature. These factors are discussed in the

following sections and are examined as they are related to the Chicago region.

Atmospheric Mixing

Atmospheric mixing can exert a powerful influence on the distribution of pollutant

concentrations in space and time and can result from thermal turbulence associated with the

redistribution of heat energy, or mechanical turbulence, often associated with weather patterns.

The temperature structure of the atmosphere is separated vertically into several layers
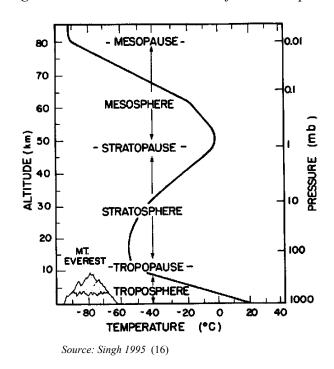
which is illustrated in *Figure 3*.(16)

Figure 3: The Vertical Structure of the Atmosphere
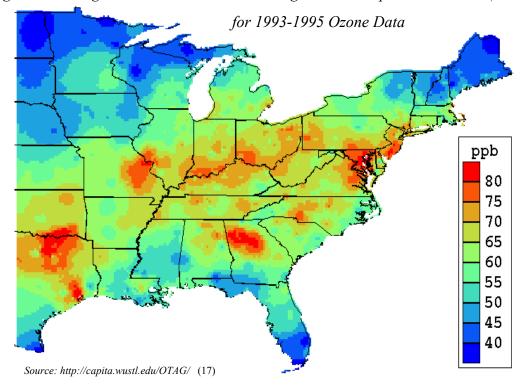

Source: Singh 1995 (16)

The thermal stability of the atmosphere is a measure of the potential of air to remain

vertically static at a constant pressure level and thus, resist overturning. The most stable layers

of the atmosphere are those known as inversion layers where temperature increases with height

and mixing rates are relatively low.   In layers where temperature decreases with height, the

static stability varies considerably. This variation occurs mainly in the planetary boundary layer

(PBL), defined as the lower layer of the troposphere in contact with the surface of the earth (1-2

km), where the majority of pollutant sources exist.

In general, thermal atmospheric mixing through the troposphere is assumed to follow a typical and predictable vertical cycle.(5) The cycle begins with a nocturnal surface inversion that forms when outflow of radiation exceeds the influx radiation. This surface layer inversion persists until surface heating becomes significant, usually 1 to 2 hours after sunrise. In this case, an elevated reservoir of pollutants, initially trapped in the inversion, could be transported vertically downward causing a rapid rise of O_3 concentrations near the ground in the morning hours. After this initial increase, surface concentrations can continue to rise as a result of photochemistry and transport of O_3 rich air to the receptor until the inversion is broken by surface heating. When surface heating decreases in the evening, a surface inversion will again begin to form. The fate of the new elevated inversion is less clear, however, for this layer is exposed to transport processes that can redistribute pollutants throughout the atmosphere.

Similarly, geography can also have a significant impact on the mixing and dispersion of pollutants along a coast or shoreline. For example, Chicago is located on Lake Michigan, where temperature gradients exist between the land and water masses and the air above the land and water masses. In this case, when the water is cooler than the land, the cool air near the water will tend to increase the stability of the boundary layer in the coastal zone, and, as a result, decrease the mixing processes that act on the pollutant emissions. The opposite condition occurs if the water is warmer than the land, which tends to increase pollutant dispersion in such areas.(5)

In the United States and Europe, the most severe regional ozone episodes occur when slow moving, high-pressure weather systems develop during the summer months.(15) These systems are characterized by the widespread sinking of air through most of the troposphere creating a pronounced inversion of the normal temperature profile, where the temperature of the air in the lower troposphere increases with height. This inversion suppresses vertical mixing and

