

## Chapter 5

# Lowering Ozone: Effect of Controlling Volatile Organic Compounds and Nitrogen Oxides

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# Lowering Ozone: Effect of Controlling Volatile Organic Compounds and Nitrogen Oxides

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## INTRODUCTION<sup>1</sup>

Ozone is not emitted; rather it is produced in the atmosphere from reactions involving two ‘precursor’ pollutants: volatile organic compounds (VOCs) and nitrogen oxides ( $\text{NO}_x$ ). To develop effective strategies for reducing ozone, an understanding of the complex relationship between ozone concentrations and VOC and  $\text{NO}_x$  emission levels is needed. Unfortunately, our ability to predict the effectiveness of control strategies is limited by uncertainties in emissions inventories, especially for VOCs (see chapter 6); lack of atmospheric concentration data for VOCs,  $\text{NO}_x$ , and rural ozone; and deficiencies in air quality models that have been applied to most cities. Moreover, generalizations are difficult to make because of the fact that the relationship depends strongly on local conditions such as topography, and spatial distributions and types of emission sources, which vary from one city to another, and on meteorological conditions that vary from day-to-day.

The focus of efforts to reduce urban ozone has historically been on controlling local VOC emissions. We assume that this focus will be continued. However, as discussed in chapter 6, we project that in many cities, currently available VOC control measures will fall short of providing the reductions needed to meet the ozone standard. In some cases, controlling  $\text{NO}_x$  emissions in addition to VOCs might reduce ozone more than controlling VOC emissions alone. In other situations, however, a combined strategy of  $\text{NO}_x$  and VOC controls might actually reduce peak ozone less than reducing VOCs alone. For many cities, the modeling and data gathering needed to reliably predict whether  $\text{NO}_x$  controls would be helpful have yet to be done. Reducing emissions in upwind areas as well as locally might also help reduce peak ozone concentrations in some nonattainment cities. Some studies have indicated where controls in upwind areas might be important, but we cannot yet quantify how much they would help.

To date, no control efforts have been undertaken expressly to reduce ozone concentrations in rural areas. However, a few recent modeling studies have attempted to simulate rural conditions. The studies suggest preliminarily that outside of pollution plumes downwind of urban and industrial areas, reducing  $\text{NO}_x$  emissions will generally be a more effective strategy for lowering ozone than reducing VOC emissions.

In this chapter, we first present an overview of the relationship between ozone levels and VOC and  $\text{NO}_x$  emissions. We then present estimates of the amounts that VOC emissions need to be reduced to enable cities with different design values to meet the ozone standard, and the amount that ozone concentrations could be reduced in these cities using available VOC control measures. The question of whether reducing  $\text{NO}_x$  emissions in addition to VOCs is likely to be beneficial or not is considered next. After that we look at the role of transported ozone and precursors. Finally, we discuss how VOC and  $\text{NO}_x$  emission reductions might affect ozone in rural areas, where it can damage trees and annual crops.

## THE RELATIONSHIP OF VOLATILE ORGANIC COMPOUND AND NITROGEN OXIDE EMISSIONS TO OZONE

Ozone is produced through chemical reactions involving nitrogen oxides and volatile organic compounds. <sup>1</sup>Ozone concentrations tend to be highest on hot, sunny days for three reasons: 1) the chemical reactions depend on sunlight and temperature; 2) emissions from some sources increase with outdoor temperatures; and 3) stagnant air that tends to limit pollutant dispersal is often associated with high temperatures. Ozone concentrations exceeding the standard occur almost exclusively between May and September in most areas of the United States, although California and the gulf coast have longer seasons with high ozone [32]. The highest concen-

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<sup>1</sup>Carbon monoxide and methane are also involved in ozone production. However,  $\text{NO}_x$  and VOCs are most important in urban areas.

trations are often observed after more than 1 day of hot, sunny conditions. Multi-day episodes can lead to concentrations that approach or even exceed the ozone standard over large areas of the Eastern United States, encompassing rural areas as well as cities [35,36,37]. Ozone levels observed at a given location can be influenced significantly by transported pollutants as well as local emissions. Plumes of elevated ozone concentrations have been observed 200 or more miles downwind of urban areas, under some circumstances [21,8,30].

Nitrogen oxides are products of fossil fuel combustion. On a nationwide basis, approximately 35 percent of  $\text{NO}_x$  emissions are from highway vehicles, another 35 percent are from utilities, and 12 percent are from industrial fuel combustion.  $\text{NO}_x$  emissions from natural sources are negligible [16]. About 60 percent of the  $\text{NO}_x$  in the Northeastern United States is emitted in nonattainment cities. In the South and Midwest, however, most of the  $\text{NO}_x$  originates in rural areas or small cities, with only about 30 percent coming from nonattainment areas.  $\text{NO}_x$  has an atmospheric lifetime in summer of about 6 to 10 hours [28] and thus is unlikely to be transported more than about 100 miles.

VOCs are a broad class of organic gases such as vapors from solvents and gasoline. In urban areas, approximately 45 percent of manmade VOCs are emitted from highway vehicles, about 25 percent from surface coatings and other organic solvent use, and smaller fractions from other categories including gasoline evaporation from gas stations, solid waste disposal, chemical manufacturing, and petroleum processing. The proportion of manmade VOC emissions originating in nonattainment cities rather than attainment areas varies from 60 percent in the Northeast to about 30 percent in the South. Evaporative emissions of VOCs tend to be especially high in hot weather.

Individual VOCs differ substantially in how quickly they react in the atmosphere. In summer, the atmospheric lifetimes of common organic gases range from less than an hour to several days [1], and correspondingly, transport distances for various VOCs range from a few to hundreds of miles. The fastest reacting VOCs tend to produce the most ozone, however, so VOCs from distant sources tend to be less important than “fresh” emissions.

