Observational and Mechanistic Studies of Tropospheric
Studies of Tropospheric Ozone/Precursor Relationships:
Comparisons of UAM and AIRTRAK Analyses of Ozone
Control Strategies

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by

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Summary

A major issue associated with the study of tropospheric photochemical air pollution is the relationship between ozone and its precursor species, i.e. nitrogen oxides (NOx) and volatile organic compounds (VOC). This report aims at cross-evaluating the ozone/precursors relationship through the complementary application of mechanistic photochemical modeling and of the “semi-empirical” approaches. The semi-empirical approach of the AIRTRAK model, developed by Johnson and coworkers [Johnson and Quigley, 1989], is implemented in this report to infer the sensitivity of ambient ozone to the reductions of precursor (NOx and VOC) emissions based on observational data. The mechanistic model analyses of the effectiveness of VOC and NOx emission controls in reducing ozone are then compared using the results from the AIRTRAK approach. It is shown that the assessment from the AIRTRAK model corroborates the predictions of ozone-NOx-VOC sensitivity obtained by a 3-d mechanistic Urban Airshed Model (UAM-IV).

Keywords

Semi-Empirical Approach, mechanistic models, Photochemical Models
1 INTRODUCTION

Tropospheric ozone and related photochemical oxidants are the most prevalent harmful air pollutants in many industrialized and developing countries [Georgopoulos, 1995; Lippmann, 1989]. High ozone levels not only play a role in damage to plant species, materials and manufactured goods, but also lead to the damage of lung tissues in humans. The earlier ozone National Ambient Air Quality Standard (NAAQS) was set at 120 ppbv, a level which was compared to the second daily one-hour maximum concentration to determine compliance with the standard. The current ozone standard (NAAQS), announced in 1997, is set at eight hour averaged concentration of 80 ppbv. An exceedance in the present standard is said to have occurred if the fourth highest eight hour averaged ozone concentration over a three-year period, is above 80 ppbv [Walia, 1998]. The Clean Air Act of 1990 requires that for the non-attainment areas, where ozone levels do not comply with the NAAQS, the responsible state agencies must prepare and implement ozone attainment State Implementation Plans (SIPs). These plans should document ways and means to meet and maintain ozone NAAQS in non-attainment areas. To assess if a region will be in compliance with the ozone air quality standard at some future date, it is necessary to be able to predict how the peak ozone concentration for the region will change in response to prescribed changes in source emissions. To predict how the peak ozone concentration will change requires an air quality model.

Air quality models are the means of relating changes in contaminant emissions to the resulting air quality. Typically, there are two basic types of models. Those which are based on a fundamental description of the physics and chemistry occurring in the atmosphere are classified as “mechanistic” (deterministic) approaches. Mechanistic models normally incorporate a mathematical treatment of the chemical and meteorological processes, and utilize information about emission distributions. Another class of methods involves the use of “phenomenological”, i.e. “observation-based” approaches in which empirical relationships are deduced from smog chamber or atmospheric measurements. These models are usually very simple and typically reflect the patterns in the actual data upon which they are based. This report examines the relationship between tropospheric ozone and precursor species (NOx and VOC) through both mechanistic and observational approaches.

A key question which is addressed here is whether mechanistic and observational approaches can achieve the same understanding of the relationship between tropospheric ozone and precursor species (NOx and VOC). Although mechanistic approaches incorporated in grid-based photochemical air-quality simulation models (PAQSMs) are recognized as the best available tools for analyzing tropospheric ozone problems, reliable applications of PAQSMs in some areas may not be feasible due to limitations in data or modeling resources. The semi-empirical AIRTRAK model, developed by Johnson and his coworkers, has been proposed as a means of qualitatively assessing the sensitivity of ambient ozone to reduction of precursor emissions (NOx and VOC) based on observed data of O₃, NO, and NOₓ (NOx + gas-phase oxidation products of NOx) concentrations. Therefore, the AIRTRAK model is used in this report as a complementary tool for PAQSMs to assess ozone/precursors relationships.
1.1 The Semi-Empirical Observation-Based Approaches

Although PAQSMs must play a role in the regulatory implementation of ozone abatement efforts, there remain very significant scientific uncertainties in their use. These uncertainties include the emission inventories and meteorological wind fields used to drive the models and derive concentration fields for ozone and its precursors. Because ozone precursor relationships are critically sensitive to the ratio of atmospheric concentrations of VOC and NOx, errors in calculating precursor concentration can cause PAQSMs to grossly misrepresent the sensitivity of ozone to changes in precursors emissions. Thus, it is desirable to have alternative methods for diagnosing ozone precursor relationships that do not depend upon emission inventories or meteorological parameterizations.