acts as a strong lid to contain pollutants in a shallow layer in the troposphere, for cooler air below does not mix with warmer air above.
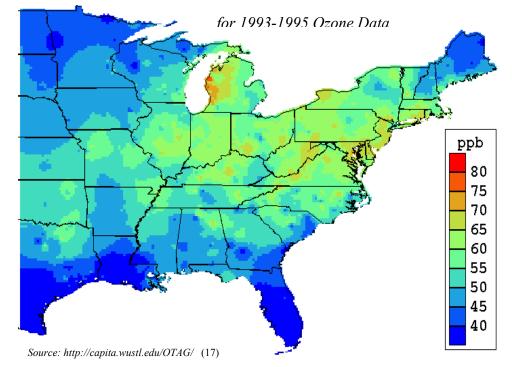
Major high-pressure systems are also frequently associated with low wind speeds, < 3 m/s, and stagnant circulation during the ozone season. When the slow moving airflow of a high-pressure system surrounds a major metropolitan area, a regional air mass that exhibits the characteristics of that region is created. Thus, if a region is considered an emissions source area, a pollutant air mass will be created in which there exists the potential for the accumulation of O_3 and its precursors near local source areas. This phenomenon is illustrated in *Figure 4*.(17)

Figure 4: Average Ozone Concentration During Low Wind Speed Conditions (< 3 m/s) for 1993-1995 Ozone Data

Source: http://capita.wustl.edu/OTAG/ (17)

The movement of these air masses facilitates the transfer of O_3 and its precursors beyond the urban scale to neighboring rural and urban areas creating episodes of high O_3 in areas which themselves generate few emissions. Thus, high ozone episodes in an area are often terminated by the passage of a front that brings cooler, cleaner air to a source region moving the polluted air

downwind.(15) High wind speeds, > 6 m/s, generate strong ventilation which helps to prevent

the local build-up of pollutants near their sources, but contributes to long-range transport and

regional ozone episodes. This phenomenon is illustrated in *Figure 5*.

Figure 5: Average Ozone Concentration During High Wind Speed Conditions (> 6 m/s)
for 1993-1995 Ozone Data

Source: http://capita.wustl.edu/OTAG/ (17)

The relationship between wind and O_3 varies from one part of the country to another

because the transport of ozone manifests itself differently at the local, sub-regional, and regional

scales. Through closer inspection of the Lake Michigan region, as illustrated in time series

ozone maps in *Figure 6* (20), it can be observed that ozone level distribution varies throughout

the day with the greatest degrees of exceedances occur in the late afternoon, in areas other than

Chicago. Initially, elevated ozone levels are located primarily over the highly industrial source

areas in Indiana and Ohio. However, as the day progresses, the elevated levels appear over

western Michigan, the Upper Peninsula of Michigan, and eastern Wisconsin, regions that have

relatively few emissions sources. Thus, it is suspected that the observed ozone levels in this

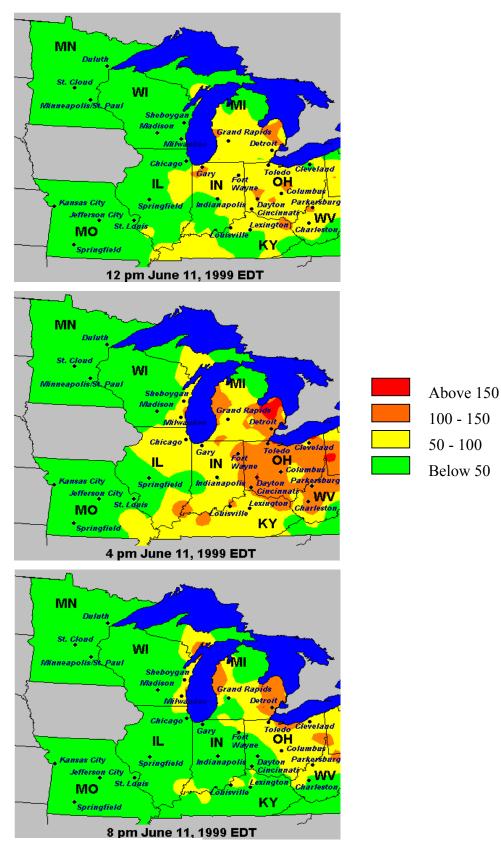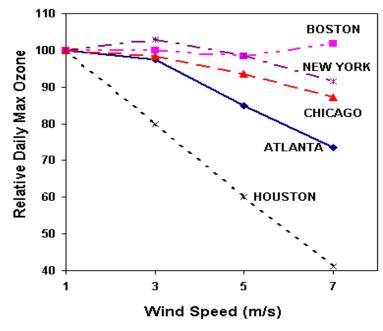region are primarily a result of transport processes.

