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A Global sensitivity analysis of photochemical models used for predicting tropospheric ozone

Daniel Wimer

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By

Daniel R. Wimer

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A Global Sensitivity Analysis of Photochemical Models Used for Predicting Tropospheric Ozone

Thesis submitted in partial fulfillment
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of

Master of Science

in

Environmental, Health & Safety Management

Approved by:

Maureen Valentine, P.E. , Department Chair,

Signature: ______________________ Date: 4/4/02

Dr. John Morelli, Thesis Advisor,

Signature: ______________________ Date: 4.4.02

Thesis Committee Members:

Dr. Joseph Norbeck, Director CE-CERT. University of California at Riverside.

Mr. Kenneth Osborn, Delphi Automotive Systems. Site Service Manager, Technical Center Rochester.

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Dedication

This study is dedicated to my wife Rene'

My Daughter Lindsay

And my son Geoff

For their continued support during my time of study.

Acknowledgements

This study was made possible through the direct interaction
and input from the University of California at Riverside
with direction from

Dr. Joseph Norbeck

And

Research Assistance from

Otto Mejia & Xiaona Zhu

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ABSTRACT

The Clean Air Act requires the use of complex photochemical models to predict future ozone concentrations and the impact of current and future regulations. In many instances uncertainty in the data input parameters used to operate these models results in uncertainty in the prediction of future air quality. The degree of this uncertainty is often greater than the degreee of air quality improvements proposed by regulations.

This study evaluates the sensitivity of a photochemical model to predict future ozone air quality with respect to the uncertainty of several critical input parameters. These parameters are: Transported ozone (ozone aloft) Biogenic emissions (naturally occurring in nature) and anthropogenic (man-made) emissions of oxides of nitrogen (NOx), volatile organic compounds (VOCs) and carbon monoxide (CO). Global sensitivity analyses were done using the United States Environmental Protection Agency (USEPA) Empirical Kinetic Modeling Approach (EKMA) photochemical model to assess the sensitivity in predictions of past (1990), present (1999), and future year (2010) air quality downwind of New York City.

Our results show that for present and future years, the uncertainty in the model's prediction of future air quality, (a consequence of the uncertainty in biogenic emissions and ozone aloft) is significantly greater than the difference in emissions as a result of different control strategies proposed by industry and the regulatory agencies for mobile source emissions. The model therefore is not accurate enough to be used to predict changes in air quality that are driven by the proposed more stringent regulations.

Chapter 1: Introduction

The one-hour National Ambient Air Quality Standard (NAAQS) for ozone of 0.12 ppm (120 parts per billion, ppb) has been the most difficult to achieve. One hundred (100) urban areas within the United States were classified to be in non-attainment for ozone when the initial Clean Air Act was promulgated in 1990. In 1998, 38 areas of the U.S. were still in non-attainment. These 38 areas are home to almost 100 million Americans. Reaching attainment for this standard requires continual reduction of precursor emissions (i.e., those emissions which are components of tropospheric ozone formation) into future years. Considerable debate exists between industry and the regulatory community on how to reach attainment for tropospheric ozone. (Office of Air Quality Planning and Standards. 67)

Ozone, the primary component of smog, is formed in the troposphere as a result of photochemical reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NOx) in the presence of sunlight. This process is non-linear and highly influenced by meteorological conditions, transport of ozone generated upwind (ozone aloft) and, at times, biogenic emissions.

Ozone concentrations are higher during summer months on warm summer days with abundant sunshine and under favorable meteorological conditions. A stagnant air mass over a metropolitan area in the summer will generally increase ozone levels from day to day as the air mass remains over the area and keeps the pollutants below the inversion level of the atmosphere.

Ozone aloft and biogenic emissions are beyond the reach of existing control strategies designed to reduce ozone. As ozone is transported by the wind, it reacts with biogenic emissions. These reactions vary depending on factors such as cloud cover, ambient temperatures, and the type of biogenic species present. Anthropogenic emissions are added to the overall chemical mixture. These factors combined compound the problem of reducing ozone to acceptable levels.

A continual debate exists between industry and the regulatory community concerning the steps to take to reduce ozone. Each area of the country has concerns on polices and methods to control ozone precursor emissions that are unique to its geographic location. For example, New York City lies in an area known as the Ozone Transport Region. This geographic area begins near Washington D.C. and extends along the Atlantic Coast to the lower portion of Maine. In the Ozone Transport Region (OTR), ozone is created daily from both anthropogenic and biogenic sources in each major metropolitan area. Meteorological factors transport ozone aloft and ozone precursors along this ridge from day to day. Precursor pollutants that are not consumed during the previous day react to form ozone in a geographic location downwind from where they are created.

Within the OTR, New York, Pennsylvania, New Jersey, Rhode Island, Connecticut and Massachusetts are besieged with requirements to develop State Implementation Plans (SIPs) to reduce the level of ozone to or below the one-hour standard. To accomplish this task therefore, these states must regulate local industry to reduce precursor emissions in order to offset chemical compounds being transported into the region. At the present time the New York State Department of Environmental Conservation (NYDEC) is considering adopting California's Low Emissions II (LEV II) motor vehicle emissions standards in an attempt to meet the ozone air quality standard.

Each state is required to demonstrate ozone attainment through the process of photochemical modeling. These models need to include emissions inventories for the state and then predict the maximum ozone concentrations into the future years. These models are data and labor intensive. In most instances, as a result of the complexity of the problem, uncertainties exist in the model. These uncertainties can be as large as 20% while control strategies designed by decision makers to reduce ozone attempt to reduce ozone precursor emissions by as little as 1%.

The objective of this study was to evaluate the sensitivity of a photochemical model to the uncertainty of the emission amounts used as input to the model. For the purposes of this study the 10 counties that make up the New York City Metropolitan Area (NYCMA) were chosen for on-road mobile source emissions inventories. The emissions of interest for a base, current and future year were biogenics (BIO), carbon monoxide (CO), volatile organic compounds (VOCs), oxides of nitrogen (NOx), and ozone aloft. VOC, NOx and CO are highly associated with mobile source emissions, while ozone aloft and biogenic emissions are large contributing factors to overall ozone quantities in the troposphere.

A major element of SIPs is a means to relate VOC and NOx emissions to ozone concentration. This relationship is elucidated through an air-quality model that is a mathematical simulation of atmospheric transport, mixing, chemical reactions, and removal processes. A one-dimensional photochemical box model, Empirical Kinetic Modeling Approach (EKMA) was used in this study. (Rethinking Ozone 84)

EKMA has been used in the past by the Environmental Protection Agency (EPA) and NYSDEC to predict future ozone air quality.

The method used to evaluate the model's sensitivity was the Fourier Amplitude Sensitivity Test. FAST provides the means to conduct a non-linear model global sensitivity analysis. FAST provides an estimate of the sensitivity of a model's output with respect to the uncertainty in the model's input parameters. Global sensitivity measures the sensitivity of the model's results to the uncertainty and considers the total range of uncertainty of the input parameters. (McRae 15)

FAST associates each uncertain parameter with a specific frequency in the Fourier transform space of the system. The sensitivity of each parameter (Ozone aloft, VOCs, NOx, Biogenics and CO) is determined by solving the system equations for discrete values of the Fourier transform variable and then computing the Fourier coefficients associated with each parameter frequency. This allows for the total variability of the model's output to be determined along with the percentage of the variability attributed to each of the input parameters.

This study evaluated the predictions of future maximum ozone concentrations downwind of New York City and the uncertainty of these predictions given the uncertainty in the emissions inventory.

Chapter Two: Literature Review

Criteria Pollutants

The EPA is required by the Clean Air Act to set air quality standards for pollutants considered harmful to public health and the environment. The Act established two types of national air quality standards, primary and secondary.

Primary standards set limits to protect public health, including the health of sensitive populations such as elderly, children and asthmatics. Secondary standards set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation and buildings. These standards are reviewed every five years. (NARSTO 2 – 6)

An air quality standard establishes an acceptable exposure time and a concentration level of exposure. The current standard for ozone is 1 hour of exposure to less than 0.12 ppm (120 ppb) daily maximum concentration. (USEPA 1– 5)

Humans exposed to levels of ozone above the health-based standard will experience chest pain, coughing, sneezing and pulmonary congestion. When ozone reacts with humans it destroys lung tissue, reduces lung function and causes the lungs to become sensitized to other irritants. (Air Quality Criteria for Ozone and Related Photochemical Oxidants. 1-18, 1-21)

Measurements are taken at geographic locations throughout the nation on a regular basis to determine the level of these pollutants. The measurements are then compared to the standard and the area is then categorized as an 'attainment' or 'non-attainment area' for each pollutant.

A 'non-attainment' area is defined as that geographical area that does not meet the health based standard for air quality of a given pollutant. When an area is determined to be out of attainment the state that governs that area is required to write and implement a 'State Implementation Plan', or SIP, for remediation. In order to develop a SIP, the state must propose and evaluate control strategies. Control strategies are evaluated using selected air-quality modeling systems.

The EPA is required to set NAAQS standards for a total of six 'Criteria Pollutants,' which are: ozone (O_3), carbon monoxide (CO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), particulate matter (PM), and lead (Pb). The pollutant that was focused on in this study is Ozone. Pollutant Standards for all six Criteria Pollutants can be found in the Appendix, Table 2.

Ozone is a secondary pollutant in that for the most part it is not emitted directly into the atmosphere. It is formed through complex series of photochemical reactions between precursor pollutants, volatile organic compounds (VOCs) and oxides of nitrogen (NOx) in the presence of sunlight.

VOCs and NOx are created by the burning of fossil fuels. VOCs can also be emitted from the transfer of fuels from one storage facility to another, from motor vehicle refueling, or from painting and solvent-use operations. NOx are created in internal combustion engines when chamber temperatures exceed 1371 C. (Knowles 221)

Biogenic precursor emissions occur naturally in the atmosphere. Isoprene is a VOC that is a by-product of photosynthesis. Lightning produced NO and biogenic emissions from unmanaged soils are sources of natural NOx. (NARSTO 3 – 33) These uncontrolled precursors and their distribution play an important role in the ozone forming process.