One of the alternatives is provided by semi-empirical (diagnostic) approaches, which are based on the analyses of ambient data to infer the sensitivity of ambient ozone to changes in precursors emissions. Semi-empirical (diagnostic) approaches are built by establishing empirical relationships between ozone and precursor species (NOx and VOC) with the incorporation of the “smog-forming” concept as illustrated below. The photochemical processes responsible for ozone formation are the oxidation of VOC in presence of the nitrogen oxides. The “smog-forming” process starts from the conversion of nitric oxide (NO) by the reaction with peroxo species to produce nitrogen dioxide (NO\(_2\)). Then nitrogen dioxide is photolysed resulting in the production of ozone and the regeneration of an equal amount of nitric oxide. Finally, ozone reacts with nitric oxide to regenerate nitrogen dioxide.

Johnson and his coworkers have developed the smog production (SP) algorithm to infer the sensitivity of ambient ozone to reduction of precursor emissions (NOx and VOC) based on the measure of photochemical process extent comprised of observed O\(_3\), NO, and NO\(_y\) (NOx + gas-phase oxidation products of NOx) concentrations [Johnson and Quigley, 1989; Johnson and Azzi, 1991; Johnson and Azzi, 1992]. This semi-empirical AIRTRAK model, based on the SP algorithm, is used in this report to examine the ozone sensitivity to changes of precursor emissions.
2 COMPARISON OF UAM AND AIRTRAK ANALYSES OF OZONE CONTROL STRATEGIES

2.1 Background

Grid-based photochemical air quality simulation models (PAQSMs) have been recognized as the best available tools for development of ozone control strategies. However, the effort needed to obtain suitable data and properly apply PAQSMs can be substantial, and the costs of applying these models can be high. Furthermore, the accuracy of the application of PAQSMs may be significantly limited due to limitation of input data. It is therefore necessary to supplement PAQSMs using approaches that are independent of PAQSMs in analyzing air quality problems and in developing control strategies.

It is generally known that for certain conditions the rate of ozone formation will increase with increasing NOx and will be insensitive to VOC, while for other conditions the rate of ozone formation will increase with increasing VOC and will be unchanged (or perhaps even decrease) with increasing NOx. Analysis of the relative effectiveness of VOC versus NOx reductions has relied primarily on the predictions of PAQSMs.

A common criticism of this approach is that model predictions are often not linked sufficiently to observations. Although the models are usually evaluated for their ability to match observed O3 concentrations, there has been no direct way to evaluate model responses to reductions in VOC or NOx emissions. This problem has been especially critical when different models have given contradictory results on the effectiveness of VOC versus NOx control, for reasons that have not been clear [Sillman et al., 1993; Scheffe, 1990; Rao and Sistla, 1993].

To help address this shortcoming, considerable interest exists in finding observable “indicators” of how real air masses are likely to respond to emission controls. If these types of “indicators” can be identified, then ozone-NOx-VOC sensitivity could be determined directly from measurements rather than from models. Comparisons between model predictions and measured values for the indicators would also provide a test of the accuracy of model sensitivity predictions.

Recent studies suggest that analyses of ambient data on the extent of atmospheric chemical reactions may offer a means of qualitatively assessing the sensitivity of ambient ozone to reductions in emissions of volatile organic compounds (VOC) and nitrogen oxides (NOx) [Hess et al., 1992; Blanchard et al., 1993; Chang and Rudy, 1993; Chang and Suzio, 1995]. In particular, a semi-empirical model developed by Johnson and his coworkers, which is called the AIRTRAK model, relates NOx emissions to smog formation using observed O3, NO, and NOy (NOx + gas-phase oxidation products of NOx) concentrations [Johnson and Quigley, 1989; Johnson and Azzi, 1991; Johnson and Azzi, 1992]. Therefore, the effectiveness of VOC and NOx emission controls in reducing ozone can be evaluated approximately by applying the AIRTRAK model.
2.1.1 Overview of Relevant Chemistry