Figure 6: Time Series Ozone Maps

Most of the ozone 120 ppb nonattainment episodes can be attributed to short range local transport (30-150 miles).(17) Local scale transport conditions can be examined through the breakdown and comparison of ozone and wind correlation for different cities, as depicted in *Figure 7*. In general, for southern urban areas, ozone levels decline rapidly with increasing wind speed. This indicates that ozone episodes are caused primarily by local stagnation conditions. The trends shown in *Figure 7* suggest that in northern cities, however, ozone levels decrease much less rapidly with increasing wind speeds. This indicates that these areas are more heavily influenced by atmospheric transport mechanisms.(17)

Figure 7: Relative Change of Ozone Concentration with Wind Speed of Different Cities

Source: http://capita.wustl.edu/OTAG/ (17)

Figure 8, which was generated from data collected during our study, provides a more detailed illustration of this phenomenon for Chicago. It can be observed that when the wind speeds in Chicago are relatively low, less than about 5 m/s, there exists a greater tendency for an ozone episode to occur. Once wind speeds rise above 5 m/s, the number of ozone exceedances begins to drop with increasing speed. This shows that local source emissions are particularly

active in the augmentation of ozone noncompliance days during low wind conditions. As wind

speeds increase, the emissions that help generate the ozone problem are carried out of the

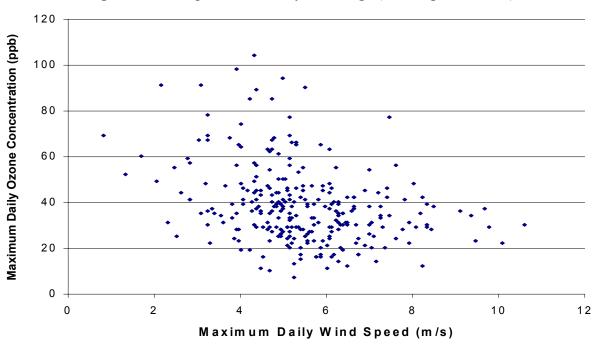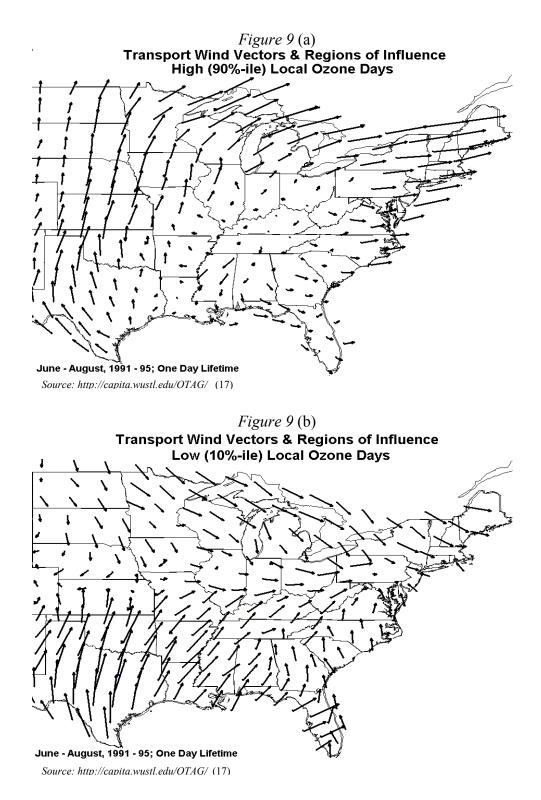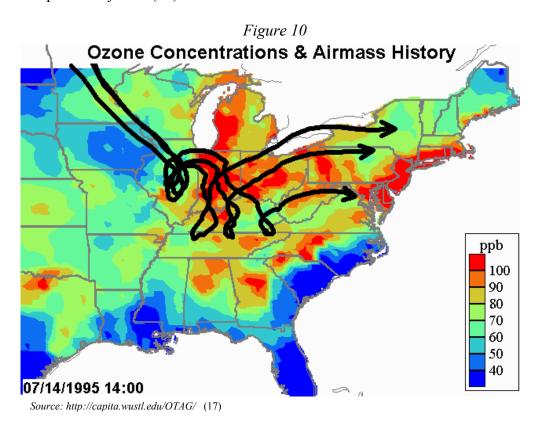Chicago region, hence lowering the overall incidence of ozone exceedances.