The levels of ozone-forming gases in the atmosphere can be estimated as a function of anthropogenic (human related) and biogenic (natural) activity. Specifically, biogenic NOx emissions are relatively small compared to anthropogenic NOx. However biogenic VOCs can make up the majority of statewide VOC emissions while anthropogenic VOC emissions represent the larger portion of urban area emissions. (NESCAUM 4)

Motor vehicle use is a large contributing factor to the creation of precursor pollutants because both VOC and NOx are emitted. The automobile industry has made significant progress in pollution control technology and reducing precursor emissions over the past two decades. However, other factors such as increased miles of travel and consumer vehicle purchasing trends toward less fuel-efficient Sport Utility Vehicles work against these efforts. These changing factors increase the difficulty involved with designing and implementing control strategies to reduce ozone.

Difficulties associated with meeting attainment for the 1 hour ozone standard

The current 1-hour standard for ozone exposure is 120 ppb measured as the 1-hour average concentration daily maximum concentration.

A geographic area meets the NAAQS standard for ozone if there is no more than one day per year when the highest hourly value exceeds the threshold. Additionally, the estimated total number of days above the threshold must be one or less. To be in attainment an area must meet the ozone NAAQS for three consecutive years.
The air quality ozone value is estimated using the EPA's guidance for calculating design values. This value is obtained from the fourth highest monitored value when three complete years of data are available. These three years are then selected as the updated air quality for the area. (USEPA Criteria Pollutants)

NAAQS standards are reviewed every five years in an attempt to determine if control strategies are being effective in keeping air quality at healthy levels. As the standards are reviewed, a geographic location is classified as 'attainment' or 'nonattainment.'

States are required to review and change control strategies for the sources of air pollutants that are the major contributing factors of the pollutants that cause air quality degradation. Control strategies need to be evaluated for effectiveness, which is done through varying air-quality modeling systems.

The ultimate goal of the SIP process is to lay out a plan that will achieve attainment to the NAAQS for a given year. SIPs must use air quality models to demonstrate that proposed emissions reductions will result in attainment.

Difficulties have existed in modeling air quality and applying it to a geographic area in an attempt to provide clean air since the Clean Air Act was written in 1970. Revisions were made to the Act in 1977 and 1990.

Congress set the first attainment deadline for 1975. When this deadline passed, and the standard was not met, Amendments were written again in 1977, which extended the deadline for attainment to 1982. Included in this Amendment were allowances to let certain areas that were not yet in attainment delay their deadline until 1987. (NARSTO 2-6)

Congress established new standards for ground level or tropospheric ozone that were to be adhered to beginning in 1990. In 1990 over 100 areas in the United States were in violation of the one-hour standard. Under this new regulation, state SIPs were to be submitted to the Environmental Protection Agency by 1994. Almost all areas were unable to submit an approvable SIP at that time. (NARSTO 2-6)

Following twenty years of attempts to formulate effective SIPs, it became apparent to government agencies and states that attainment of ozone standards was more complex than had been anticipated. The ozone problem was beginning to be recognized as one a of serious nature and one that was not clearly understood at that time.

In the 1960s and 1970s it was believed that ozone pollution could be mitigated most effectively through controls of VOC emissions. By the late 1980s, there was a growing appreciation for the potential efficacy of NOx controls in some areas. (NARSTO 3-11)

However, since the early 1990s an increasingly complex picture has emerged that supports the idea that there is no simple answer to whether a VOC or NOx based strategy should be adopted to reduce ozone in a given locale.

The chemical compounds that create ozone, VOCs, NOx and biogenic emissions were common knowledge to scientists when the Clean Air Act was implemented. They knew that the sources of these compounds were industrial processes including painting, use of solvents and burning of fossil fuels to produce electricity or power motorized vehicles. They did not know exactly how the chemical compounds reacted in the atmosphere to create ozone.

The elusive nature of ozone creation cannot be defined by the location of the sources or the emissions generated within a given geographic locale. The chemical make up of the ingredients that create ozone can depend on the characteristics of an air parcel. This air parcel can vary a great deal with the distance the air parcel is transported and the nature of how it disperses.

Scientific measurements must be taken within geographic locations to determine if the area is or is not within attainment guidelines. Most air quality monitoring sites are located in heavily populated areas and are designed simply to determine whether or not the area is in compliance with current air quality standards. (Global Air Quality 22). Measurements are taken during the ozone season for a certain locale. Ozone seasons vary in length from state to state. Most areas determine their ozone season depending on the amount of warm and sunny weather for the region.

Typically, a state will establish ground level stationary monitoring sites that are equipped with instruments to measure ozone levels on a daily basis during the ozone season. Ground level monitoring stations are cost effective and able to collect data on a daily basis. One disadvantage of ground level monitoring is that these sites measure only the air parcel directly surrounding the monitoring site within a few kilometers of the earth's surface known as the atmospheric boundary layer.

Another method of measuring ozone is by using balloons that are released into the atmosphere with scientific measuring equipment on board. Using balloons to measure ozone provides a method of vertical measurement that is above the earth's surface. This method is cost prohibitive in many locations and can prevent daily measurements.

Meteorological factors that contribute to the difficulty in meeting attainment for the 1 hour ozone standard.

Meteorological factors transport ozone and ozone precursor pollutants downwind from the source depending on the conditions during weather patterns. Studies have shown that the ozone problem in some areas of North America is complicated by interactions between meteorological processes on small to large scales that take place in the presence of precursor pollutants and their chemical behavior. These interactions create situations where ozone levels are the result of emissions that are created locally or ozone levels that are primarily the result of precursor pollutants that are transported into the region from upwind sources. Ozone that is transported into a region from upwind is more commonly referred to as Ozone Aloft.

Meteorological forces controlling atmospheric mixing, dilution, radiation, and heating can affect the local speed and intensity of this photochemistry as well as rates of biogenic and evaporative emissions. This phenomenon adds to the difficulty of assessing ozone quantities and making decisions to control precursor emissions.

Atmospheric stability and wind speed are two meteorological parameters that affect air pollution. A stable atmosphere with low windspeeds leads to the highest ground-level pollution concentrations. Conversely, unstable atmospheres and high wind speeds lead to the lowest ground-level pollutant concentrations. A relationship between temperature and elevation exists that determines the stability of the atmosphere. At night, when the sun is not heating the surface of the earth, the ground cools. As this occurs, the air layer directly above the earth also cools. This process continues and layer after layer of air is cooled. (De Nevers 83 - 96)

When the sun begins to warm the earth in the morning temperatures increase up to an elevation of 305 meters. At that point the cool air from the ground meets with the warm air remaining from the previous day. Below 305 meters temperature increases with height. By mid-afternoon the sun has changed the temperature of the air to an elevation of about 1830 meters. At this point the warmer air encounters the more stable air mass above. The altitude at 1830 meters is known as the mixing height. Mixing heights during summer are higher than they are in the winter. On a warm summer afternoon mixing heights range from 600 to 4000 meters. Vigorous vertical mixing occurs on summer days when temperatures approach 32 C, which induces large-scale turbulence in the atmosphere. Pollutants released at ground level will be mixed up to the mixing height but not above it. (De Nevers 97-100) The mixing height can be different from one season to the next, from one day to the next, and from morning to afternoon of the same day.

Wind speed affects air pollution by moving parcels of air from one geographic location to another. Wind velocity and direction contribute to the amount of air pollution in an area and wind speed increases as elevation increases. A certain amount of ground friction exists that slows wind closer to the surface of the earth and allows wind speeds to increase at higher elevations.

A layer of atmosphere approximately 1 to 2 meters from the surface of the earth known as the planetary boundary layer (PBL) is the region where surface friction plays an important role in understanding ozone movement. (NARSTO 3 – 33)

Immediately above the PBL layer up to 500 m is the area where wind does not meet with ground friction. This frictionless area is known as the geostrophic layer. Wind speed is largely determined by how well the planetary boundary layer and the geostrophic layer are coupled to each other. This coupling changes depending on the speed of the geostrophic layer. When the planetary boundary layer is stable there is little vertical movement or low wind, and the coupling between these two layers is weak. The opposite is obvious, when the planetary boundary layer is unstable a great deal of vertical movement or high wind exists and a large transfer takes place between the two layers. (De Nevers 106)

So it can be stated that unstable air and high wind velocities in the PBL allow mixing from lower altitudes to mix with higher velocity winds in the geostrophic layer and that the mixing of the PBL and geostrophic layers are affected by temperatures of the air mass that is closest to the surface of the earth.

Ozone aloft is ozone that remains above the inversion layer of the atmosphere. In the inversion layer the temperature inversion prevents the air below it from rising thus trapping any pollutants that are present. When the sun goes down, ozone in this layer does not react after ultra-violet light from the sun stops a process of photolysis of certain forms of nitrogen oxides. (Air Quality Criteria 1-3) Ozone aloft is then transported at night into another geographic region. As the sun rises the next day, the mixing layer forms downwind from the previous day and the photochemical process to create ozone begins again.

Stable atmospheres and low wind speeds lead to the highest ground-level pollution concentrations while unstable atmospheres and high wind speeds lead to the lowest ground-level pollution concentrations.

High-pressure systems in the atmosphere contribute to air stagnation conditions. High pressure systems are slow moving air masses that travel from west to east across the continent. They can settle into place during the summer months and heat the PBL. This high-pressure area is surrounded by weak winds that fail to move the air mass from the region. It is during long extended periods of high pressure that a major portion of ozone can remain in a given geographic location and continue to grow in magnitude. (NARSTO 3 – 34)

Chemical Makeup of Ozone

Ozone generation in the troposphere is nonlinear in nature. This stems from the complexities in the chemical system that creates ozone. A secondary pollutant that is nonlinear has a property where the output is not proportional to the input.

Many factors in the creation of ozone contribute to its nonlinear nature. Rate constants of compounds, dependant reactions that are necessary to start other reactions and reactions that scavenge molecules from other compounds contribute to the complexity of this nonlinear phenomenon.

The rate of ozone production is a nonlinear function of the mixture of hydrocarbons and nitrogen oxides in the atmosphere depending on the concentrations of these compounds in the atmosphere, ozone can be sensitive to hydrocarbon reduction or it can be sensitive to nitrogen oxide reduction. (The Atmospheric Sciences 121)

It is imperative to consider biogenic sources of hydrocarbon emissions and the difficulty they may add to reducing ozone. Controlling emissions from natural sources is a technology that does not currently exist. Considering this nonlinear nature, if control strategies were written to reduce ozone by reducing anthropogenic hydrocarbons and nitrogen oxides then biogenic sources of hydrocarbons could make the control strategies ineffective.