The origin of ozone in the clean, unpolluted troposphere is due to the downward transport from stratospheric ozone. The chemistry of stratospheric ozone is briefly illustrated by the Chapman reactions as follows.

\[ \text{O}_2 + \text{hv} \rightarrow 2\text{O}^{(3\text{P})} \] (1)
\[ \text{O}^{(3\text{P})} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} (\text{M = air}) \] (2)
\[ \text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O} \] (3)

In the troposphere, ozone reacts with NO from biogenic emission to form NO\(_2\), which would undergo rapid photolysis to regenerate NO radical and O\(^{(3\text{P})}\) atom. Then, the O\(^{(3\text{P})}\) atom reacts with molecular oxygen to regenerate ozone. This process is illustrated as following reactions:

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \] (4)
\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}^{(3\text{P})} (\text{phot}) \] (5)
\[ \text{O}^{(3\text{P})} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} (\text{fast}) \] (6)

At photo-equilibrium, the ozone concentration in the clean, unpolluted troposphere can be calculated by,

\[ [\text{O}_3] = \frac{k_{\text{phot}} [\text{NO}_2]}{k_1 [\text{NO}]} \] (7)

where \(k_{\text{phot}}\) and \(k_1\) are the photolysis rate of NO\(_2\) and the rate constant for the reaction of NO with O\(_3\), respectively. Therefore, any processes converting NO to NO\(_2\) would result in enhancing ozone levels in the troposphere. Indeed, there are such processes present in the troposphere, which are the VOC oxidation reactions mostly initiated by OH radical.

The OH radical initiation is almost always a photolysis process. A significant fraction of radical initiation to generate the fresh OH radical comes from the photolysis of ozone.

\[ \text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O}^{(1\text{D})} \] (8)
\[ \text{O}^{(1\text{D})} + \text{H}_2\text{O} \rightarrow 2\text{OH} \] (9)

The VOC oxidation reactions initiated by OH radical can be treated as the propagation steps for OH radical.

\[ \text{OH} + \text{VOC} \rightarrow \text{RO}_2 \cdot + \text{H}_2\text{O} \] (10)
\[ \text{RO}_2 \cdot + \text{NO} \rightarrow \text{NO}_2 + \text{RO} \cdot \] (11)
\[ \text{RO} \cdot + \text{O}_2 \rightarrow \text{carbonyls} + \text{HO}_2 \cdot \] (12)
\[ \text{HO}_2 \cdot + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \] (13)

The net outcomes of the above cycle are just the degradation of VOC and the conversion of NO to NO\(_2\). In this sequence, a VOC molecule is converted to carbonyl molecules and two
molecules of NO are converted to two molecules of NO$_2$. Finally, the free radical emerges as OH radical again at the end of the chain.

The most obvious OH radical termination reaction is the following reaction:

$$\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$$  \hspace{1cm} (14)

Since radical propagation steps produce NO$_2$, it makes NO$_2$ available during the time that a large flux of radicals is also available. Therefore, the above reaction dominates the termination step.

Other possible termination reactions are as following:

$$\text{HO}_2 \cdot + \text{HO}_2 \cdot \rightarrow \text{H}_2\text{O}_2$$ \hspace{1cm} (15)

$$\text{RO}_2 \cdot + \text{HO}_2 \cdot \rightarrow \text{ROOH}$$ \hspace{1cm} (16)

$$\text{RO}_2 \cdot + \text{RO}_2 \cdot \rightarrow \text{ROOR}$$ \hspace{1cm} (17)

$$\text{RO}_2 \cdot + \text{NO} \rightarrow \text{RONO}_2$$ \hspace{1cm} (18)

$$\text{RO}_2 \cdot + \text{NO}_2 \rightarrow \text{ROONO}_2$$ \hspace{1cm} (19)

where RONO$_2$ is an organic nitrate and ROONO$_2$ is an organic peroxy nitrate.