Figure 8: Wind Speed vs. Ozone for Chicago (Jun-Aug,1994-1996)

On a regional level, the examination of dispersion conditions can be attained through the

analysis of national wind speed and direction trends, which are illustrated in *Figure 9*. During

high-ozone days (90th percentile), dispersion in the Southeast is typically poor due to stagnating

air masses, shown by the region of small arrows in *Figure 9 (a)*. Whereas, the western and

northern sections of the domain experience stronger and more persistent southerly and westerly

winds, respectively. This supports the idea that ozone exceedances in the central and

southeastern areas are predominantly the result of local emissions, while exceedances in other

regions are also influenced by regional transport. In contrast, on low-ozone days (10th

percentile), the transport is predominantly from the regions outside the U.S., such as Canada and

the Gulf of Mexico. This is illustrated in *Figure 9 (b)*. (17)

Figure 9 (a)
Transport Wind Vectors & Regions of Influence
High (90%-ile) Local Ozone Days

June - August, 1991 - 95; One Day Lifetime
Source: http://capita.wustl.edu/OTAG/ (17)

Figure 9 (b)
Transport Wind Vectors & Regions of Influence
Low (10%-ile) Local Ozone Days

June - August, 1991 - 95; One Day Lifetime
Source: http://capita.wustl.edu/OTAG/ (17)

Regional scale ozone transport episodes often result from several days of air stagnation over multi-state areas and end with the subsequent transport of the elevated O_3 concentrations to downwind states. *Figure 10* illustrates this phenomenon for the Midwestern region of the U.S.

where an atmospheric flow visualization is superimposed on observed ozone concentration

patterns. Stagnant atmospheric flow patterns create an air mass that lingers over the Midwest, a

high NO_X emission region, causing the accumulation of high ozone concentrations. Near the end

of the episode, Midwestern concentrations drop, as the polluted airmass is swiftly transported

eastward, carrying high ozone concentrations toward the Northeastern seaboard where regional

ozone levels peak a day later.(17)

Figure 10

Source: http://capita.wustl.edu/OTAG/   (17)

Temperature

The relationship between tropospheric ozone concentration and temperature has been

demonstrated through the examination of the correlation between ambient air ozone

concentrations and maximum temperature measurements. A graphical representation of the

results from five different cities, including our study of Chicago, is presented in *Figure 11*. This

figure shows the maximum daily ozone concentration verses maximum daily temperature for the

summer months (May to October) for Chicago, IL, Atlanta, GA, New York, NY, Detroit, MI, and Phoenix, AZ, respectively.
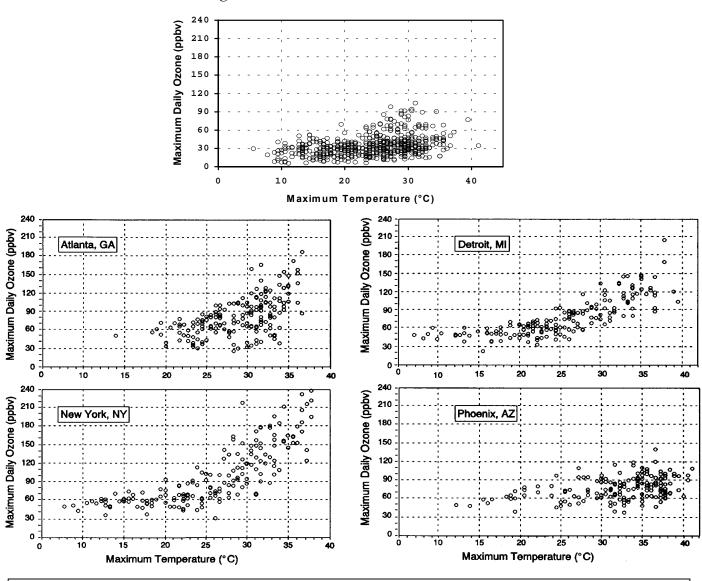
Figure 11: Maximum Daily Ozone Concentration verses Maximum Daily Temperature for Chicago[*], Atlanta, New York, Detroit, and Phoenix[†]

* Scatter plot for a single ozone monitoring station in downtown Chicago, IL for May-October, 1994-1996
† Scatter plot for Atlanta, GA, New York, NY, Detroit, MI, and Phoenix, AZ for May-October, 1988-1990. *Source: Air Quality Criteria for Ozone and Related Photochemical Oxidants, volume I* (5)