The chemical constituents of the atmosphere are not processed independently of each other. They are linked through a complex array of both chemical and physical processes. As a result of these linkages, a perturbation of one component of the atmospheric chemical system can lead to significant, nonlinear effects that ripple through the other components of the system and, in some cases, to feedbacks that can either amplify or damp the original perturbation. (The Atmospheric Sciences 121)

The chemical nature of ozone and the reactions that create it in the troposphere is a major component that impacts control strategies designed to reduce it. Ozone chemistry is a very complex science. It is beyond the scope of this study to examine and explain all of the reactions that take place to create ozone. A general explanation of ozone chemistry will be discussed to emphasize the difficulties associated with measuring ozone quantities and designing control strategies to obtain NAAQS. The chemical reactions that create ozone can be found in the Appendix in Table 1.

Anthropogenic and biogenic activities are responsible for depositing large quantities of chemical compounds into the atmosphere every day. VOCs and NOx in the presence of sunlight combine to form ozone. However, the reaction of these compounds is a very complex array of chemical and physical processes that lead to photochemical air pollution.

VOCs are complex in themselves. There are numerous classes of VOCs such as alkanes, alkenes and aromatic hydrocarbons. Each of these classes has their own unique chemical makeup that adds to the complexity of the problem. The speed at which the different species react in the atmosphere is also a contributing factor in how they create or inhibit the production of ozone.

Very important compounds that contribute to the creation of ozone in the troposphere are OH radicals. OH radicals can be considered the atmosphere's primary oxidizing agent. (Global Air Quality 12) As OH radicals form they lead to cycles of reactions that degrade organic compounds from anthropogenic and biogenic origin and enhance the formation of ozone. The OH radical has a certain lifetime in the troposphere and reacts differently with VOCs than it does with NOx. The OH radical is both spatially and temporally dependent. (National Research Council, Rethinking the Ozone Problem. 110) Certain species of NOx, VOCs and ozone are short-lived and more reactive in the atmosphere due to their large spatial and temporal variations. (Global Air Quality 21) The kinetics of these species determine their atmospheric lifetimes in a column of air that exists for a time period time in a geographic area.

When the use of automobiles and the internal combustion engine are added into the mix of atmospheric pollutants, a higher degree of difficulty is added to the existing problem of designing control strategies that will effectively reduce air pollution.

The automobile emits a wide spectrum of inorganic and organic chemical compounds into the atmosphere. The source of these emissions is from combustion and evaporative processes. These compounds transform into other compounds as some gain and others lose compounds through chemical reactions. These compounds are composed of different chemical structures with different rate constants. This introduces a time factor related to how these compounds react in the atmosphere.

Automotive emissions include water, carbon dioxide, carbon monoxide, oxides of nitrogen, oxides and oxyacids of sulfur, reduced sulfur compounds, and a wide variety of volatile organic compounds comprising fuel components and partially oxidized products of combustion, and particulate matter. (Health Effects Institute 100)

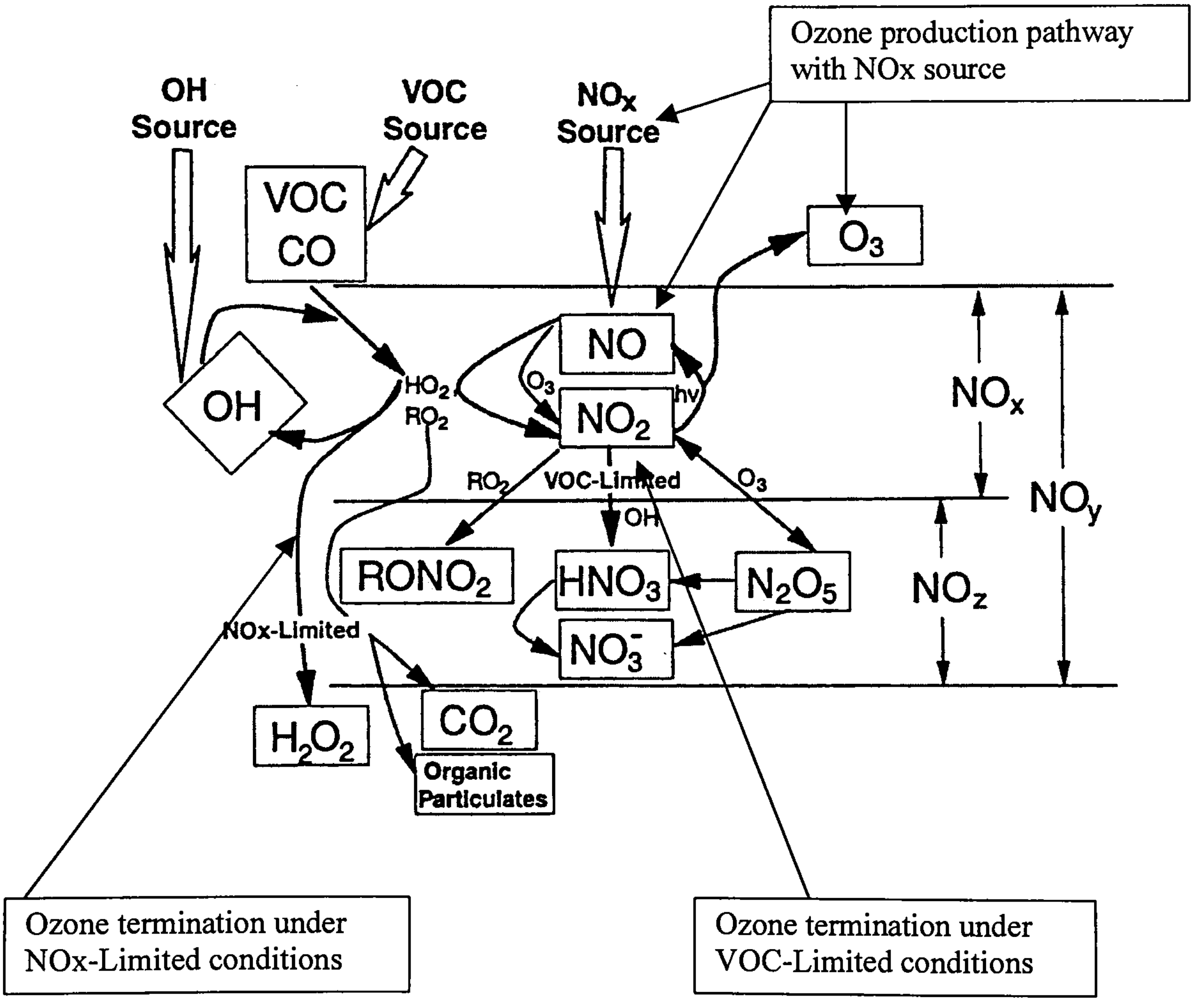
Stationary sources such as power plants and industrial complexes, and natural sources such as forests also contribute to the overall chemical composition of reactive pollutants in the atmosphere. A few of these pollutants are hydrocarbons, nitrogen oxides, sulfur oxides, particulate matter, ammonia and carbon monoxide.

Automobile use in large metropolitan areas contributes to a higher concentration of air emissions in these areas. Also apparent from heavier automobile use in these areas is the possibility that downwind from metropolitan areas the potential exists for ozone to be present in quantities that exceed NAAQS.

Automotive emissions mix in the atmosphere with emissions from stationary sources. It is very difficult to isolate automotive emissions inventories from the entire mix of atmospheric pollutants. Changes in emissions rates from all sources combined with meteorological factors, the spatial and temporal factors of air pollutants and photochemical reactions created by solar radiation are only a few of the problems decision makers face when choosing control strategies.

Photolysis requires that a chemical compound absorb light. This process explains why ozone is created mostly in the summer months on days with a great deal of sunlight. The wavelength for this to happen falls between ~ 290 – 1,000 nm, and the energy content must be a minimum of ~ 40 kcal/mole. Therefore, photolytic wavelengths of ≤ 700 nm are necessary. (Health Effects Institute 102)

Figure 1
Ozone Photochemical Schematic
(NARSTO 3 – 15)



Ozone production pathway with NOx source

Ozone termination under NOx-Limited conditions

Ozone termination under VOC-Limited conditions

The schematic in Figure 1 shows the photochemical reactions that take place to form ozone in a polluted environment. Ozone production occurs via the free-radical-initiated oxidation of, VOC or CO in the presence of NOx and sunlight. In general, ozone production can be limited by either VOC or NOx. The existence of these two opposing regimes, often schematically represented in an EKMA ozone isopleth diagram (shown in figure 2 on page 18), can be mechanistically understood in terms of the relative sources of OH and NOx. When the OH source is greater than the NOx source, termination is dominated as shown in the NOx-Limited region. (Lower left text-box) This means that ozone concentrations are most effectively reduced by lowering the emission concentrations of NOx instead of VOC. When the OH source is less than the NOx source, termination proceeds as shown in the VOC-Limited region. (Lower right text-box) In this region, ozone is most effectively reduced by lowering VOC. Between these two extremes lies the transitional region, sometimes referred to as the 'ridge-line' in an EKMA isopleth diagram. (NARSTO 3 – 14)

Considering the wide array of automotive exhaust compounds, the atmospheric lifetimes of these compounds from automotive sources vary a great deal. Each compound has a different rate constant based on its chemical nature. As we have seen from the reactions in Figure 1, these compounds react in the atmosphere where they are consumed. The presence of one compound and its reaction in the presence of sunlight can change the rate at which other compounds react to form ozone.

Control Strategies

Control strategies for mobile source emissions have been in effect for the past three decades. (Air Pollution the Automobile and Public Health 3) These control strategies have historically been aimed at the automobile industry due to the fact that on-road mobile sources are the largest contributing factor to the mobile source emissions category. Non-road mobile source emissions have recently become an additional area of concern and control strategies are taking shape to reduce emissions from these sources in the near future. (DeNevers 472)

The on-road mobile source emissions category is complex in nature and needs to be considered. Automobiles are classified in fleets depending on vehicle age, weight, type of fuel used and mechanical emissions control devices inherent to the vehicle. It is also necessary to identify the types of pollutants emitted from each vehicle category.

The broad classification of on-road vehicle categories is divided into Light-duty Vehicles (LDV) and Heavy-duty Vehicles (HDV). The classification is separated by vehicle weight typically at 8,500 pounds. Vehicles above 8,500 pounds gross vehicle weight (GVW) are HDV.

HDVs are sub-divided into those fueled by gasoline and those fueled by diesel fuel. Typically HDVs above 26,000 (Heavy HDVs) pounds are fueled with diesel fuel. This classification of vehicle is a rather small population numerically when compared to other classes but it is a significant number of total vehicle miles traveled, fuel consumption and emissions.