The newly produced NO$_2$ from VOC oxidation reactions can either photolyse to generate a free oxygen atom or react with radicals to terminate the free radical chain reactions. The produced free oxygen atom would be distributed among O$_3$ and oxidized nitrogen species. This series of free radical chain reactions is actually comprised of two chain reaction cycles, the OH-cycle and the NO-cycle. The net outcome of the OH-cycle is the production of the free oxygen atom. The function of the NO-cycle is to determine the partition of the free oxygen atom among O$_3$ and oxidized nitrogen species. In the whole photochemical reacting system, these two cycles are coupled together to regulate the ozone formation.

In general, ozone production is proportional to the total production of the free oxygen atom, which can be determined by the total number of VOC molecules that react with OH and by the availability of NO to react with peroxy radicals to produce NO$_2$. If only low level of NO can be cycled, it indicates that the produced free oxygen atom is mostly present in the form of oxidized nitrogen species, caused by the fact that there are sufficient amount of NOx in the air. Therefore, ozone sensitivity is controlled by the amount of VOC molecules that react, which can be denoted as the VOC-sensitive regime. If very high level of NO can be cycled, it indicates that there are plenty of peroxy radicals and limited amount of NOx present in the air. Thus, ozone sensitivity is controlled by NOx emissions, and can be denoted as the NOx-sensitive regime.

2.1.2 Development of the AIRTRAK Model

An important characteristic of the photochemical cycle process is that for each ozone molecule produced a nitric oxide molecule is regenerated. This is the confounding cycle which complicates the interpretation of ozone concentration data. However, this complication can be
removed from consideration by taking the measure of the photochemical process extent to be the sum of the ozone concentration plus the concentration of nitrogenous products formed from nitric oxide. The concentration of “Smog Produced” (SP) is defined in this manner to represent the extent of the photochemical process as follows:

\[
(SP)_t = (O_3)_t - (O_3)_0 + (NO)_0 - (NO)_t
\]  

(20)

where \((SP)_t\), \((O_3)_t\), and \((NO)_t\) denote concentrations at time \(t\); and \((O_3)_0\) and \((NO)_0\) represent the initial concentrations, respectively.

The AIRTRAK model is based on the “smog-production” (SP) algorithm defined above by Johnson [Johnson and Azzi, 1991; Johnson and Azzi, 1992]. From the above definition of “Smog Produced” concentration, SP is implicitly expressed in terms of nitric oxide oxidation. Based on a series of smog-chamber runs, Johnson reported that SP displays a linear relationship to cumulative-incident light flux under the light-limited regime where both VOC and NOx are available for oxidant formation, and then reaches its maximum value, which is proportional to the initial concentration of NOx, in the NOx-limited regime where NOx has been depleted.

The cumulative-incident light flux is defined as follows:

\[
\text{cumulative - incident light flux} = \int_{t=0}^{t} k_{\phi(NO_2)} \cdot dt
\]  

(21)

where \(k_{\phi(NO_2)}\) is the rate coefficient for photolysis of NO\(_2\), a common measure of light intensity.

These linear relationships can be described by the following formulas: (a) in the light-limited regime,

\[
(SP)_t = R \int_{0}^{t} k_{\phi(NO_2)} e^{\alpha(1/T - 1/316)} \cdot dt
\]  

(22)

where R is the reactivity-adjusted VOC concentration; \(\alpha\) is a parameter; and T is temperature in K; consequently, R is approximately constant during the light-limited regime and can be expressed as

\[
R = A (VOC)_0
\]  

(23)

where A is the reactivity coefficient for oxidant formation by VOC and \((VOC)_0\) is the initial concentration, (b) in the NOx-limited regime,

\[
(SP)_{max} = \beta(NOx)_0
\]  

(24)

where \(\beta\) is the NOx stoichiometric coefficient for maximum SP formation.

In order to facilitate the assessment of relationships between ozone and precursors (NOx and VOC), the extent of reaction (E) was defined by Johnson as:

\[
\text{Extent}(t) = \frac{SP(t)}{SP_{max}}
\]  

(25)

Extent \((E)\) reaches a maximum value of unity when the concentration of NOx approaches zero, thus denoting a condition of NOx limitation. By calculating the extent parameter \((E)\),
the control preference can be determined. When the extent value (E) is less than one, the air parcel is in the light-limited regime and VOC control is preferred for reducing the peak ozone concentration. When the extent value (E) reaches one, the air parcel is in the NOx-limited regime and NOx control is preferred for reducing the peak ozone concentration.