Along with manmade sources, trees and other plants also produce VOCs, with especially high emissions in hot weather. Estimates of VOC emissions from vegetation are extremely uncertain—a recent study suggests they might be either high or low by a factor of 3 or more due to questions about emission rate measurements and land use estimates [11]. If current estimates of vegetative emissions are correct, though, totaled over the contiguous 48 States, peak summertime emissions from vegetation exceed manmade VOC emissions by about a factor of 2 [11]. The national totals reflect the vast amount of rural area in the United States where, in summertime, vegetation is the dominant source of VOCs. Vegetative emissions are generally highest in the rural Southeast, but are also high in forested parts of the Southwest, Northwest, and Northeast. In summer in nonattainment areas, we estimate that ratios of manmade-to-vegetative VOC emissions range from about 1 to 1, in wooded suburbs, to more than 20 to 1, in densely developed urban cores [11,20].

A useful way of thinking about how effective VOC and/or  $\text{NO}_x$  reductions are likely to be in a given area is to look at the balance in concentrations of VOCs and  $\text{NO}_x$  found in the ambient air, given existing emissions levels and pollutant transport from upwind. Generally, VOC reductions are effective and  $\text{NO}_x$  reductions ineffective where the concentration of  $\text{NO}_x$  is relatively high compared to the concentration of VOCs (i.e., ozone production is “VOC-limited”). Under such conditions, which are most likely to occur in high emissions areas such as urban or industrial centers, reducing  $\text{NO}_x$  can actually increase ozone concentrations. Conversely,  $\text{NO}_x$  reductions are most effective and VOC reductions least effective where the concentration of VOCs is relatively high compared to the concentration of  $\text{NO}_x$  (ozone production is  $\text{NO}_x$ -limited). Conditions tend to be increasingly  $\text{NO}_x$ -limited as a polluted air mass is transported out over suburban and rural areas downwind of high emissions regions, because chemical and physical processes tend to remove  $\text{NO}_x$  more rapidly than VOCs. Although measurements are sparse, conditions in rural areas tend to be  $\text{NO}_x$ -limited [1,31,10].

The relationship between ozone and its precursors is actually much more complicated than implied by the simple description of VOC-limited v.  $\text{NO}_x$ -limited conditions. Atmospheric concentrations of

ozone, VOCs and  $\text{NO}_x$ , vary from place-to-place and day-to-day, making it difficult to reliably predict the impact of VOC and/or  $\text{NO}_x$  reductions in a given city. Computer models used to predict the effect of emissions changes on ozone levels usually include mathematical representations of VOC,  $\text{NO}_x$ , and carbon monoxide emissions; chemical reactions among 30 or more chemical compounds; meteorological conditions including wind speed and direction, temperature, humidity, cloud cover, and atmospheric mixing; and pollutant concentrations at the start of the simulations and along the boundaries of the region being modeled. Various models differ greatly in how detailed their inputs are (e.g., whether they use emissions totaled over an urban area or require them to be “gridded,” i.e., broken out for small subdivisions of the area).

The most detailed urban models perform reasonably well in replicating observed ozone concentrations over episodes lasting 1 to 3 days, provided that adequate emissions inventories, boundary and initial pollutant concentration data, and meteorological data are available [26]. Unfortunately, application of these models is time-consuming and expensive (costing on the order of \$500,000), and their use has been limited. To date, most cities have used EPA’s Empirical Kinetic Modeling Approach (EKMA) model instead.<sup>2</sup> EKMA was designed to minimize input requirements, and allows use of default values for many parameters. Consequently, it often oversimplifies the relationship between precursor emissions and ozone.

EPA has historically encouraged exclusive reliance on VOC emission controls to ensure compliance with the air quality standard for ozone.  $\text{NO}_x$  emission controls have mostly been used only to the extent necessary to comply with the standard for nitrogen dioxide. Part of the reason for the emphasis on VOC controls is that laboratory (smog chamber) experiments and computer modeling studies have shown that reducing  $\text{NO}_x$  emissions could increase ozone concentrations under some conditions found in urban areas. (See ref. [17,9,2] for reviews of some of these studies.) However, recent measurements of

VOC and  $\text{NO}_x$  concentrations in a number of areas, new modeling analyses, and new estimates of the impact of VOC emissions from vegetation have elicited speculation that in rural areas [27,31] and in some cities [3,7,5],  $\text{NO}_x$  controls may be more effective in reducing photochemical pollution than previously thought. In short, the issue of whether reducing  $\text{NO}_x$  emissions would generally help lower ozone is still controversial.

## EFFECT OF CONTROLLING VOLATILE ORGANIC COMPOUNDS

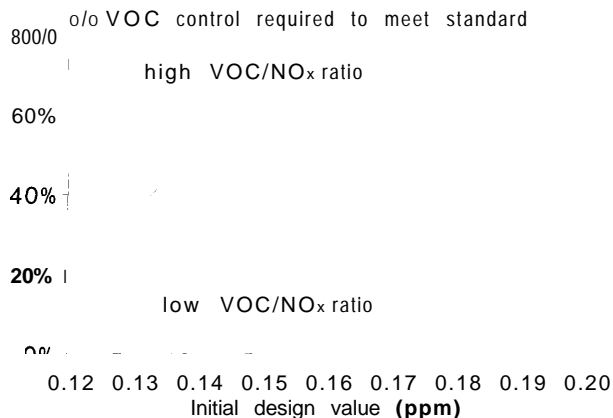
### *Local Volatile Organic Compound Reductions Required To Meet the Standard*

This section presents estimates of local VOC emission reductions needed to reduce local peak 1-hour average ozone concentrations or “design values” down to 0.12 parts per million (ppm), the maximum concentration allowed under the ozone standard. For areas with design values up to 0.20 ppm, the control requirements presented in figure 5-1 were estimated using EPA’s EKMA model, with the Agency’s default set of “typical” meteorological, emissions, and transport conditions [18]. A moderate amount of ozone (0.07 ppm) is assumed to be transported from upwind, and VOC emissions from vegetation are assumed to be negligible.  $\text{NO}_x$  emissions were assumed to be unchanged from 1985 levels.