LDVs are also sub-divided into two main categories: passenger cars and Light-duty Trucks (LDTs). Until the recent upward trend in Sport Utility Vehicle (SUV) usage, LDTs were primarily used for commercial purposes and the LDV category was divided into two different exhaust emissions standards. This difference in the LDV category will diminish with new regulations designed to more closely control emissions from a larger population of SUVs. For the first time in mobile source emissions control strategy regulations, SUVs and certain LDTs are combined into the passenger car emissions category under Low Emissions Vehicle II (LEV II) regulations. (The California Low-Emissions Vehicle Regulations)

Two mobile source emissions control strategies that automobile manufacturers must design vehicles to comply with today are Tier 2 and LEV II. Both strategies direct emissions reductions through vehicle classifications. Tier 2 is the Federal program supported by the United States Environmental Protection Agency. LEV II is the control strategy used in California that was written initially to reduce mobile source emissions in heavily populated and polluted areas in California. LEV II is hailed as the more stringent control strategy.

Efforts to evaluate mobile source emissions are interdisciplinary and require interaction of different areas of expertise. Travel demand models, emissions models, and air-quality models all need to be evaluated when designing emissions control strategies.

Travel demand consists of determining the amount of transportation activity that takes place in a region based on daily travel routines of the area residents. This includes measuring the number of trips, time of day, length of trip, mode of transportation, route or location of trips, average speed of travel, and age of the vehicle. The number of transit trips, automobile occupancy, and vehicle miles of travel (VMT) are common performance measures used to measure transportation activity.

Emissions models are based on emission rates. These data are based on vehicle type, (Passenger car, Light Duty Vehicle, Heavy Duty Vehicle, etc.) average speed, ambient temperature and other factors. Emissions estimates are collected for each pollutant emitted from on-road mobile sources in each category.

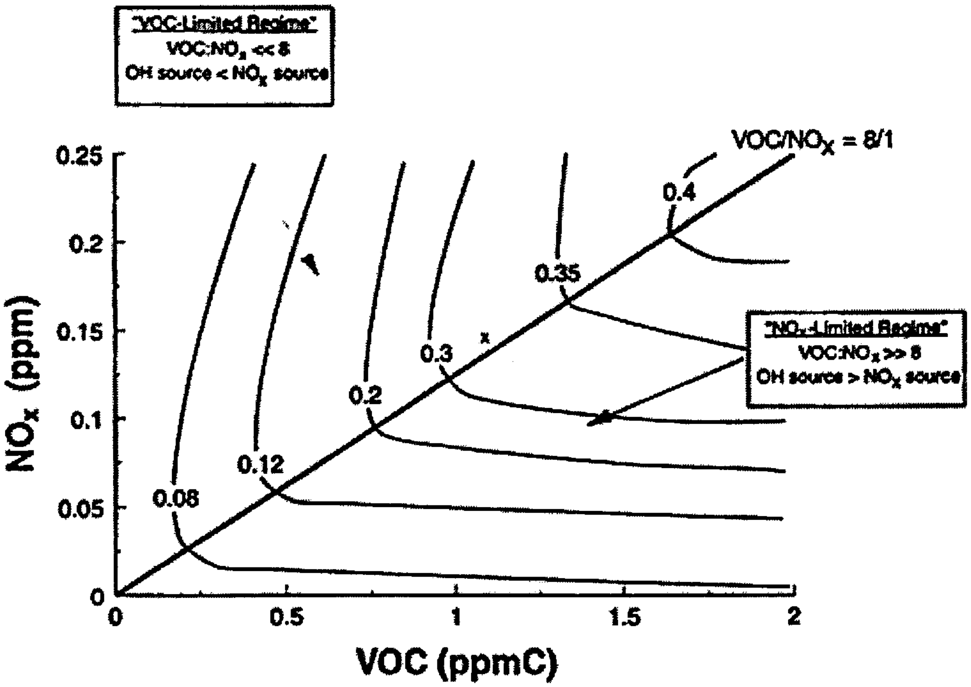
The effectiveness of control strategies to reduce ozone is directed at reducing VOCs or NOx in a given location. Limiting VOCs or NOx is not defined by location or emissions, it is, rather, a chemical characteristic of an air parcel that varies dynamically with transport, dispersion, and photochemical aging.

When designing control strategies for ozone it is necessary to determine if reducing VOCs or NOx will provide the most benefit. This is due primarily to the sensitivity of ozone to the species and combination of species for VOCs and NOx. Therefore, considerable uncertainty exists when determining whether ozone is primarily VOC-sensitive or NOx-sensitive. (Photochemical Indicators 1)

Figure 2 below shows an ozone isopleth diagram of the 1 – hour maximum ozone concentrations (in ppm) calculated as a function of initial VOC and NOx concentrations and the regions of the diagram that are characterized by VOC or NOx limitation.

Figure 2

Ozone Isopleth Diagram (NARSTO 3 – 15)



The ozone isopleth diagram is commonly used with the EKMA model in ozone NAAQS demonstrations. The model simulates ozone formation in a hypothetical box of air that is transported from the region of the most intense ozone source emissions to a downwind point of maximum ozone accumulation. Emissions of VOCs and NOx are assumed to be well mixed in the box, which varies in height to account for dilution caused by changes in height of the mixed layer of air, ozone formation is simulated using a photochemical mechanism. By simulating an air mass as a box of air over its trajectory for a large number of predetermined combinations of initial VOC and NOx concentrations, EKMA generates ozone isopleths that are, to a varying degrees, specific to particular cities. Once the maximum ozone concentrations in a city has been identified, the VOC and NOx reductions needed to achieve NAAQS are determined in EKMA from the distances along the VOC and NOx axes to the isopleth that represents the 120 parts per billion (ppb) peak ozone concentration mandated by the NAAQS. (Rethinking Ozone 164)

A few characteristics of the ozone isopleth diagram are worthy of explanation. A ridgeline runs diagonally from the lower left corner to the upper right corner of the graph. Generally speaking, the VOC/NOx ratio along the ridgeline is 8:1.

The ridgeline divides the graph into two areas. Areas to the right of the ridgeline are referred to as NOx-limited. In this area VOC/NOx ratios are above 8:1 which is typical of rural areas and suburbs that are downwind of large metropolitan areas. In the NOx-limited region, lowering NOx concentrations at a constant VOC concentration, or in conjunction with lowering VOCs, results in lower peak concentrations of ozone.

Areas to the left of the ridgeline are VOC-limited. In this area, VOC/NOx ratios are less than 8:1. This region is typical of highly polluted metropolitan areas. In this region lowering VOC at constant NOx results in lower peak ozone concentrations. This is also true if VOC and NOx are decreased proportionally at the same time. However, lowering NOx at constant VOC will result in increased peak ozone concentrations until the ridgeline is reached, at which point ozone begins to decrease. (Rethinking Ozone 167)

This prediction that lowering NOx can, under some conditions, lead to increased ozone seems to be counter intuitive. However, this is possible if consideration is given to the nonlinear nature of ozone formation and its chemistry. It has been mentioned earlier that certain molecules are scavenged during ozone formation, which makes predicting ozone levels difficult. In the region of ozone formation, the radicals that propagate VOC oxidation and NO-to-NO_2 conversion are scavenged by high concentrations of NOx. The NO2 competes with the VOCs for the OH radical, which slows down production of RO_2 and HO_2 when compared to the same situation with lower NOx concentrations. As a result, as NOx is decreased, more of the OH radical pool is available to react with the VOCs leading to greater formation of ozone. (Rethinking Ozone 168)

Decision makers responsible for designing SIPs to reduce ozone are faced with this situation as they compare existing ozone values and attempt to predict future ozone values.

Sensitivity-Uncertainty Analysis

One of the greatest uncertainties in photochemical modeling of ozone is the estimation of emissions. This is due in part to the kinetics of the different species of compounds that exist in the atmosphere. Recent studies on the uncertainties in absolute ozone are on the order of 25%. (Markar et al 6) VOC and NOx emissions also contribute to the overall uncertainty. Studies in the Los Angeles area have found uncertainties in VOC emissions inventory at 8% of total uncertainty. Global uncertainties of both anthropogenic and natural NOx emissions have been found to range from 22 – 81%. (J.G.J Oliver et al 138)

Sensitivity analysis incorporates the systematic study of the behavior of a model over ranges in variation of inputs and parameters. It can be used to determine whether the predictive behavior of a model is consistent with what is expected on the basis of the underlying chemistry and physics of the individual species and if they respond properly when varied. The analysis determines how an environmental system will respond to both inputs and system parameters.

Sensitivity-uncertainty analysis can be described as a sensitivity analysis in which the variations in inputs and parameters correspond to their estimated uncertainties. It is used to determine the uncertainty in a model prediction. First, it should determine qualitatively whether a model responds to changes in a manner consistent with what is understood in the basic chemistry and physics of the system, and secondly it should estimate quantitatively the uncertainty in model predictions that arise from uncertainties in the inputs and parameters. (Rethinking Ozone 345)

Decision makers of control systems to improve air quality often depend on air quality models to make final conclusions as to the programs they will implement in a region to reduce pollutants from point and non-point sources.

These models are complex mathematical summations of air samples taken in the region over select periods of time. The mathematical model examines the presence of air pollutants, many parameters of atmospheric transport, and chemical and physical processes that predict the impact of emissions on human health and other end receivers of air pollution. Ozone falls into the category of these models as a secondary pollutant. In order to reduce ozone, projections must be made as to the reactions between several factors and how these reactions will affect ozone formation in the troposphere.

Air quality models, also referred to as photochemical models, calculate input data from various factors that create air pollutants in a region. Included in the calculations are the rate constant parameters of air molecules at given temperatures and altitudes, dry or wet deposition factors, precursor pollutants, atmospheric conditions, and meteorological factors.

Considering the non-linear nature of ozone formation and the variables associated with the other input data, uncertainties can exist that will heavily impact the outcome of the model and subsequently the control mechanism chosen by decision makers to improve air quality from the data generated by the model.

Therefore, ozone formation is heavily dependent on the reactions of several factors. Determining mechanisms to reduce ozone are then also dependent on the accuracy of the data that predicts ozone levels for future years.

Related Work

Studies by Dr. G.S. Tonnesen

A study was done by Dr. Gail S. Tonnesen on the effects of uncertainty of the hydroxyl radical (OH) with nitrogen dioxide (NO_2) on model-simulated ozone control strategies. Her purpose was to evaluate the effect of a 20% reduction in the rate constant of the reaction of the hydroxyl radical with nitrogen dioxide to produce nitric acid (HNO_3) on model predictions of ozone mixing ratios and the effectiveness of reductions in emissions of volatile organic compounds (VOC) and nitrogen oxides (NOx) for reducing ozone.