In general, two consistent trends are observed: the correlation for temperatures below approximately 20°C is a relatively flat line and the upper bound limit for ozone concentrations

tends to increase with temperature. The first observation holds for all the cities, including Chicago. However, above 20°C, a linear increase in maximum daily ozone concentration as a function of increasing temperature is observed in Atlanta, New York, and Detroit. This linear relationship is not seen upon analysis of the data gathered in Chicago or Phoenix

The data in *Figure 11* shows that at any given temperature, an extensive range of ozone concentrations can exist, and this range of ozone levels differs from region to region. For example, at 30°C, the approximate range of possible ozone values in Atlanta is 35–160 ppb; whereas in New York this 30°C range is about 85-220 ppb. In addition, the slope of the ozone verses temperature function also varies. These phenomena are a direct result of the effect of the variation of meteorological factors, other than temperature, and precursor source emissions between different regions of the country. Thus, the upper bound evidently represents the maximum O_3 concentration achieved under the most favorable production conditions within a specific area.(5)

There are numerous reasons hypothesized to explain the positive correlation between ozone and temperature. One of these is the related to the increase in photolysis rates of ozone production with increasing temperature and under meteorological conditions associated with high temperatures. This follows from the fact that an increase in photolysis rates would augment a key source of OH radicals (E8), whose availability plays a key role in the photochemical production of O_3. If the availability of this energy source is enhanced as a result of meteorological conditions associated with high temperatures, more ozone will be produced. Another reason could be attributed to an increase in the production of ozone precursors, such as NO_x and VOC, at high temperatures. This hypothesis arises from the fact that higher temperatures create an increased energy use, mostly due to a greater demand for air conditioning

in buildings and automobiles. Thus, as power plants burn more fossil fuels to meet this increase in energy demand, they generate greater a quantity of emissions which increases the levels of ozone precursors present at ground level. In addition, the relationship between high temperatures and stagnant circulation patterns, as discussed previously, can be used to account for the notable trend between ozone and temperature. Unfortunately, an exact mechanistic understanding as to the exact relationships between all these factors causing elevated ozone concentration does not currently exist.

Ground Level Emissions

The photochemical production of the ozone found at the earth's surface is the result of a series of chemical reactions that involve nitrogen oxides (NO_x) and volatile organic compounds (VOCs). The formation of O_3 from its precursors is a complex, non-linear function of many factors: spectral distribution of sunlight, atmospheric mixing, meteorological conditions, temperature, concentrations and reactivity of precursor compounds in ambient air.

Ground-level ozone production and control depends on the emissions of NO_x and VOC from many sources. Until about 150 years ago, the levels of these pollutant precursors were quite low and the sources were mainly natural. As urbanization and industrialization began to grow, the pollution levels in these areas also increased as a result of supplementary man-made sources.(H) Thus, in order to rectify the pollution problem and devise the most appropriate pollution regulations and control strategies, it is important to understand both the sources and source strengths of O_3 precursor species. In the following sections, anthropogenic and biotic NO_x and VOC sources and their relative influence on ambient conditions in the Chicago area will be described.

<u>*Nitrogen Oxides (NO$_x$)*</u>

Nitrogen gas (N$_2$) is an abundant and inert gas, which makes up almost 80 percent of the earth's atmosphere. In this form, it is harmless to humans and essential to plant metabolism, but due to its abundance in the air, it is a frequent reactant in many combustion processes where it combines with oxygen (O$_2$) to form various oxides of nitrogen (NO$_x$). Of these, nitric oxide (NO) and nitrogen dioxide (NO$_2$) are the most important contributors to air pollution and the term NO$_x$ is generally used to represent these two nitrous oxide forms.(21)

Major NO$_x$ source categories include mobile sources, external fuel combustion, stationary internal combustion, other combustion, industrial processes, and biogenic sources. *Table 3* gives a more detailed summary of what is included within each of these categories, and *Figure 12* provides a pie chart that illustrates the typical summer day contribution of each source category to the total daily NO$_x$ emissions in the Chicago area.(22) Appendix A provides the complete and detailed inventory.