A key parameter in an EKMA calculation is a ratio of the VOC and  $\text{NO}_x$  concentrations measured at a central location in a given city, and averaged over the period from 6 to 9 a.m. on the day when the city’s highest ozone concentration occurred. This VOC-to- $\text{NO}_x$  ratio is assumed to be a measure of the precursor balance that initially exists in the parcel of air that produces the peak ozone concentration later in the day. In figure 5-1, the range of VOC control requirements shown for each design value corresponds to the range of VOC-to- $\text{NO}_x$  ratios expected to prevail on most days, in most cities—from about 8:1 (8 ppb carbon to 1 ppb  $\text{NO}_x$ ) to 15:1 [3]. For two

<sup>2</sup>The EKMA model consists of a single cell, or box, in which chemical reactions take place, and which is moved in a straight line at a constant velocity during the course of a day. The box leaves the center of a city at 8 a.m. and arrives in the afternoon at the location where the peak ozone concentration was observed. En route, the contents of the box are diluted with comparatively clean air, and emissions are added as the box moves over sources. Problems with the model include its unrealistic treatment of the horizontal movement of the box and the mixing of freshly emitted pollutants into it; lack of spatial resolution; and sensitivity to difficult-to-measure starting concentrations of VOCs and  $\text{NO}_x$ .

**Figure 5-1-VOC Emissions Reductions Estimated To Be Required To Reduce Ozone From the Initial Peak Concentrations or "Design Values" Shown, Down to 0.12 ppm**



Control requirements were estimated using EPA's standard "EKMA" model, with meteorological, emissions, and transport conditions set to approximate conditions in a typical area where transport from upwind cities is not the principal cause of nonattainment. The range of estimates shown for each design value corresponds to the range of VOC and NO<sub>x</sub> ratios expected to prevail across different cities. The percentage reduction needed to meet the standard in an individual city will typically fall somewhere between the two curves shown.

SOURCE: Adapted from E.L. Meyer, Jr., U.S. Environmental Protection Agency, personal communication, September 1987.

cities (or 2 days in the same city) with the same peak ozone concentration, the level of VOC control required to meet the standard will generally be highest for the city (or day) with the highest VOC-to-NO<sub>x</sub> ratio, i.e., the most VOC-rich conditions. However, local conditions that deviate from the default values used in our calculations could lead to different results. For example, a higher level of pollution transported into a city from upwind could lead to a relatively high control requirement even if the city had a low VOC-to-NO<sub>x</sub> ratio.

To illustrate how to interpret figure 5-1, for a city with a design value of 0.16 ppm, with no change in NO<sub>x</sub> emissions levels, the model predicts that VOC reductions ranging from about 45 to 70 percent will be needed to meet the ozone standard. As used here, the EKMA model is intended to provide only rough estimates of control requirements. In our judgment, it seems reasonable that control requirements for

most cities would fall within the ranges shown in figure 5-1. However, control requirements for individual nonattainment areas could deviate substantially from those presented here.

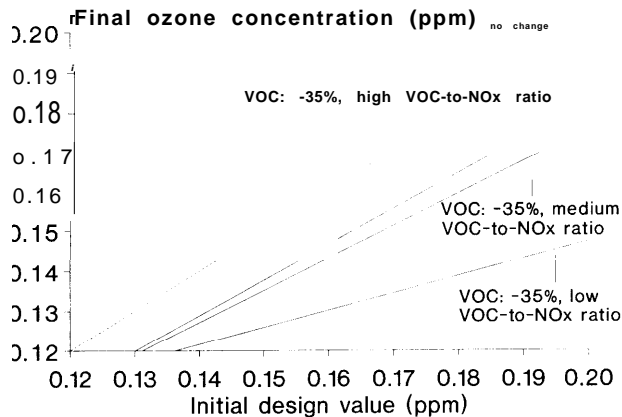
### *The Effect of Lowering Volatile Organic Compound Emissions by 35 Percent*

As we will discuss in detail in chapter 6, if all VOC controls we consider to be currently available were to be imposed, the total reductions in VOC emissions estimated for most areas by 1994 would be between 20 and 50 percent of 1985 levels, falling short of the amounts estimated to be required to attain the standard in many cities.

Figure 5-2 shows peak ozone concentrations predicted to result when VOC emissions are reduced by 35 percent (with NO<sub>x</sub> emissions unchanged), plotted against initial design values. The solid lines represent estimates of the range of peak ozone concentrations expected to result from a 35-percent reduction in VOC emissions with no change in NO<sub>x</sub> emissions. The dashed line represents "no change" in ozone concentrations, i.e., the final concentration is the same as the initial concentration or design value. Note that the ozone standard, 0.12 ppm, is at the bottom of the graph, so that the relative position of a control scenario line between the "no change" diagonal and the bottom of the graph indicates what fraction of the reduction in ozone that is needed to obtain the standard is predicted to be achieved. The range of reductions shown for each design value in figure 5-2 is based on the range of 6 to 9 a.m. VOC-to-NO<sub>x</sub> ratios expected in most cities.

As shown in figure 5-2, we predict that currently available VOC reductions would be sufficient to enable most areas with design values equal to 0.13 ppm to meet the standard. Some areas with design values equal to 0.14 ppm are also predicted to be able to attain. Reducing VOC emissions by 35 percent is predicted to lower ozone concentrations in areas with design values higher than 0.15 ppm by about one-third to two-thirds of the amounts needed to meet the standard. As with the control requirement calculations, the impact of VOC reductions in individual nonattainment areas could deviate substantially from the results shown in figure 5-2.

**Figure 5-2-Ozone Concentrations Predicted To Result When VOC Emissions Are Reduced by 35 percent, With No Change in NO<sub>x</sub> Emissions Levels**



The three solid lines indicate the ozone concentrations predicted to result in cities with low, medium and high VOC to NO<sub>x</sub> ratios. The dashed line illustrates the "no control" case, i.e., the final ozone concentrations are the same as the initial design values.

SOURCE: Adapted from E.L. Meyer, Jr., U.S. Environmental Protection Agency, personal communication, September 1987.