The study emphasizes that the reaction of the hydroxyl radical with nitrogen dioxide to produce nitric acid plays a significant role in the photochemistry of ozone. A model simulation compared a new rate constant to a base case scenario. The study found that ozone increased between 2 and 6% for typical rural conditions and between 6 and 16% for typical urban conditions. Conclusions of the study found that the increases in ozone were less that proportional to the reduction in the $OH + NO_2$ rate constant which can be attributed to negative feedbacks in the photochemical mechanism.

The study used two different approaches to evaluate how the new $OH + NO_2$ rate constant changed the effectiveness of reductions in emissions of VOC and NOx. In the first step Tonnesen evaluated the effect on ozone sensitivity to small changes in emissions of VOC and NOx. In the second step Tonnesen used the Empirical Kinetic Modeling Approach, EKMA to evaluate the effect on the level of emissions reduction necessary to reduce ozone to a specified level.

Both methods showed that reducing the $OH + NO_2$ rate constant caused control strategies for VOC to become less effective relative to NOx control strategies.

Studies by Gao et al.

Research performed by Gao, Stockwell, and Milford evaluated local sensitivity of O_3, HCHO, H_2O_2, PAN and HNO_3 to various rate constants and stoichiometric coefficients. The research examined first-order sensitivity and uncertainties in the second-generation Regional Acid Deposition Model (RADM2) gas phase chemical mechanism, which comprises 157 reactions involving 63 chemical species. Simulation conditions for the study were for a typical summer day at ground level. Temperature was 298K (76.7° F) with an atmospheric pressure of 1.0 ATM, and relative humidity of 50%. Photolysis rates were calculated at a zenith angle of 60° (which is approximately the 12-hour daytime average for surface conditions on June 21, at a latitude of 40°N).

In the study, ranges of ambient conditions are examined for both urban and rural conditions. Reactive organic gases (ROG) and oxides if nitrogen (NOx) were input as initial conditions, with no emissions added during the simulations. An initial O_3

concentration of 30 ppb was used for all simulations that have the effect of providing an initial source of radicals. Initial conditions for both urban and rural conditions were also used as data input for the study.

Uncertainty estimates were complied for the kinetic and stoichiometric parameters of RADM2 along with photolysis rates, thermal reaction rates, nonstandard reaction rates, and stoichiometric coefficients.

Six simulated cases were studied using different ratios of ROG: NOx at surface conditions. The initial conditions chosen were:

Urban: ROG = 1000ppbC	ROG:NOx = 12:1, 6:1, 24:1
Rural: ROG = 160ppbC	ROG:NOx = 24:1, 12:1, 100:1

The initial concentrations were set high in the simulations compared to observed concentrations because the initial concentrations were used to constitute the total input with no subsequent emissions.

Results of the study found that the O_3 concentrations are highly sensitive to the rate parameters for the reactions:

$$HO + NO_2 \longrightarrow HNO_3,$$
$$NO_2 + h\nu \longrightarrow O(^3P) + NO,$$
$$O_3 + NO \longrightarrow NO_2 + O_2 \text{ and,}$$
$$HCHO + h\nu \longrightarrow 2HO_2 + CO$$

The highest uncertainty contribution is about 37% from the rate constant for the reaction $HO + NO_2 \longrightarrow HNO_3$ in the urban 6:1 case. Other uncertainty contributions were in the urban 12:1 and 24:1 cases that were about 18% and 15% respectively. The highest uncertainty contributions in the rural 12:1, 24:1, and 100:1 cases were about 14%, 9%, and 7%, respectively.

The data finds that uncertainty contributions are primarily determined by sensitivity coefficients rather than by rate parameter uncertainty estimates. For example, ozone sensitivity coefficients with respect to different parameters range over 12 orders of magnitude, whereas uncertainty estimates range over a factor of 30.

A follow-up study was performed by Gao et al. in 1996 that examined a regional-scale gas-phase chemical mechanism. The study extends first-order research by Gao et al. mentioned previously.

In the study uncertainties are estimated for predicted concentrations of O_3, HCHO, H_2O_2, HNO_3 and peroxyacetyl nitrate (PAN). Also, in three urban cases, uncertainties are estimated for reductions in ozone associated with reducing ROG or NOx emissions, or both.

Three different control cases were considered in the study. A 25% reduction in emissions and initial concentrations of ROG, a 25% reduction in emissions and initial concentrations of NOx, and a 25% reduction in both ROG and NOx.

The results of the research found that uncertainties in absolute ozone concentrations range from 23% at the ROG: NOx ratio of 24:1 to 55% at the ROG : NOx ratio of 6:1. Also, relative uncertainties in O_3 are highest for simulations with low input ROG:NOx ratios.

It is important to notice that other species had similar uncertainties in the study. For example, HNO_3 uncertainties ranged from 15 to 30 %, HCHO ranged from 20 to 30%, and PAN uncertainties ranged from 40 to 70%.

Considering the range of uncertainties studied by Gao et. al., control mechanisms for reducing ozone that rely on estimates of input parameters of different species and their reactions in the atmosphere may prove to be ineffective.

Research has been done on different control mechanisms to reduce air pollution and concentrations of ozone in the atmosphere adopted by federal and state governments.

The effective control parameter of these mechanisms is very small when compared to the uncertainties associated with chemical and physical behaviors of precursor pollutants in the atmosphere.

Studies by AIR Incorporated

Air Improvement Resources (AIR), conducted a study in New York State analyzing New York States Department of Environmental Conservation recent adoption of the California LEV II standards over the Federal EPA's Tier 2 emissions control strategies for mobile source emissions.

The analysis found very small benefits to the LEV II program over Tier 2. Data for the report were taken directly from the NYDEC Regulatory Impact Statement (RIS). Emissions were projected through the year 2020. The data are shown in Table 1 below.

Table 1

Statewide HC and NOx Inventories in tons per day (TPD)

Year	LEV II	Tier 2	Difference	% Difference
2007	938.8	985.0	1.2	0.1%
2010	690.9	692.6	1.7	0.2%
2015	425.7	428.3	2.6	0.6%
2020	308.5	311.7	3.2	1.0%
			Total	1.9%

Given the information and projections of emissions changes with either the LEV II or Tier 2 the total emissions reduction through the year 2020 is only 1.9% difference in LEV II or Tier 2 methods of control.

Studies by ENVIRON International Corp. Inc.

ENVIRON International Corporation Inc. performed a study for General Motors Corporation (GMC) due to a concern that GM had about Environmental Protection Agency (EPA) Tier 2 modeling analysis for future years. Their concerns focus around the issue of the EPA incorrectly stating future ozone non-attainments that calls for the proposed Tier 2 fuel sulfur regulations. Also, GMC is concerned that coarse OTAG databases used by EPA in the Tier 2 sulfur regulations do not adequately represent urban scale ozone formation. GMC retained Air Improvement Resources, Inc. (AIR), Alpine Geophysics LLC (AG), and ENVIRON International Corporation to:

- Estimate the emissions benefits of different tailpipe emission standards and gasoline fuel sulfur content using the AIR MOBILE model,
- Using the new emissions estimates and the OTAG episodes (91-93-95) estimate the future-year residual nonattainment counties using AIR mobile source emissions and EPA's Rollback Method,
- Analyze EPA's Rollback Method and develop alternative methods as appropriate, and
- Perform high resolution fine-grid modeling to estimate future year nonattainment and the benefits of different tailpipe standards and gasoline fuel sulfur content.

The study performed fine-grid photochemical modeling for three scenarios surrounding the Northeast Corridor, Lake Michigan, and Houston, TX. Three different vehicle technology control scenarios were analyzed: the National Low Emissions Vehicle (NLEV) program; the EPA proposed Tier 2 vehicle standards (Tier 2); and the Alliance of Automobile Manufacturers (AAM) proposed alternative vehicle standards. Three different gasoline sulfur content levels were also analyzed. For the 2007 NLEV scenario, a 150 ppm sulfur gasoline fuel was assumed in the Federal Reformulated Gasoline (FRG) areas and a 339 ppm sulfur fuel was assumed elsewhere.

For each of the three fine-grid modeling databases, a 1995 Base Case scenario was prepared to estimate current ozone air quality. For the Northeast Corridor and Lake Michigan July 1995 episodes, the current 1995 baseline emissions inventory was updated from MOBILE 5 to the AIR Tier 2 MOBILE model (T2MM) to account for the missing mobile source emissions. It was necessary to update the data due to the fact that the MOBILE 5a source emissions model used to develop Tier 2 /sulfur modeling inventories fails to account for numerous unknown mobile source emissions sources such as off-cycle emissions.

The ENVIRON report will be used in this study to compare effectiveness of control strategies with reference to chemical and physical uncertainties of input parameters. The data for the Northeast Corridor will be referenced primarily.

For the Northeast Corridor, the emissions reductions predicted by control mechanisms are shown in Table 2 below.

Table 2

Predicted Emissions Reductions by Control Strategies

Control Mechanism	**VOC Emissions**		**NOx Emissions**	
	Tons per day	**% reduction** [1]	**Tons per day**	**% reduction**[1]
Base Case	1408	--	2896	--
2007 ROTR/NLEV	472	0	1204	0
2007 AAM/30	462	2	1070	11
2007 T2/30	462	2	1054	12
2007 AAM/5	448	5	1013	16
2007 T2/5	448	5	1003	17

The control mechanisms mentioned in the table 2 are defined as follows.

- ROTR: Regional Ozone Transport Rule. This control strategy is aimed particularly at point source emissions of NOx.
- T2: Federal EPA Tier 2 emissions control strategy.
- AAM: Alliance of Automobile Manufacturers control strategy.
- T2/5; T2/30: Federal Tier 2 emissions control strategy with a fuel sulfur content of 5 and 30 ppm respectively.

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[1] Percent reduction from 2007 ROTR/NLEV base case.

- AAM5; AAM/30: Alliance of Automobile manufacturers control strategy with a fuel sulfur content of 5 and 30 ppm respectively.

(T2 and AAM are automotive tailpipe control strategies)

The peak ozone benefits from the control strategies are shown in Table 3 below.