Table 3: Source Categories Used to Inventory Nitrogen Oxide Emissions

Mobile Sources	External Fuel Combustion	Stationary Internal Combustion	Other Combustion	Industrial Processes	Biogenic Sources
Highway Vehicles: • Gasoline autos and trucks • Diesel autos and trucks • Motorcycles Non-Highway Vehicles • Rail • Aircraft • Vessels • Service, Recreational, Agricultural, Industrial, and Commercial equipment	Utility Boilers Oil Boilers • Industrial • Commercial • Institutional • Residential Gas Boilers • Industrial • Commercial • Institutional • Residential	Reciprocating Engines Gas Turbines	Waste Disposal • Industrial • Governmental • Commercial • Institutional • Residential Open Burning • Structure • Forest • Agricultural • Other	Manufacturing • Chemical • Iron and Steel Coke Ovens Mineral Products Petroleum Refining	Soil • Nitrification • Denitrification

Source: Illinois Statewide Ozone Precursor Emissions Inventory (22)

Figure 12: Typical Summer Day Emissions of NO$_x$ for Chicago the Area (1996)

Anthropogenic NO$_x$ is primarily associated with combustion processes. The principal pollutant emitted is NO, which is formed at high combustion temperatures from the nitrogen and oxygen in air and from nitrogen in combustion fuel. Anthropogenic emissions of NO$_x$ on a typical summer day in 1996 totaled 1026.58 tons. As shown in *Figure 12*, over 93% of these emissions are from two source categories: mobile sources, at 705.20 tons/day, and external fuel combustion, at 252.84 tons/day.(22)

Natural NO$_x$ sources, which include lighting, soils, wildfires, stratospheric inversion, and oceans, constitute only a small percentage of the total NO$_x$ emissions for the Chicago area and are included within the biogenic slice in *Figure 12*. However, of these natural sources of NO$_x$, lightning and soils are the only two significant contributors within the United States. Lightning produces high enough temperatures to allow N$_2$ and O$_2$ to be converted to NO in the atmosphere, and soils contain both nitrifying and denitrifying organisms, which produce NO$_x$ as a by-product of natural mechanisms.(23) The relative importance of these two pathways varies greatly from organism to organism and is dependent upon soil temperature and fertilization levels.(5)

Volatile Organic Compounds (VOCs)

The term volatile organic compounds (VOCs) is used to denote the entire set of vapor phase atmospheric organics, excluding CO and CO_2. The U.S. National Acid Precipitation Assessment Program (NAPAP) inventory of VOC emissions includes, for example, over 600 different compounds.(15) The major classes of VOCs in the ambient air are alkanes, alkenes, aromatic hydrocarbons, carbonyl compounds, alcohols, and esters.(5) Characterizing VOC emissions ideally requires not just the total VOCs but the individual chemical compounds that constitute the entire mixture since the atmospheric behavior of individual species can vary enormously.
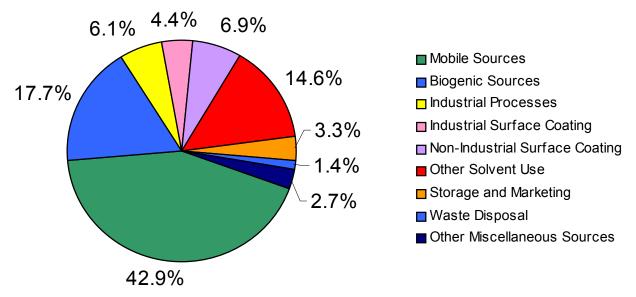
Major VOC source categories include industrial processes, industrial surface coating, non-industrial surface coating, other solvent use, storage and marketing, waste disposal, mobile sources, biogenic sources, and other miscellaneous sources. *Table 4* gives a more detailed summary of each of these categories, and *Figure 13* provides a pie chart that illustrates the typical summer day contribution of each source category to the total daily VOC emissions in the Chicago area.(22) Appendix B provides the complete and detailed inventory.