2.1.3 Application of AIRTRAK Model to the Ambient Atmosphere

Johnson and Azzi suggested that the smog production equation could be expressed in terms of instantaneous ozone and NOy concentrations alone, which would allow the AIRTRAK model to be applied to ambient monitoring data [Johnson and Azzi, 1992]. The SP concentration defined in above section cannot be measured directly at a monitoring site, since measured concentrations of species represent concentrations of air parcels passing by during the measurements. Therefore, [NO] is not known in the atmosphere and it must be replaced by [NO], representing the concentration of all NOx emission inputs into an air parcel.

Thus, smog concentration [S], which can be measured by AIRTRAK or conventional monitors, is defined as follows to supplement the representation of SP in the ambient atmosphere.

\[ [S] = [O_3] + [NO_y] - [NO] \]  \hspace{1cm} (26)

[S] is lower than [SP] because of the removal processes of NOy from the gas phase. Johnson assumed that the amount of NOy lost from the gas phase, [PNOy], is proportional to the SP for the light-limited regime

\[ [PNOy] = P[SP] \]  \hspace{1cm} (27)

where P is the proportionality constant. Also, in the ambient atmosphere a portion of NOx emissions is in the form of NO2.

Considering these factors, Johnson and Azzi (1992) derived the following two equations for [SP] during light and NOx-limited regimes, [SP] and [SP]NR, to permit application of the SP algorithms to ambient data:

\[ [SP]_{LR} = \frac{[O_3] - [NO] + F[NO_y]}{1 - FP} \]  \hspace{1cm} (28)

\[ [SP]_{NR} = [SP]_{max} = \frac{\beta[O_3]}{\beta - F} \]  \hspace{1cm} (29)

where F is the fraction of NOx emitted as NO.

In addition, it is possible to determine the type of regime by estimating the corresponding NOx emissions from following two equations:

Light – limited regime : \[ [NOx]_{LR} = \frac{[NO_y] + P([O_3] - [NO])}{1 - FP} \]  \hspace{1cm} (30)

\[ NOx – limited regime : [NOx]_{NR} = \frac{[O_3]}{\beta - F} \]  \hspace{1cm} (31)
Each of the above two equations for estimating NOx emissions is valid only when applied in the appropriate regime and each underestimates NOx emissions when applied to the wrong regime. The reason for underestimating NOx emissions when applied \([\text{NOx}]_{\text{NR}}\) formula in the light-limited regime is that it does not account for any NOy losses once SP reaches SP\(_{\text{max}}\). The other way around here is that when applied \([\text{NOx}]_{\text{LR}}\) formula in the NOx-limited regime, the estimated SP is less than the actual SP\(_{\text{max}}\).

Therefore, a quantity \(G\) is defined as an alternative of \(E\) to determine the sensitivity regime.

\[
G = \frac{[\text{NOx}]_{\text{NR}}}{[\text{NOx}]_{\text{LR}}} = \frac{[\text{O}_3]/(\beta - F)}{([\text{NOy}] + P([\text{O}_3] - [\text{NO}])/((1 - FP) (32)
\]

When \(G \leq 1\), smog formation for the air parcel is in the light-limited regime; if \(G \geq 1\), smog formation is in the NOx-limited regime.

### 2.1.4 Limitations of the AIRTRAK Model

The development of the AIRTRAK model is based on limited smog chamber data and several assumptions. The adaptation of this model from smog chambers to the real atmosphere is not totally straightforward and needs to be carefully examined. For instance, in the ambient atmosphere, NOx emissions along a trajectory reaching a receptor are unknown and the dilution and mixing of air masses reaching a receptor are unknown. Thus, the ambient measurement recorded in the monitoring site represents the successive states of different air parcels. However, the assumptions of the AIRTRAK model need to be reconsidered to ensure the applicability of this model to the ambient data.