### *Sensitivity to Emissions From Vegetation*

Figures 5-1 and 5-2 were generated using a model that assumes VOC emissions from vegetation are negligible. However, rough estimates suggest that the fraction of total VOC emissions in nonattainment areas that come from vegetation actually ranges from a few percent up to about 50 percent, with areas where the contribution appears to be greater than about 25 percent located almost exclusively in the Southeast.<sup>3</sup> If they comprise a significant fraction of total VOCs, vegetative emissions can substantially reduce the apparent effectiveness of controlling manmade VOC emissions. In Atlanta, for example, where over 50 percent of the 11-county nonattainment area is wooded, summertime emissions from vegetation are estimated to be about equal to manmade VOC emissions [7]. Neglecting emissions from vegetation, simulations with a version of EPA's EKMA model predict that a 40 percent reduction in manmade VOC emissions would be needed to attain the ozone standard in Atlanta. When vegetative emissions are considered,

a 70-percent reduction in manmade VOCs is predicted to be required [7]. Although the Atlanta case is an extreme example, it suggests that for some cities, control requirements may exceed the range shown in figure 5-1, and reducing manmade VOC emissions by 35 percent may be less effective than indicated in figure 5-2.

## **EFFECT OF CONTROLLING NITROGEN OXIDES**

In its post-1987 policy proposal, EPA has suggested that some areas may be required to consider reducing emissions of NO<sub>x</sub> in addition to VOCs [33]. And, the State of California has promulgated new, more stringent limits on NO<sub>x</sub> emissions from motor vehicles, primarily to meet nitrogen dioxide and particulate matter (PM-10) standards, but to help reduce ozone as well [6]. This section considers the option of controlling NO<sub>x</sub> emissions in addition to VOCs.

### *Balance of Volatile Organic Compounds and Nitrogen Oxides*

The ratio of the average VOC and NO<sub>x</sub> concentrations measured over the period from 6 to 9 a.m. at a downtown location is often used as a rough measure of the precursor balance that exists in the parcel of air that is expected to produce a city's peak ozone concentration later in the day. The higher the ratio of VOCs to NO<sub>x</sub>, the more NO<sub>x</sub>-limited is the air parcel, and the more likely it is that reductions in NO<sub>x</sub> will be beneficial. Conversely, the lower the ratio, the more likely it is that reducing NO<sub>x</sub> will be counterproductive. Because they depend on emissions, meteorology, topography, and upwind precursor levels, VOC-to-NO<sub>x</sub> ratios are expected to differ from one city to another. However, the actual balance can also vary significantly from day-to-day in a given city, as meteorological conditions and emissions vary, and can also depend significantly on monitor location.

As a screening method, EPA has suggested that cities for which the median ratio over the summer is 10:1 (10 ppb carbon per 1 ppb NO<sub>x</sub>) or greater will be required to consider reducing NO<sub>x</sub> emissions in addition to VOCs. EPA has compiled 6 to 9 a.m.

<sup>3</sup>Based on average levels of VOC emissions from vegetation estimated for five regions of the United States [12] and manmade VOC emissions estimated for each nonattainment area.

VOC-to-NO<sub>x</sub> ratios for about 40 cities, for summers between 1984 and 1987 [4]. Of the 40 cities, about one-third had median VOC-to-NO<sub>x</sub> ratios lower than 10:1, indicating that they would not be required to consider NO<sub>x</sub> controls. Most of these cities were located in the upper Midwest or Northeast. The remainder of the cities had median ratios higher than 10:1, with the highest VOC-to-NO<sub>x</sub> ratios generally observed in the South (Texas and east), where no cities consistently had VOC-to-NO<sub>x</sub> ratios less than 10:1.

VOC-to-NO<sub>x</sub> ratios give only a preliminary indication of the potential effect of controlling NO<sub>x</sub>. The variability mentioned above is one limitation. A second is that there is no single ratio that clearly separates NO<sub>x</sub> and VOC-limited conditions, but rather a transition range extending from about 8:1 to 15:1, encompassing the median ratios of most cities. Most importantly, additional factors such as the size of a city, its spatial distribution of emissions sources, and the reactivity of the mix of VOCs present also influence whether or not NO<sub>x</sub> controls would be beneficial. As recommended by EPA, detailed air quality models are ultimately needed to reliably estimate the impacts of controls [33].

### ***The Effects of Nitrogen Oxide Controls in Urban Areas***

Over the past 15 years, urban-scale models have been used to predict the impacts of NO<sub>x</sub> controls for a half dozen United States cities (for example, see [17,5,24,29]). The conclusions of the studies have been mixed: compared to VOC control alone, adding NO<sub>x</sub> control was found to be counterproductive in some studies and beneficial in others. A key point from these studies is that in many urban areas, with both VOC and NO<sub>x</sub> reductions, peak ozone concentrations will be higher at some locations and lower at others than if VOC emissions were controlled alone. Thus a key question is whether controlling NO<sub>x</sub> is beneficial or counterproductive for an area as a whole, not just at a single location. A Los Angeles-area study illustrates how complicated this question can be.

Figure 5-3 illustrates the complexity of reducing NO<sub>x</sub> emissions, as predicted using an urban-scale model, for a 1982 episode in the Los Angeles area [19]. The figure shows the predicted impact of

uniformly reducing NO<sub>x</sub> emissions by 35 percent and holding VOC emissions constant, compared to estimated 1982 levels. The gray area shows where peak ozone concentrations were predicted to increase when NO<sub>x</sub> emissions were lowered. This area is centered on Los Angeles County, the portion of the region where NO<sub>x</sub> emission rates are highest. Downwind of this area, in San Bernardino and Riverside Counties, reducing NO<sub>x</sub> is predicted to reduce peak ozone.

For the case simulated, the highest ozone concentrations occurred in the eastern part of the Los Angeles basin, and reducing NO<sub>x</sub> emissions by 35 percent was predicted to lower the area-wide peak ozone concentration by slightly more than 10 percent. However, Los Angeles County is the most densely populated part of the basin, and a 35-percent reduction in NO<sub>x</sub> was predicted to lead to about a 5-percent increase in population exposure to ozone concentrations above 0.12 ppm.