Table 3

Ozone Benefits From Control Strategies

Control Strategy	Ozone Benefit
1995 base case	99.9%
2007 base	88.4%
2007 AAM/30	88.2%
2007 T2/30	88.3%
2007 AAM/5	88.2%
2007 T2/5	88.3%

The ozone benefits in 2007 of the Tier 2 mobile source control strategy over the AAM alternative method are minimal, ranging from 0.1 to 0.3 ppb reductions in the peak ozone concentrations downwind of New York City. These results demonstrate that the AAM alternative and the Tier 2 tailpipe control strategies have essentially identical ozone air quality benefits.

Chapter Three: Methodology

In this study six different model scenarios were performed for 10 of the counties that comprise the New York City Metropolitan Area (NYMA). These model simulations were run to see if uncertainties in the input parameters of a simple model would have an impact on the output parameter, in this case, ozone. Uncertainties were randomly chosen for all of the precursor pollutants.

The base year chosen was 1990 mobile source emissions inventory. Simulations were run which span two decades for the years 1990 base case, 1999 current year, and 2010 future year. Emissions inventory data was obtained from the New York State Department of Environmental Conservation's Environmental Specialist Kevin Watz.

The inventories are for a typical ozone season day. The data is reported each hour of the day beginning at 8:00 A.M. and commencing at 7:00 P.M. The data for the report was converted from kg/hr to tons per day (tpd).

The 10 counties used in this report are: Bronx, Kings, Nassau, New York, Putnam, Queens, Richmond, Rockland, Suffolk and Westchester.

Emissions inventory summaries for the 10 counties are shown in table 4 below. Ozone design values shown are for the Tri-State region of New York, New Jersey and Connecticut. (Ozone Attainment Demonstration 7)

Table 4

Emissions Inventory Summary and Ozone Design Values

Year	Ozone Design Value (ppb)	Emission Inventories in Tons per Day (tpd)		
		VOC	CO	NOx
1990	201	402	3245	295
1999	147	343	2538	358
2010	Estimated	116	1175	255

Emissions inventory data was used to run a simple EKMA model. This was done to predict the changes in ozone if uncertainties in emissions were programmed into the input data. These calculations were performed at The University of California at Riverside under the direction of Dr. Joseph Norbeck.

The model results will be compared with the base year inventory. The model shows that ozone emissions have improved in the 10 county NYMA area over the time period chosen.

There were two major programs used to calculate the data, Fourier Amplitude Sensitivity Test (FAST), and Ozone Isopleth Plotting Program Research (OZIPR). The calculation method of OZIPR named CALC was chosen to perform the calculations.

FAST technology provides global sensitivity analysis instead of local sensitivity analysis. Sensitivity analysis provides a measure of the change of the output variables with respect to changes in the model's input parameters. Global sensitivity measures the sensitivity of the model's results and considers the total range of uncertainty of the input parameters. This technique is more useful in assessing the overall uncertainty of the model. (McRae 15)

FAST associates each uncertain parameter with a specific frequency in the Fourier transform space of the system. The sensitivity of each parameter chosen, Ozone aloft, VOCs, NOx, Biogenics and CO is determined by solving the system equations for discrete values of the Fourier transform variable and then computing the Fourier coefficients associated with each parameter frequency. This allows for the total variability of the model's results to be determined along with the percentage that is attributed to each input parameter.

The calculations performed by EKMA for this study are considered 'global sensitivity analysis.' Global sensitivity encompasses a measure of sensitivity of the solution to variations of a parameter's value combined in an appropriate manner with a measure of the actual degree of uncertainty of the parameter's value. It may then be determined through the parameter's sensitivity and uncertainty which parameters have the most influence on the solution. Another analysis technique used in sensitivity analysis of a model is 'local sensitivity analysis.' This technique is only capable of measuring small perturbations in parameters. (McRae 15).

FAST can be thought of as two programs. The first program generates points in Fourier space if given the uncertainty of a parameter like ozone. FAST generated 5 Fourier frequencies for the parameters chosen.

For this study the five critical parameters chosen were: Ozone aloft, VOC, NOx, CO and biogenic emissions. Uncertainties in these parameters were assumed in the six different model simulations. These parameters were selected due to their significance to mobile source emissions control strategies. Ozone aloft and Biogenic emissions are beyond any control strategies. VOCs, NOx and CO are emitted from mobile source categories and the primary targets of control strategies.

Two OZIPR models were used in the study, EKMA and CALC. OZIPR is based on EPA's Ozone Isopleth Plotting Program (OZIP), but it contains improved and expanded capabilities that make the model useful for research purposes. OZIPR serves the dual purpose of providing: (1) a simple trajectory model capable of utilizing complex chemical mechanisms, emissions, and various meteorological parameters of the lower atmosphere, and (2) procedures through which the Empirical Kinetics Modeling Approach (EKMA) can be implemented for calculations of emissions reductions needed to achieve compliance with NAAQS. (Users Guide iii)

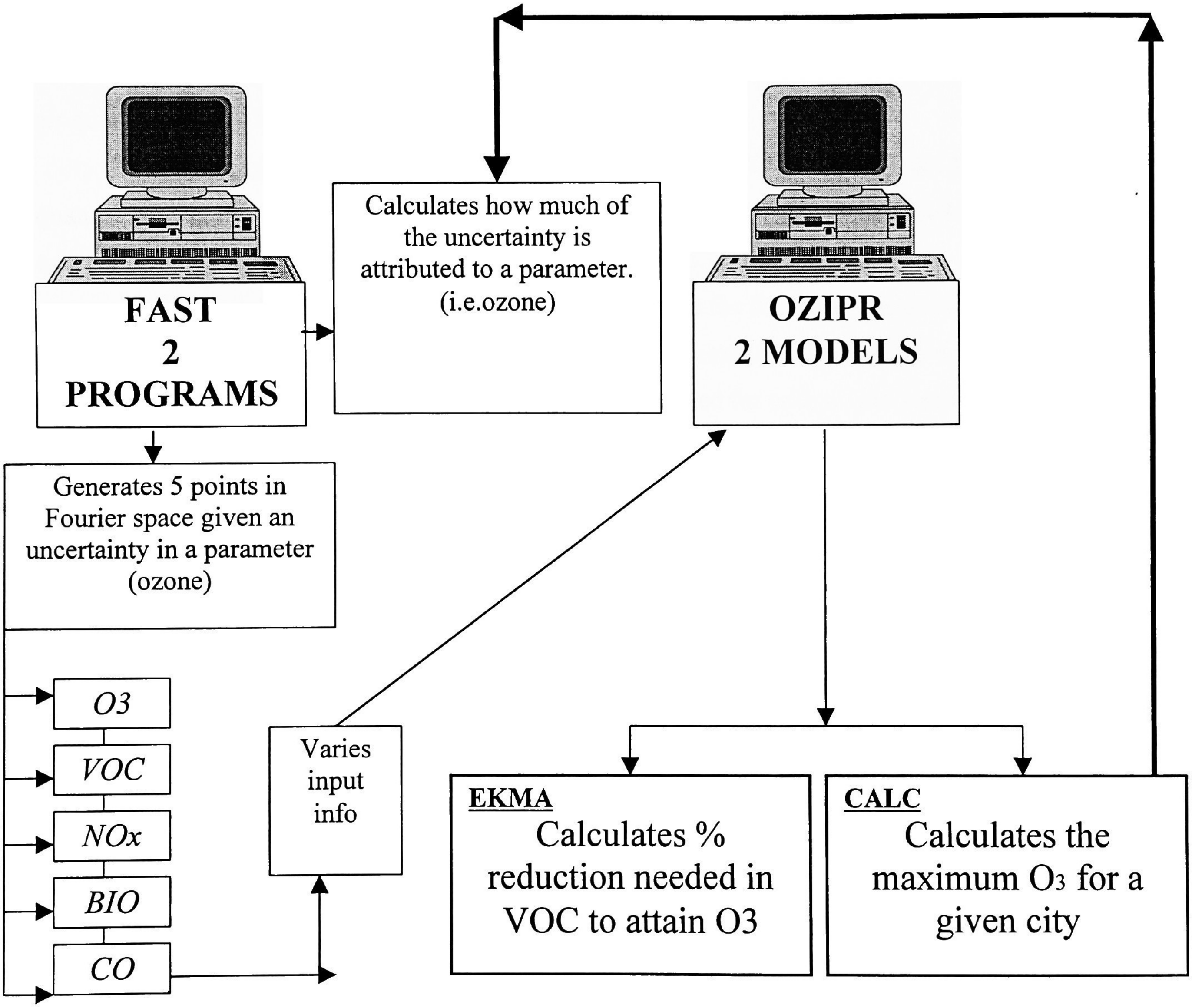
EKMA calculates the percent reduction in VOC needed to reach attainment of the 1 – hour ozone standard of 120 ppb. It is a program that is largely used in ozone NAAQS attainment demonstration which simulates urban ozone formation in a hypothetical box of air that is transported from the region of the most intense source emissions, the center of a city for example, to the downwind point of maximum ozone accumulation. (Rethinking Ozone 164)

Calculations performed for this study used the EKMA procedure along with OZIPR to perform multiple simulations with different levels of VOC and NOx precursor emissions to estimate the effect of reduced emissions on maximum ozone concentration.

A map that shows how the data is calculated is shown in figure 3 below.

Figure 3

Data Calculations Map



Chapter Four: Results

EKMA model results are shown in the following five model simulation tables. Each data set is described below.

Ozone Design Value is the pollutant concentration used by air quality managers as the basis for determining attainment of an air quality standard, generally by using an air quality model. This data was provided by the NYDEC.

The Emissions Inventories in tons per day for the year of the simulation are the quantities of mobile source emissions received from the NYDEC. Future year 2010 is the estimated mobile source emissions provided by the NYDEC.

The Uncertainty in Emissions Inventory table shows the five input parameters that can be attributed to mobile source emissions and the uncertainty attributed to each parameter. (i.e ± 20%, 50% etc.) Uncertainty values are varied for each model simulation. This is done to determine how the model will respond to these changes.

The Statistics for the Output Parameter table shows the average in ozone (O_3) predicted by EKMA for the time period in each table. The variance in this section of the table represents how far from predicted ozone the model actually varied. The variance is the plus or minus value that is applied to average O_3 aloft.

The Partial Sensitivity of the Input Parameter table shows the percentage of uncertainty each variable contributed to the variance. For example in the base year 1990 data NOx contributed to 75% of the variance of 60 ppb (59.7 rounded).

The Percentage of the variance explained is the sum of five parameters in the Partial Sensitivity of the Input Parameters.

All figures are normalized to 1 from the raw data. For purposes of discussion, some figures are rounded to the nearest whole number and indicated by the symbol ~.