The key assumptions and limitations of the AIRTRAK model are summarized as follows:

- The most critical assumption in the AIRTRAK model is the linear relationship between maximum SP concentration and NOx emissions. This assumption implies that maximum O\(_3\) and SP concentrations are linearly related to NOx emissions. From other smog chamber studies and a modeling study [Chang and Rudy, 1993], it has been shown that maximum ozone concentrations in the NOx-limited regime are linearly related to a square root of initial NOx concentrations for a wide range of initial NOx concentrations. Thus, a nonlinear relationship between ozone maximum and NOx emissions has been obtained:

\[
[\text{O}_3]_{\text{max}} = \gamma \sqrt{[\text{NOx}]} 
\]

Also, it should be noted that values of parameters \(\beta\) and \(\gamma\) are dependent on VOC compositions. Therefore, it is important to establish the range of validity of this assumption with representative VOC mixtures.

- The SP algorithm assumes that SP concentrations are independent of temperature. From other smog chamber studies and photochemical modeling results [Chang and Rudy, 1993], it has been shown that maximum SP and O\(_3\) concentrations are dependent on temperature in the NOx- and light-limited regimes.
• The SP algorithm does not take the effect of dilution into account. Hess et al. [Hess et al., 1992] performed a series of chamber experiments involving dilution or injection of fresh emissions. These chamber studies suggested that the SP algorithm could be extended to situations involving dilution or injection of fresh emissions by introducing linear dilution factors. However, if maximum SP concentrations in the NOx-limited regime are significantly nonlinear for the concentration range of NOx emissions, the linear effect of dilution needs to be reconsidered.

• Another critical assumption in the SP algorithm is that the loss processes of NOy from the gas phase is linearly related to SP concentration. The governing processes for the loss of NOy from the gas phase are dry deposition, secondary organic aerosol formation, and inorganic nitrate formation. The effects of these processes on the loss of NOy from the gas phase are varying among different areas. Thus, a better method of estimating the parameter P or a different way of estimating the NOy loss is needed.

### 2.2 A Case Study: Analysis of Ozone Control Strategies

The objective of this case study is to estimate the relative effectiveness of controlling VOC or NOx emissions in reducing ground-level ozone through the application of a PAQSM (UAM), and then cross-evaluate the result from the UAM and the assessment from AIRTRAK model. The UAM application domain, as shown in Figure 1, covers an area of $210 \times 275$ km with a grid resolution of 25 km$^2$. The ozone episode days considered here were July 6-8, 1988. This episode was characterized by high ozone levels in the entire northeastern part of the United States, and the observed ozone maximum within the domain was 210 ppb on July 7 at Philadelphia and Chester, Pennsylvania. The application of the AIRTRAK model is through the implementation of the Mapper program [Map, 1994]. The input data files for this program include an air quality datafile and a geometric information file for the monitoring stations. The air quality file contains the $O_3$, NO and NOy concentrations measured at the monitoring stations.

#### 2.2.1 Methodology

The first step is to perform the base case UAM simulation for the 1988 ozone episode at the Philadelphia/New Jersey modeling domain. From performance evaluations of different base case studies [EPA, 1991; Tesche et al., 1990], a combination of wind fields from the Diagnostic Wind Model [EPA, 1990] and spatially varying mixing heights from the MIX-EMUP [SAI, 1994] algorithms was chosen for use here. As the demonstration examples, the wind fields obtained from the Diagnostic Wind Model are shown in Figure 2 for a morning hour (4:00 a.m.) and Figure 3 for an afternoon hour (15:00 p.m.). Since the maximum ozone concentration during this episode was observed at July 7, the further analyses of sensitivity tests were focused on July 7, 1988. From the base case simulation output of July 7, as shown in Figure 4, the ozone plumes appeared to be located around the areas northwest of Philadelphia and north of New York city. In order to analyze the effects of precursors (NOx
and VOC) on the two major ozone plumes, the whole modeling domain was divided into four sub-domains, as shown in Figure 1.