### ***Combined Volatile Organic Compound and Nitrogen Oxide Control in the Northeast***

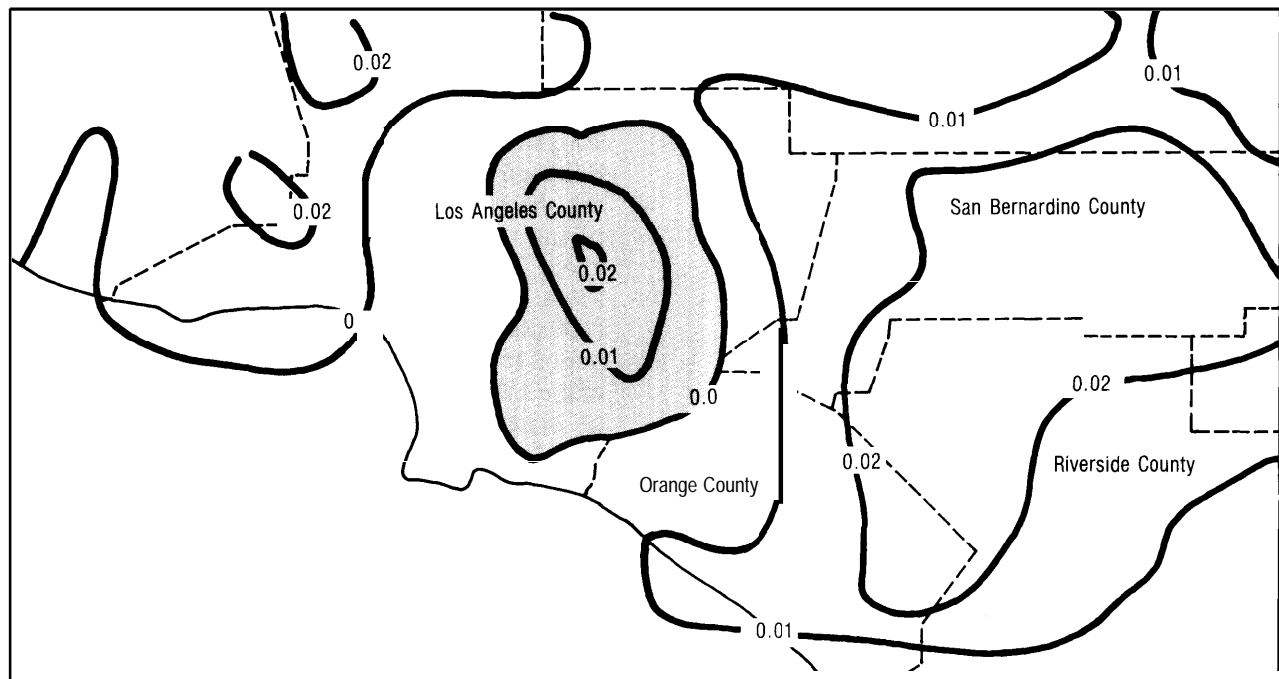
EPA has used a regional-scale air pollution model, its Regional Oxidant Model (ROM), to study the effect of reducing VOC and NO<sub>x</sub> emissions in the Northeastern United States. The ROM modeling region is shown in figure 5-4. The region is divided into cells with horizontal dimensions of approximately 11.5 miles X 11.5 miles. Emissions, air quality and meteorological inputs and outputs are averaged within each cell. Averaging over this scale is necessary to keep computational requirements down, but can lead to underprediction of peak ozone concentrations in urban areas, and may also bias how ozone levels respond to changes in VOC and NO<sub>x</sub> emissions levels. Representation of such large point sources as utility and industrial boilers is especially problematic [13].

EPA has used ROM to examine control strategies involving both VOC and NO<sub>x</sub> control alone, and combinations of the two. In keeping with our premise that future efforts will focus first on reducing VOCs, but that NO<sub>x</sub> controls may also be imposed, we present results here for the following strategies [23]:

- VOC control alone—reductions of manmade VOC emissions by 42 percent, averaged over



**Figure 5-3—Change In Peak Ozone Concentrations in the Los Angeles Basin, Predicted to Result From Reducing  $\text{NO}_x$  Emissions by 35 Percent Below 1982 Levels**



The gray area shows where ozone concentrations are predicted to increase. Ozone concentrations are predicted to decrease throughout the rest of the region. The predictions were made using an urban-scale model, with emissions and meteorological conditions corresponding to the August 30-31, 1982 period.

SOURCE: J.B. Milford, A.G. Russell, and G.J. McRae, "Implications of Spatial Patterns in Pollutant Responses to Reductions in Nitrogen Oxides and Reactive Organic Gas Emissions," *Environmental Science and Technology*, accepted, 1989.

the entire ROM domain, with reductions in cells in nonattainment cities ranging from 27 to 70 percent and uniform 30-percent reductions outside of nonattainment areas.

- Combined VOC and  $\text{NO}_x$  control—the same VOC reductions plus 27-percent reductions in  $\text{NO}_x$  emissions, averaged over the entire modeling region.

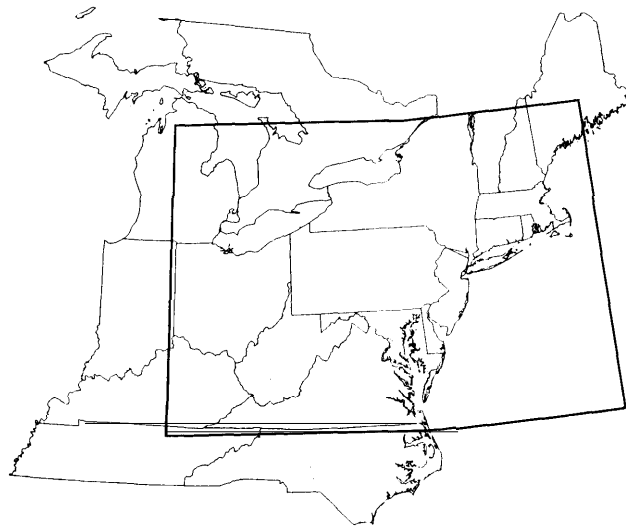
The results reported here are for a 16-day period in July, 1980, when winds were generally from the west or southwest.<sup>4</sup> Base case emissions estimates for manmade VOCs,  $\text{NO}_x$ , and CO were from the 1980 National Acid Precipitation Assessment Program (NAP') inventory. VOC emissions from vegetation are also included.