Table 4: Source Categories Used to Inventory Volatile Organic Compound Emissions

Industrial Processes	Industrial Surface Coating	Non-Industrial Surface Coating	Other Solvent Use	Storage and Marketing of VOC
Petroleum Refining Manufacturing • Lube Oil • Chemical • Iron and Steel • Pharmaceutical • Plastics • Polymer Coke Ovens	Transportation Vehicles • Autos • Trucks • Ships • Aircraft Furniture Large Appliances Other Products • Metal • Paper • Textile • Wood • Plastic	Architecture Auto Refinishing Traffic/Maintenance Painting	Degreasing Dry Cleaning Graphic Arts Adhesives Emulsified Asphalt Paving Solvents • Commercial • Consumer	Production • Oil and Gas Processing • Oil and Gas Storage • Gasoline • Crude Oil • Volatile Organic Liquid Transfer and Refueling • Gas • Volatile Organic Liquid Leaking and Breathing

Waste Disposal	Mobile Sources	Biogenic Sources	Other Miscellaneous Sources
Municipal Combustion • Residential • Commercial • Institutional • Governmental • Industrial Landfills Hazardous Wastes	Highway Vehicles: • Gasoline autos and trucks • Diesel autos and trucks • Motorcycles Non-Highway Vehicles • Rail • Aircraft • Vessels • Service, Recreational, Agricultural, Industrial, and Commercial equipment	Vegetation	Fuel Combustion • Utilities • Industrial • Commercial • Institutional • Residential Open Burning • Structure • Forest • Agricultural • Other Pesticide Applications Stationary Internal Combustion Engines Bakeries

Source: Illinois Statewide Ozone Precursor Emissions Inventory (22)

Figure 13: Typical Summer Day Emissions of VOC for Chicago the Area (1996)

Source: Illinois Statewide Ozone Precursor Emissions Inventory (22)

VOCs emitted into the atmosphere are primarily the result of evaporative and combustion processes, from a large number of source types. The total Chicago area VOC emissions, for a typical summer day in 1996, amounted to 963.23 tons. As shown in *Figure 13*, the two largest source categories include, once again, mobile sources, at 413.67 tons/day, and, in contrast to the

NO$_x$ emissions, biogenic sources, at 170.71 tons/day. Emissions of VOCs from highway

vehicles result from the incomplete combustion of fuel or from its vaporization and account for

approximately 65% of the transportation related emissions. In addition, studies have shown that

the majority of these VOC emissions originate from only about 20% of the automobiles in

service, many of which are poorly maintained older cars.(5) In addition, it is interesting to note

that asphalt pavement itself emits 13.41 tons/day, approximately 1.5% of the total daily VOC

emissions. Vegetation also emits significant quantities of VOCs into the atmosphere, however,

because biogenic emissions are extremely dependent on temperature and the extent of vegetation

growth, they vary greatly by season. Coniferous forests are the largest vegetative contributors on

a national basis because of their extensive land coverage.(5)

2.3.3   Implications For Chicago

It has been shown that there is a very weak, if any, correlation between ozone levels and

temperature in the Chicago area. This suggests that there are other factors present that dictate the

level of Chicago's air quality. In fact, our analysis, in conjunction with studies conducted by the

Ozone Transport Assessment Group (OTAG), established that Chicago's ozone problem is

strongly correlated with wind patterns and atmospheric transport. As a result, the control and

reduction of ozone and its precursors requires addressing regional mobile, area, and point

sources, and continuing to establish programs and practices that work towards an overall

improvement in regional air quality.

3. MITIGATION ALTERNATIVES - COOLING OUR COMMUNITIES

Research on the effects of urban heat islands is progressing at a time of immense public concern about air quality and human health issues. Specifically, the urbanization of the natural landscape through the replacement of vegetation with roads, bridges, houses, and commercial buildings has dramatically altered the temperature profile of cities. In fact, even within a city, different areas have different temperatures, depending on specific surroundings, type of exposed surface, and ground cover.

It is evident that urban heat islands have major effects on the surface energy balance, heating/cooling costs, and quality of urban life. While many of the factors which influence the formation of urban heat islands, including climate, topography, and weather patterns, can not be changed or altered, it is apparent that efficient and cost-effective ways of mitigating heat islands exist. There are two heat island factors, attributable to human activities, which can be readily controlled: the amount of vegetation and the color of surfaces.(3)   Increasing vegetative cover through strategic landscaping around buildings and throughout cities can absorb solar radiation, provide shade, and control wind flow benefits. Changing dark colored surfaces to light colored ones would more effectively reflect, rather than absorb, solar energy and emit stored heat energy at a higher rate, thus reducing the cooling energy loads and ground level air temperatures influenced by these surfaces.

In general, it is observed that parks and areas with significant amounts of vegetation are cooler than neighborhoods full of paved surfaces and buildings. These differences may seem obvious, but they illustrate the fact that the climate in cities is greatly affected by human activities and the creation of the urban landscape.