Further analyses focused on sub-domains 2 and 3 where the two major ozone plumes were located. Then, a matrix set of UAM simulations, corresponding to varying levels of across-the-board reductions in NOX and VOC emissions, was performed to test the sensitivity of ozone levels to precursors’ levels [Georgopoulos et al., 1997]. Finally, the AIRTRAK model calculations were performed using measured O₃, NO and NOy concentrations at six air quality stations located within sub-domain2 and sub-domain3. Since there are no NOy measurement data available at the monitoring stations, we used the output from UAM simulations to represent the measured NO and NOy concentrations at the monitoring stations. Thus, we can test the consistency of control preferences for the AIRTRAK model and UAM.

The geographical information of the six stations considered is presented in Table 1.

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2.2.2 Results

The UAM simulation results

The area of sub-domain2 covers the north of New York metropolitan area and Northern New Jersey. As shown in Figure 5, it was seen that NOx control appeared counter-productive in reducing the peak ozone concentration at this sub-domain, while VOC control tended to uniformly decrease the peak ozone concentration. Comparison of maximum ozone predictions indicated that at 25% and 50% VOC reductions, decreasing NOx in this sub-domain has adverse effects on reducing the peak ozone concentration.

The area of sub-domain3 covers most of southeastern Pennsylvania and parts of Maryland and Delaware. As shown in Figure 5, it was seen that both NOx and VOC controls were beneficial to reduce the peak ozone concentration in this sub-domain. Therefore, it was suggested that within the whole domain VOC control is more efficient in lowering the peak ozone concentration. This point can be further confirmed by checking the ozone isopleth plots, as shown in Figure 6.

The AIRTRAK model calculations
From the results shown in Figure 7, the extent values exhibited by air quality stations were significantly different between sub-domain2 and sub-domain3 during the time period of occurring peak ozone concentration. For the three stations located in sub-domain2 (NYC2, QUEE, WHIT), the extent values were significantly less than one, indicating VOC control is effective. For the three stations located in sub-domain3 (PHIL, CAM2, GLOU), the extent values are about 0.9 to 0.95, indicating both VOC and NOx controls are effective. Thus, the results from this semi-empirical approach corroborated the application of a PAQSM (UAM).

2.2.3 Discussion

This case study leads to the following recommendations:

1. The UAM and AIRTRAK model are in agreement in that reductions in VOC levels are more efficient in lowering the calculated peak ozone concentration.

2. The assessment from the AIRTRAK model can corroborate the control strategies developed from a PAQSM (UAM), and justify the rationale of control strategies in terms of the extent of photochemical reactions occurring in the atmosphere. For instance, from UAM matrix simulations on sub-domain2 it was suggested that NOx control is counter-productive in reducing peak ozone concentrations. According to the assessment from the AIRTRAK model, the extent values in sub-domain2 were significantly less than one, indicating there were significant amounts of NOx present in the environment. Therefore, peroxy radicals were consumed by NOx species, thus blocking the photochemical process. Once NOx was reduced, peroxy radicals would have a better chance to promote the photochemical process. That is why NOx control is counter-productive in this case.

3. The results presented here are only valid for this particular domain and combination of meteorological inputs and emission inventories; the trends might change for different scenarios.

Although the AIRTRAK model can provide a route to the evaluation of photochemical smog which is based on the measured properties of the air rather than estimates of the emissions into the air, its application is highly dependent on the siting of monitoring stations and measurement data of NO and NOy. It should also be noted that the reported NOx measurements from monitoring stations are often used to approximate NOy measurements. Since the chemiluminescent analyzer with a heated converter, used in monitoring stations, can convert NO2 and most other oxidation products of NO to NO, reported NOx are close to NOy. It is noteworthy that direct measurements of NOx at the time of high ozone levels are the most useful data for determining the sensitivity regimes of the air parcels. In the troposphere, no additional ozone is formed until NOx reaches some threshold levels. To determine threshold levels of NOx in urban and downwind areas, some chamber experiments with pollutant mixtures corresponding to photochemically aged air masses in urban and downwind areas would be needed. Currently, specific NOx measurements are not made, generally due to the difficulties of species measurements of NO2.
Figure 1: Philadelphia/New Jersey UAM Modeling Domain with grid cell resolution of 5 kilometers (42x55 cells)
Figure 2: Wind field during 4:00 - 5:00 a.m. at July 7, 1988
Figure 3: Wind field during 15:00 - 16:00 p.m. at July 7, 1988
Figure 4: The UAM’s Base case simulation output for July 7, 1988
Figure 5: Daily maximum ozone concentration from Matrix set of UAM simulations on July 7, 1988 at (a) sub-domain 2 (b) sub-domain 3
Figure 6: Predicted ozone isopleth plots for (a) sub-domain 2 (b) sub-domain 3
Figure 7: Diurnal pattern of the extent values for 6 air quality stations located at sub-domain 2 and 3: NYC2, QUEE, and WHIT in sub-domain 2; PHIL, CAM2, and GLOU in sub-domain 3
3 CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