Table 5

Model Simulation #1 NYMA Base Year 1990

Data Summary:

Data in this model simulation show uncertainties of ± 20% in Ozone aloft, VOC, NOx and CO from actual values for the base year 1990. Biogenic emissions uncertainties are ± 50%.

Ozone Design Value for 1990: 201 parts per billion (ppb)

Emissions Inventories in tons per day for 1990.

VOC	CO	NOx
402	3245	295

Uncertainty in Emissions Inventory

VARIABLE	LOWER	UPPER
Ozone Aloft	80 %	120 %
VOC	80 %	120 %
NOx	80 %	120 %
Biogenics	50 %	150 %
CO	80 %	120 %

Statistics for Output Parameter

Average O_3	Variance	Std. Dev.
201 ppb	~ 60 ppb	7.73

Partial Sensitivity of the Input Parameters

VARIABLE	VARIANCE
NOx	75 %
VOC	15 %
Ozone Aloft	8 %
Biogenics	2 %
CO	0 %

Percentage of the Variance explained 99.4%

Table 6

Model Simulation #2

NYMA with 1% variation in NOx Year 1990

Data Summary:

Data in this model simulation show uncertainties of ± 20% in Ozone aloft, VOC and CO from actual values for the base year 1990. Biogenic emissions uncertainty was set at ± 50%. Uncertainty in NOx was set at ± 1% , which essentially eliminated NOx.

Ozone Design Value for 1990: 201 parts per billion (ppb)

Emissions Inventories in tons per day for 1990

VOC	CO	NOx
402	3245	295

Uncertainty in Emissions Inventory

VARIABLE	LOWER	UPPER
Ozone Aloft	80 %	120 %
VOC	80 %	120 %
NOx	99 %	101 %
Biogenics	50 %	150 %
CO	80 %	120 %

Statistics for Output Parameter

Average O_3	Variance	Std. Dev.
201 ppb	~ 19 ppb	4.32

Partial Sensitivity of the Input Parameters

VARIABLE	VARIANCE
VOC	42 %
Ozone Aloft	25 %
NOx	7 %
Biogenics	6 %
CO	0 %

Percentage of the Variance explained 79.1%

Table 7

Model Simulation # 3

NYMA Current Year 1999

Data Summary:

Data in this model simulation show uncertainties of ± 20 % in Ozone aloft, VOC, NOx and CO. Biogenic emissions uncertainty was set at ± 50 %.

Ozone Design Value for 1999: 147 parts per billion (ppb)

Emissions Inventories in tons per day for 1999

VOC	CO	NOx
343	2538	358

Uncertainty in Emissions Inventory

VARIABLE	LOWER	UPPER
Ozone Aloft	80 %	120 %
VOC	80 %	120 %
NOx	80 %	120 %
Biogenics	50 %	150 %
CO	80 %	120 %

Statistics for Output Parameter

Average O3	Variance	Std. Dev.
194 ppb	~ 53 ppb	7.25

Partial Sensitivity of the Input Parameters

VARIABLE	VARIANCE
NOx	50 %
VOC	33 %
Ozone Aloft	11 %
Biogenics	5 %
CO	0 %

Percentage of the Variance explained 98.9%

Table 8

Model Simulation #4

NYMA Future Year 2010

Data Summary:

Data in this model also show uncertainties of ± 20 % in Ozone aloft, VOC, NOx and CO with Biogenic emissions uncertainty at ± 50 %.

Ozone Design Value for 2010: Estimated

Emissions Inventory (estimate) in tons per day for 2010

VOC	CO	NOx
116	1175	255

Uncertainty in Emissions Inventory

VARIABLE	LOWER	UPPER
Ozone Aloft	80 %	120 %
VOC	80 %	120 %
NOx	80 %	120 %
Biogenics	50 %	150 %
CO	80 %	120 %

Statistics for Output Parameter

Average O3	Variance	Std. Dev.
118 ppb	~ 26 ppb	5.12

Partial Sensitivity of the Input Parameters

VARIABLE	VARIANCE
Ozone Aloft	40 %
BIO	32 %
VOC	14 %
NOx	12 %
CO	0 %

Percentage of the Variance explained 98.8%

Table 9

Model Simulation #5

NYMA Future Year 2010

Data Summary:

Data in this model show uncertainties of ± 20 % in Ozone aloft, and CO. Uncertainties in VOC and NOx were changed to ± 1% and biogenic emissions uncertainty remained at ± 50 %.

Ozone Design Value for 2010: Estimated

Emissions Inventory (estimated) in tons per day for 2010

VOC	CO	NOx
116	1175	255

Uncertainty in Emissions Inventory

VARIABLE	LOWER	UPPER
Ozone Aloft	80 %	120 %
VOC	99 %	101 %
NOx	99 %	101 %
Biogenics	50 %	150 %
CO	80 %	120 %

Statistics for Output Parameter

Average O3	Variance	Std. Dev.
118 ppb	~ 19 ppb	4.3

Partial Sensitivity of the Input Parameters

VARIABLE	VARIANCE
Ozone Aloft	55 %
BIO	44 %
VOC	0.0 %
NOx	0.0 %
CO	0.0 %

Percentage of the Variance explained 99.8%

Chapter Five: Analysis and Discussion

The five EKMA model simulations performed for this study clearly show that average ozone levels are sensitive to uncertainties in estimates of the precursor pollutants of volatile organic compounds (VOCs), and oxides of nitrogen (NOx). Carbon monoxide (CO) did not play an important role in estimating ozone. Ozone aloft and Biogenic emissions are also large contributing factors to the formation of ozone when NOx and VOCs are better understood over a period of time.

Models simulations 1 and 2 in tables 5 and 6 are base year simulations from actual emissions numbers obtained from the NYDEC for 1990. Simulation 1 sets the basis for uncertainties in all five of the input parameters. As EKMA calculated the data, the average ozone value was 201 ppb with a large variance of 60 ppb. In this simulation the NYMA could not have reached the 1 – hour ozone attainment regulation for 1990. NOx contributed the most uncertainty to the variance with a value of 75%. Reviewing this information and comparing it to the ozone isopleth diagram, it could be assumed that the area fell into the NOx-Limited range.

Model simulation 2 in table 6 is similar to simulation 1 with the exception of the NOx value. In this simulation the assumption was made that New York had a better understanding of NOx with an uncertainty of only ± 1%. Average ozone remains at 201 ppb but the variance is smaller at 19 ppb and the variable that contributes the most uncertainty has changed from NOx to VOCs. It should also be noted that Ozone aloft has increased 17% from Simulation 1. Overall the area remains a considerable distance from reaching the 1 – hour attainment regulation.

Model simulation 3 in table 7 emissions inventories are almost one decade later than simulations 1 and 2. During that time period control strategies have been effective in lowering pollutants with the exception of NOx, which has seen a slight increase (See table 4). The uncertainties in the emissions inventory input parameters are unchanged from the base year. In this simulation, average ozone has fallen slightly to 194 ppb with a variance of 53 ppb. The variable that contributes the most uncertainty is again NOx with a value of 50%. It should be noted that VOCs are a significant factor also. The area is still out of attainment for ozone.

Another decade of control strategies has elapsed in model simulation 4 table 9. Emissions inventories are lower than 1990 and 1999. Uncertainties remain unchanged from the base year. Average ozone has fallen considerably to 118 ppb, which is below the 1 – hour NAAQS standard of 120 ppb. Total success cannot be claimed however due to the variance of 26 ppb, which could raise the ozone value to 144 ppb. It is important to notice that NOX and VOCs are no longer the largest contributing factors to the uncertainty of the variance. Instead, Ozone aloft and Biogenic emissions contribute a combined total uncertainty of 72%. Individually, Ozone aloft contributes the larger portion at 40% with Biogenic emissions at 32%.

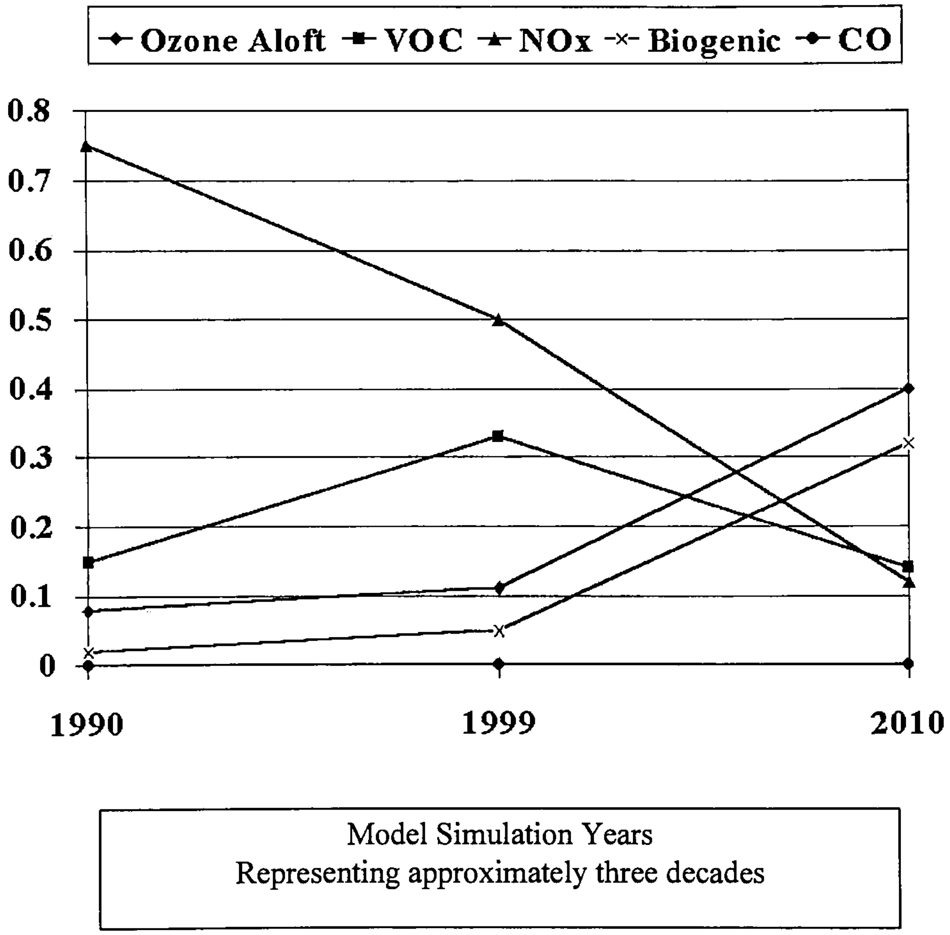
As NOx and VOC control strategies have obviously had an impact on emissions inventories by 2010, and uncertainties for NOx and VOCs are better understood, the data in Model simulation 5 was changed for these two variables to ± 1%. With this change, average Ozone is within the 1 – hour attainment regulation of 120 ppb with a value of 118 ppb. As in Simulation 4 total success cannot be claimed with a variance of 19 ppb.