ROM's development and evaluation are ongoing, so the results presented here should be considered preliminary. Uncertainties in the estimates of both manmade VOC emissions and VOC emissions from vegetation are significant. VOC emissions from both mobile sources and area sources were probably underestimated in the 1980 NAPAP inventory, since emissions associated with running losses and waste treatment, storage, and disposal facilities (TSDFs) were not included. Evaluations of the model conducted to date indicate a tendency to overpredict low concentrations and underpredict peaks, especially near major point sources; and to overpredict low concentrations in remote areas [14].

Table 5-1 shows the results for cities (Metropolitan Statistical Areas or MSAs) in the ROM modeling

<sup>4</sup>Along the urbanized eastern seaboard, during this period, surface winds often flowed from the southwest while winds at higher altitudes came from the west [22].

**Figure 5-4—Region Covered by the U.S. Environmental Protection Agency's Regional Oxidant Model (ROM)**



ROM is being used to study the effect of reducing VOC and NO<sub>x</sub> emissions.

SOURCE: W. Battye, L. Langstaff, M. Smith, N. Possiel, E. Meyer and K. Baugues, "Regional Ozone Modeling For Northeast Transport—Development of a Base Year Emissions Inventory," paper prepared for the 82nd Annual Meeting of the Air and Waste Management Association (Anaheim, CA: June 25-30, 1989).

region. Results for rural (non-MSA) areas of New York, Pennsylvania, and West Virginia are discussed below in the section on rural ozone. Two measures of the extent of possible exposure are tabulated for the base case and for the VOC-alone and combined VOC and NO<sub>x</sub> control strategies. The first is an area-weighted measure of the occurrence of ozone concentrations above specified levels—on each day, the number of grid cells where ozone exceeds a threshold concentration is counted, and then the daily totals are added up over the 16-day modeling period. The second measure is "population-weighted"—in this case the number of people living in those parts of a city where ozone exceeds a threshold concentration is added up for each day, and then the daily 'potentially exposed' population numbers are totaled over the entire 16-day period. Two threshold levels are displayed in table 5-1: a peak daily 1-hour average concentration of 0.12 ppm

(equivalent to the standard), and a peak daily 8-hour average concentration of 0.10 ppm (a measure of multi-hour exposure).

Approximately 61 million people live within all the metropolitan areas included within the modeling region. The total metropolitan area covered is about 100,000 square miles. If the entire modeling region had been blanketed by ozone concentrations exceeding the standard for every day during the 16-day period modeled, the entries in table 5-1 would be about 976 million person-days (61 million people times 16 days) and 1.6 million square mile-days (100,000 square miles times 16 days). The 16-day period modeled represents one of the worst episodes of the 1980-88 period, with the base case occurrence of ozone concentrations above the thresholds in table 5-1 equal to about 10 percent of the theoretical maximum. This total represents a mix of conditions—some locations where the standard was never exceeded, and other locations such as New York City where the standard was exceeded on 11 of the 16 days modeled.

As shown in table 5-1, for the Northeast as a whole, the net effect of the combined VOC and NO<sub>x</sub> control strategy is predicted to be an improvement over the strategy that would control VOCs alone, in terms of reducing both the urban area and population potentially exposed to elevated ozone concentrations. The large reductions in VOC emissions alone eliminate the majority of potential exposures, with the combined strategy eliminating 3 to 13 percent more, depending on the measure of exposure considered. Consistent with the explanation that ozone is most likely to be sensitive to VOC controls in densely populated, high-emissions areas, reducing VOC emissions alone is somewhat more effective for lowering population-weighted potential exposure than area-weighted exposure.

Despite the fact that the combined strategy is predicted to be beneficial overall, for urban areas in the Northeast, the modeling results suggest that NO<sub>x</sub> reductions may be counterproductive for individual locations within the region. In other places, though, adding NO<sub>x</sub> controls is predicted to be more effective than suggested by the regionwide totals shown in table 5-1. Table 5-2 presents results for the Pittsburgh, Hartford, and New York City areas.

**Table 5-1-Predicted Effect of VOC-Alone and Combined VOC and NO<sub>x</sub> Control Strategies In Northeastern Cities, Over a 16-Day Period in July 1980**

	Base case—potential exposure to elevated ozone <sup>a</sup>	Case 1, VOC control—reduction in potential exposure (% of base)	Case 2, VOC and NO <sub>x</sub> control—reduction in potential exposure (% of base)
Areal exposure:			
>0.12 ppm, 1-hr average . . . . .	115,000 square miles*days	64%	72%
Population exposure:			
>0.12 ppm, 1-hr average . . . . .	117 million people*days	76%	79%
Areal exposure:			
>0.10 ppm, 8-hr average . . . . .	149,000 square miles*days	500/0	63%
Population exposure:			
>0.10 ppm, 8-hr average . . . . .	141 million people*days	63%	70%

<sup>a</sup>About 61 million people live in about 100,000 square miles of urban area in the ROM (Regional Oxidant Modal) region. If ozone concentrations had exceeded the specified thresholds every day, throughout all of these urban areas, the entries in this column would have been 1.6 million square-miles-days and 976 million people-days.  
 NOTE: The first column indicates "potential exposure" to elevated ozone (i.e., the occurrence of ozone levels above the indicated threshold concentration) for the base case, by area and population. The second and third columns give percentage reductions in "potential exposure" compared to the base case, for two control cases: 1) a 42 percent reduction in manmade VOC emissions; and 2) the same 42 percent reduction in manmade VOCs plus a 27 percent reduction in NO<sub>x</sub> emissions.