3.1 Summary Conclusions

The analysis of ambient data for the extent of atmospheric chemical reaction offers a means of developing a qualitative understanding of a particular area’s sensitivity to reductions in VOC and NOx emissions. The semi-empirical approach of the AIRTRAK model, developed with the incorporation of the “smog-forming” concept, provides such means to relate NOx emissions to smog formation using observed O₃, NO, and NOy (NOx + gas-phase oxidation products of NOx) concentrations. This report has examined the methodology of using the AIRTRAK model to corroborate the UAM’s analyses on the development of ozone control strategies, where various scenarios of precursors (NOx and VOC) emissions reductions have been simulated.

The case study shown in this report suggested that the AIRTRAK model can achieve the same understanding of the ozone’s sensitivity to the reductions of precursors (NOx and VOC) emissions as the UAM analyses. However, the accuracy of the AIRTRAK model is limited, because it was developed using a small number of environmental chamber experiments, carried out at a single research facility for a limited range of conditions. Further evaluations of the underlying SP algorithms in the AIRTRAK model are needed by conducting more environmental-chamber studies and field studies for various atmospheric conditions.

3.2 Future Directions

Although the AIRTRAK approach reveals interesting features relating to control strategy assessments, its application to ambient concentration data is expected as limited, due to its underlying assumptions that have originated from chamber experiments. An alternative approach of determining ozone sensitivity is to identify individual species or species ratios that consistently assume different values under conditions of NOx-sensitive and VOC-sensitive ozone. This type of approach is called “photochemical indicators”.

For many years, it was believed that the morning VOC:NOx ratio in an urban area could be used as the photochemical indicator. However, it is now apparent that the VOC:NOx ratio is not a reliable diagnostic of ozone precursor relationships [Milford et al., 1994]. Milford et al. [Milford et al., 1994] have established a link between ozone sensitivity and total reactive nitrogen (NOy=NOx + HNO₃ + peroxyacetyl-nitrates + alkyl nitrates). In their study, low values of afternoon NOy (< 12 ppb) were consistently associated with NOx-sensitive ozone, and high values of NOy ( > 25 ppb) were associated with VOC-sensitive ozone, based on sensitivity predictions from four different PAQSMs applications to cities and regions in the United States. The drawback of this approach is that correlations between ozone sensitivity and indicator species (NOy) may shift significantly when changes in initial emission rates are made. This type of shift would suggest that this indicator-based estimate for ozone sensitivity still depend on mechanistic models assumptions rather than provide a fully independent estimate.

Sillman extended the work of Milford et al. [Sillman, 1995; Sillman, 1997] to include
other species and species ratios: \( \text{O}_3/\text{NO}_y \), \( \text{O}_3/\text{NO}_z \) (where \( \text{NO}_z = \text{NO}_y - \text{NO}_x \)), \( \text{O}_3/\text{HNO}_3 \), \( \text{H}_2\text{O}_2/\text{HNO}_3 \), and \( \text{H}_2\text{O}_2/\text{NO}_x \). Sillman found that the link between NOx-VOC sensitivity and these “photochemical indicators” was largely unaffected by changes in mechanistic models assumptions, including assumed emission rates for both anthropogenic and biogenic species. High values of these species ratios are correlated with NO\(_x\)-sensitive chemistry and low values are associated with VOC-sensitive chemistry. Sillman’s results suggested that the accuracy of mechanistic model predictions for NOx-VOC sensitivity can be evaluated by comparing model results with measured values for the indicator species. Thus, the “photochemical indicators” suggested by Sillman are recommended to supplement the AIRTRAK model for the cross-evaluation of the sensitivity to ozone predicted by PAQSMs under various atmospheric conditions.
References