The most contributing variable to the uncertainty is Ozone aloft with a value of 55%. Biogenic emissions are equally as important to consider with a value of 44%.

Figure 4 below summarizes the changes in the five input parameters used in the model simulations for this study. Beginning in 1990 NOx emissions were the most contributing factor to the uncertainty. VOCs contributed a portion of the uncertainty while Ozone aloft, Boigenic emissions and CO were significantly less contributing factors. Approximately one decade later in 1999, NOx has reduced considerably while VOCs, Ozone aloft and Biogenic emissions show an increase in contributing to the uncertainty. In future year 2010, after almost two decades of control strategies when NOx and VOC emissions are better understood, Ozone aloft and Biogenic emissions are the largest contributing factors to the uncertainty of the model and therefore the area that should receive the most consideration to improve ozone air quality.

Figure 4

Model Simulation Summary



Chapter Six: Conclusions

Overall air quality in New York State has improved over the last three decades. Mobile source emissions are less in 1999 than they were in 1990 and the Department of Environmental Conservation has predicted that mobile source emissions will be considerably lower in the year 2010. The adoption of California's Low Emissions II motor vehicle tail pipe emissions control strategy is going to provide some quantifiable improvements to air quality in the entire state.

However, according to a recent report by the American Lung Association, Upstate New York along with the New York Metropolitan Area (NYMA) still suffers from high levels of ozone pollution. In the report, Monroe and Wayne counties in the Rochester area received a grade of "F" for ozone air quality in 2001. Monroe and Wayne counties registered 11 and 15 high-ozone days for the time period between 1997 and 1999. Downstate, the counties of Chautauqua, New York, Putnam, Richmond and Suffolk, which are part of the NYMA, were the five worst areas for ozone pollution. New York County had the highest number of ozone pollution days at 37 for the time period. This level is the worst on record in the entire state. (American Lung Assoc. Appendix B) The data is summarized in tables 10 and 11 below.

Table 10

Ozone Health Classification Levels

Unhealty for Sensitive Groups	0.085 – 0.104 ppm ozone
Unhealthy	0.105 – 0.124 ppm ozone
Very unhealthy	0.125 – 0.374 ppm ozone

Table 11

Unhealthy Ozone Days in New York State

County	Number of unhealthy days between 1997 and 1999
New York	37
Richmond	36
Suffolk	31
Putnam	29
Chataqua	26
Queens	25
Dutchess/Westchester	23
Orange	19
Erie/Jefferson	18
Wayne	15
Niagara	14
Bronx/Monroe/Saratoga	11

The counties in New York State that showed more than 10 unhealthy days for ozone received a grade of "F" in the report. (American Lung Association)

We have seen in this study that ozone is a tough pollutant to quantify due to its non-linearity, behavior in the atmosphere and transport over land masses by meteorological forces. Tonnesen and Gao et al emphasized that ozone cannot always be reduced in equal amounts to the same size reduction as its precursor pollutants.

Darlington and ENVIRON established that control strategies designed to reduce mobile source emissions are within 1 or 2 percent of each other therefore the overall tonnage of pollution reduction between strategies is minimal.

The pollutants that were used in the EKMA model simulations were assigned random uncertainties that range in the area of ± 20%. This random number is a modest representation of the actual conditions that can exist in the atmosphere. These uncertainties are a major contributing factor to the output data of any model used to predict ozone levels. The modeling simulations responded to changes in the uncertainties of the variables. VOCs and NOx, the two ozone precursor pollutants that contribute heavily to ozone, have been under regulation for two decades.

Considering the large uncertainties of ± 20% for NOx and VOCs in modeling simulations, and the effectiveness between more stringent control strategies of only 1 to 2 %, the tonnage reduction changes through control strategies is considerably less than the amount of the uncertainties of the input parameters. Therefore the impact in the tonnage reduction of emissions from more stringent control strategies will be much less than the uncertainties that are inherent in the precursor pollutants that are major contributors to the formation of ozone.

If the debate continues to reduce motor vehicle emissions of VOCs and NOx to lower levels through tighter emissions control strategies when only a very small benefit will be recognized, it becomes imperative to examine the concept of tighter controls that will be very costly, against a better understandings of modeling emissions and the uncertainties of the pollutants that create ozone.

The EKMA model used in this study is a simple model that provided the concept of how models respond to input parameters. More sophisticated models are currently used by decision makers at the regulatory level today. MOBILE 5B is a model that is used frequently but problems still exist for this model.

The biggest problems New York currently faces when modeling emissions from mobile sources is having a model that can do an acceptable job. MOBILE 5B, the current model used by New York, is based on data collected in the 1970's and 1980's. Motor vehicles on the highways today are more technologically advanced to reduce emissions than the vehicles of two decades ago. Another model, MOBILE 6 will be a succession to MOBILE 5B, but problems exist with the new model and it may not be available until 2002. A more serious problem exists in not being able to get the required input data for the newer models. The data needed for these models are simply not collected so assumptions need to be made that can seriously affect the amount of emissions predicted. (Watz)

The expense to consumers for stricter emissions control strategies range from the increase in the price of automobiles, to the cost of increased regulation enforcement by government bodies. It will be more prudent to focus efforts on reducing emissions by securing a better understanding of modeling air quality and the impact of precursor pollutants that cannot be controlled.

Chapter Seven: Opportunities for Improvements

New York State should focus on ozone aloft and biogenic emissions in future years for modeling based on the findings in Model simulations 4 and 5. As biogenic emissions cannot be controlled, the most obvious path for New York to take would be to try and reduce ozone aloft that is carried into the state by meteorological factors from areas upwind.

The conclusion can be made that in order to attain National Ambient Air Quality Standards for the current one-hour ozone standard, it will be necessary to develop control programs that reduce ozone-forming precursor pollutants emitted many miles upwind of the area of violation. Consideration also needs to be given to the possibility that the proposed eight-hour ozone standard may become reality in the future.

With current regulations for air quality being the responsibility of the states, no individual state or jurisdiction can be expected to fully address or resolve all of the issues that are relevant to ozone transport. The current regulations require states to develop State Implementation Plans to maintain air quality, however, as ozone transport is beyond control of state boundaries, reducing ozone transport is a federal issue. Therefore, the federal government needs to develop Federal Implementation Plans to reduce ozone transport.

This study demonstrated that current modeling techniques do not fully address all of the parameters and their uncertainties when measuring air quality. An opportunity exists to develop the technology that will provide better results from air quality models.

Industry, states and environmental groups that are effective in implementing programs to improve air quality need to recognize that consumer behavior plays an important role in the total equation that makes up the air pollution formula. Consumer awareness concerning tropospheric ozone is often confused with stratospheric ozone. Consumers hear a news report that the ozone hole is getting smaller and they feel comfortable knowing that ozone issues are improving. The consumer needs to be educated about the two levels of ozone in the atmosphere and the fact that their actions contribute to the ozone problem in the air space they occupy. A public awareness program needs to be implemented nationwide that will warn consumers on high ozone days and advise them how they can take steps to minimize the impact of ground level ozone on that particular day and the days that follow an ozone episode.

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Appendix

Table 1

Ozone Chemical Reactions

Reaction Number	Reaction
1	$RH + OH \rightarrow R + H_20$
2	$R + O_2 + M \rightarrow RO_2 + M$
3	$RO_2 + NO \rightarrow RO + NO_2$
4	$RO + O_2 \rightarrow HO_2 +$ CARBONYL
5	$HO_2 + NO \rightarrow OH + NO_2$
6	$2x(NO_2 + hv \rightarrow NO + O)$
7	$2x(O + O_2 + M \rightarrow O_3 + M)$
NET of #1 - 7	$RH + 4O_2 + 2\ hv \rightarrow$ carbonyl $+ H_2O + 2O_3$
8	$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$
9	$OH + NO_2 + M \rightarrow HNO_3 + M$

Key to chemical reactions:

Hv = Sunlight energy
HNO_3 = Gaseous nitric acid
HO_2 = Hydroperoxyl radical
M = Another particle that can absorb energy released from the previous step
OH = Hydroxyl free radical
R = Hydrocarbon chain
RH = Generic Hydrocarbon

Table 2

National Ambient Air Quality Standards (NAAQS)

The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards for pollutants considered harmful to public health and the environment. The Clean Air Act established two types of national air quality standards. ***Primary standards*** set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. ***Secondary standards*** set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings.

The EPA Office of Air Quality Planning and Standards (OAPQS) has set National Ambient Air Quality Standards for six principle pollutants, which are called "criteria" pollutants. Table 1 below lists these six pollutants. Units of measure for the standards are parts per million (ppm), milligrams per cubic meter (mg/m3), and micrograms per cubic meter of air (mg/m3).

National Ambient Air Quality Standards (www.epa.gov/air/criteria.html)

Pollutant	Standard Value		Standard Type
Carbon Monoxide (CO)			
8-hour Average	9ppm	(10 mg/m3)	Primary
1-hour Average	35ppm	(40 mg/m3)	Primary
Nitrogen Dioxide (NO2)			
Annual Arithmetic mean	0.053 ppm	(100µg/m3)	Primary & Secondary
Ozone (O3)			
1-hour Average	0.12 ppm	(235 µg/m3)	Primary & Secondary
8-hour Average	0.08 ppm	(157 µg/m3)	Primary & Secondary
Lead (Pb)			
Quarterly Average		(1.5 µg/m3)	Primary & Secondary
Particulate < 10 micrometers (PM-10)			
Annual Arithmetic mean		50 µg/m3	Primary & Secondary
24-hour average		150 µg/m3	Primary & Secondary
Particulate < 2.5 micrometers (PM-2.5)			
Annual Arithmetic mean		15 µg/m3	Primary & Secondary
24-hour Average		65 µg/m3	Primary & Secondary
Sulfur Dioxide (SO2)			
Annual Arithmetic mean	0.03 ppm	(80 µg/m3)	Primary
24-hour Average	0.14 ppm	(365 µg/m3)	Primary