SOURCE: N.C. Possiel, U.S. Environmental Protection Agency, personal communication, March 1989.

**Table 5-2-Predicted Effects of VOC-Alone and Combined VOC and NO<sub>x</sub> Controls in the Hartford, New York City, and Pittsburgh Areas, Over a 16-Day Period in July 1980**

	Base case—potential exposure to elevated ozone	Case 1 VOC control—reduction in potential exposure (% of base)	Case 2, VOC and NO <sub>x</sub> control—reduction in potential exposure (% of base)
<b>Hartford<sup>a</sup></b>			
Areal exposure:			
>0.12 ppm, 1-hr average . . . . .	12,000 square miles*days	48%	58%
Population exposure:			
>0.12 ppm, 1-hr average . . . . .	6.1 million people*days	49%	60%
<b>New York City<sup>b</sup></b>			
Areal exposure:			
>0.12 ppm, 1-hr average . . . . .	41,000 square miles*days	660/0	68%
Population exposure:			
>0.12 ppm, 1-hr average . . . . .	68.6 million people*days	81%	830/0
<b>Pittsburgh<sup>c</sup></b>			
Areal exposure:			
>0.12 ppm, 1-hr average . . . . .	6,400 square miles*days	69%	69%
Population exposure:			
>0.12 ppm, 1-hr average . . . . .	3.3 million people*days	82%	780/0

<sup>a</sup>About 1.4 million people live in the 2,900 square-mile Hartford area.

<sup>b</sup>About 16.5 million people live in the 12,000 square-mile New York City area.

<sup>c</sup>About 2.6 million people live in the 5,200 square-mile Pittsburgh area.

NOTE: See table 5-1 for a full explanation of the entries.

SOURCE: N.C. Possiel, U.S. Environmental Protection Agency, personal communication, March 1989.

Of the major urban areas in the Northeast, controlling NO<sub>x</sub> appears to be most counterproductive for Pittsburgh. As shown in the table, VOC control alone is predicted to reduce potential population exposure to concentrations above the standard by 82 percent; adding NO<sub>x</sub> control offsets some of those gains. For Pittsburgh, the net effect of combined controls is a 78-percent reduction in population exposure. In contrast to Pittsburgh, combining

NO<sub>x</sub> and VOC controls is predicted to be comparatively more effective for Hartford than for the urban Northeast overall. There, combining VOC and NO<sub>x</sub> controls is predicted to reduce both the population-weighted and area-weighted exposure measures by about 60 percent, whereas 50-percent reductions are predicted with VOC-control alone.

Finally, in the base case, more than half of the total potential exposures in northeastern cities occur

in the New York City area. Totaled over that 12,000 square mile area, the incremental effect of adding NO<sub>x</sub> control is predicted to be a relatively small improvement compared to controlling VOCs alone. VOC controls alone are predicted to reduce area-weighted exposures by 66 percent, and population-weighted exposures by 81 percent. Combined VOC and NO<sub>x</sub> controls yield additional reductions of 2 percent, by both measures.

Key limitations of these results need to be reiterated. First, they are specific to the meteorological conditions and emissions scenarios modeled. As discussed above, the emission reductions modeled are relative to an estimated 1980 baseline. Current emissions differ from those estimates due to actual changes in emissions since 1980, as well as methodological improvements in estimating emissions that have been made since 1980. The results also depend on the levels of control evaluated. Comparing a different combination of VOC and NO<sub>x</sub> control levels might have yielded different results in sign, as well as magnitude, from those presented here. In addition to the July episode, EPA has also used ROM to simulate an August 1980 episode of comparatively stagnant, recirculating flows. In that case the combined control strategy generally yielded more improvement over the VOC-alone case than for the episode considered here. Of the two, ozone episodes in the Northeast are more frequently similar to the July episode than the August episode [23]. Finally, the 11.5 X 11.5-mile resolution of the model precludes detailed analysis within cities and adds uncertainty about the effect of emissions from large sources.

## **RURAL OZONE, TRANSPORTED OZONE, AND PRECURSORS**

### *Transported Ozone and Precursors*

Even if local, manmade VOC and NO<sub>x</sub> emissions were eliminated completely, peak ozone concentrations would not be reduced to zero. A natural background concentration of 0.04 ppm is generally

assumed to contribute to peak (1-hour average) ozone concentrations. In most cases, emissions from upwind areas contribute additional ozone to observed peaks. For example, on days when the peak ozone concentrations measured downwind of Atlanta exceed 0.10 ppm, concentrations upwind of the city are typically only 0.02 to 0.04 ppm lower than the peak concentrations [15]. As another example, ozone concentrations approaching the standard are commonly observed upwind of east coast cities such as New York and Boston on days when the standard is violated downwind of these cities [21,24].

Urban "plumes" with elevated ozone concentrations have been tracked over 200 miles downwind of some cities. Aircraft observations show that the New York City plume can extend to Boston, for example [21] ozone formed from precursors emitted in urban areas within about 100 miles upwind may exacerbate nonattainment problems of cities along the Northeast corridor from Virginia to Maine (21 nonattainment areas); along the gulf coast of Texas and Louisiana (7 nonattainment areas); around Lake Michigan (5 nonattainment areas); and in California (8 nonattainment areas apparently affected by transport). Overall, of 74 consolidated metropolitan areas that did not attain the ozone standard for the 1983-85 period, 41 appear to lie within about 100 miles in directions commonly downwind of other nonattainment cities. In most of these cases, reducing both VOC and NO<sub>x</sub> emissions in the upwind nonattainment areas would probably help improve air quality in the downwind cities. Over the next 2 to 5 years, proposed or ongoing modeling studies in the four major transport areas listed above could provide quantitative information about the effect of alternative control strategies in those areas.<sup>5</sup>

### *Regional Episodes*

In association with certain types of weather systems that cross the Eastern United States several times each summer, peak ozone concentrations in the range of 0.08 to 0.10 ppm have been observed at rural locations throughout multi-state regions [25,35].

<sup>5</sup>In cooperation with the States in the Northeast, EPA is using its Regional Oxidant Model (ROM) to try to understand the impact of intercity transport there, and to evaluate coordinated control strategies. The application should be completed by the end of 1990. The Agency has also applied ROM to the gulf coast region, but plans few additional applications to this area prior to 1991, due to limited resources. The California Air Resources Board, together with local governments in the San Joaquin Valley and California industries, has planned an \$8 to \$10 million field experiment and modeling study to investigate transport and control strategies for that area. The 6-week field experiment is planned for summer 1990. State air pollution control agencies of Michigan, Illinois, Indiana, and Wisconsin have proposed, but not yet found funding for a million-dollar field study and modeling effort for the southern Lake Michigan area.

During the growing season, episodes of high ozone in rural areas are of concern due to potentially adverse impacts on crops and forests. Ozone formed during regional-scale episodes may also contribute to violations of the standard in urban areas, where additional ozone is formed from local emissions.

Based on modeling and analysis of spatial and temporal trends in ozone concentrations and air mass movement, some scientists have suggested that during multi-day episodes, pollutants emitted in major urban or industrial areas may contribute to high ozone concentrations observed several hundred miles away. In particular, they suggest that emissions from the industrial Midwest may contribute to high ozone concentrations over large areas of the South [15] and Northeast [27,8]. Carried aloft, it is plausible that slow-reacting VOCs and ozone could be carried several hundred miles. However, we are not aware of any analyses that have quantified the contributions that major urban or industrial areas make to ozone concentrations in either rural or urban areas several hundred miles away.

Rather than originating in distant urban or industrial areas, the ozone concentrations observed in regional-scale episodes could also build up over 2 or more days due to emissions from widely distributed sources, such as powerplants, or motor vehicles in rural areas or small towns. As an illustration, Trainer et al. [31] used a simple model to show that at levels estimated to occur during summer in rural Pennsylvania, manmade  $\text{NO}_x$  emissions and VOCs emitted from vegetation alone (without any manmade VOC contribution) could produce peak ozone concentrations of almost 0.12 ppm, built up over a 4-day episode. (Adding manmade VOCs at levels observed in rural areas in the Northeast was predicted to increase the peak ozone concentration by less than 10 percent, as ozone production was predicted to be  $\text{NO}_x$ -limited.)

Within the next 2 years, EPA's modeling efforts should provide some information about the potential influence of emissions from urban and industrial areas in Ohio and Pennsylvania on ozone concentrations throughout the Northeast, including the nonattainment areas along the coast. The analysis could also provide information about the impacts of

emissions from rural areas and small cities within this region. Regional-scale studies of these issues for the South and Midwest would also be useful.

### ***Reducing Rural Ozone***

Recent modeling studies that have simulated typical rural conditions suggest that outside of urban and industrial plumes, reducing  $\text{NO}_x$  emissions will generally be a more effective strategy for lowering ozone than reducing VOC emissions [27,31]. Conditions in rural areas tend to be  $\text{NO}_x$ -limited [1,10]. In rural areas where vegetative VOC emissions are high, ozone production may be particularly insensitive to changes in manmade VOC emissions [31]. As discussed in the previous section, ozone and precursors transported from urban areas also contribute to elevated ozone levels in rural areas immediately downwind of cities, and some scientists suggest that impacts of transported pollutants may extend for hundreds of miles. In these cases, reductions in urban VOC and  $\text{NO}_x$  emissions are likely to help reduce rural ozone. We cannot estimate the comparative contributions to rural ozone levels of local production versus transported pollution.

Table 5-3 shows results from the ROM simulations discussed above, for non-urban areas in Delaware, New Hampshire, New York, Pennsylvania, Vermont, Virginia and West Virginia. The total non-urban area included is about 83,000 square miles. For the non-urban results, the areal measure described above is tabulated, for 8-hour average concentrations exceeding 0.08 and 0.10 ppm, and for 1-hour average concentrations exceeding 0.10 and 0.12 ppm. Because the controls simulated were applied throughout the region, we cannot sort out the impacts of reducing precursors in rural areas versus cities.

As shown in the table, controlling  $\text{NO}_x$  emissions in addition to VOCs (in both urban and rural areas) always reduced ozone in non-urban areas more than controlling VOCs alone, at the level of aggregation considered. This result is also true for each of these states individually. Comparing tables 5-1 and 5-3, shows that the incremental benefit of the combined strategy over reducing VOCs alone is larger in rural areas than in cities. This is consistent with the expectation that  $\text{NO}_x$  controls would be more effective for reducing ozone in rural areas than in

**Table 5-3—Predicted Effect of VOC-Alone and Combined VOC and NO<sub>x</sub> Control Strategies in Nonurban Areas of the Northeast, Over a 16-Day Period in July 1980**

	Base case-potential exposure to elevated ozone <sup>a</sup>	Case 1, VOC control—reduction in potential exposure (of base)	Case 2, VOC and NO <sub>x</sub> control—reduction in potential exposure (of base)
Areal exposure: >0.10 ppm, 1-hr average . . . . .	78,000 square miles*days	48%	630/o
Areal exposure: >0.12 ppm, 1-hr average . . . . .	16,000square miles*days	68%	81%
Areal exposure: >0.08 ppm, 8-hr average . . . . .	176,000square miles*days	240/o	45%
Areal exposure: >0.10 ppm, 8-hr average . . . . .	30,000 square miles*days	5570	71%

<sup>a</sup>About 83,000 square miles of nonurban area is included in the modeling region. If this entire area had been blanketed by ozone concentrations exceeding the specified thresholds every day during the 16-day period modeled, the entries in table 5-3 would be about 1.3 million square miles-days

NOTE: See table 5-1 for a full explanation of the entries.

SOURCE: N.C. Possiel, U.S. Environmental Protection Agency, personal communication, March 1989.

urban areas, and also with the fact that most of the VOC reductions occurred in cities, rather than rural areas.

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