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Photochemical Air Pollution in the Northeast United States

William S. Cleveland and T. E. Graedel

In what is now a classic paper, Haagen-Smit (1) first described the basic mechanism of photochemical air pollution or, as it is sometimes called, photochemical smog. The primary ingredients of this form of air pollution are sunlight and emissions of nitric oxide (NO) and of a wide variety of hydrocarbons. These ingredients interact in the atmosphere to produce a host of standard, established on the basis of current information on human health effects, was set at 80 parts per billion (ppb) in 1971 and was recently revised to 120 ppb (2).] Thus the design of "control strategies" to reduce photochemical air pollution has been oriented toward O_3 . But it has become apparent within the past several years that controlling O_3 concentrations is a difficult task. The

Summary. Statistical analyses of meteorological and contaminant data and chemical kinetic modeling demonstrate that (i) the concentrations of ozone in the New Jersey-New York City metropolitan area are regional in character; (ii) ozone concentrations in Connecticut are increased by approximately 20 percent as a consequence of primary emissions in the New Jersey-New York City metropolitan region and subsequent transport; and (iii) the concentrations of a variety of products of smog chemistry in the New Jersey area are markedly increased by an increase in NO emissions, but are minimally affected by a change in hydrocarbon emissions.

undesirable secondary products. One of these is ozone (O_3) , which in sufficiently high concentrations can burn plants and damage materials such as rubber. Two other products are peroxyacetyl nitrate $[CH_3C(O)O_2NO_2]$ and acrolein (CH_2CHCHO) , both of which cause eye irritation and respiratory difficulties. Acidic products include nitric acid (HNO_3) and a group of oxidized sulfur compounds, including sulfuric acid (H_2SO_4) , referred to collectively as sulfates.

Although O_3 is only one of these undesirable secondary products, it has been endowed with a special status by virtue of its selection by the U.S. Environmental Protection Agency as the indicator of photochemical smog. [Its air quality chemical reaction chains that are involved are complicated and, despite the large amount of research that has gone on since the initial work of Haagen-Smit, there is much that is not understood. It is clear, however, that the application of what would seem to be simple logic can easily lead to incorrect conclusions. For example, it might be thought that, since NO and hydrocarbons are the building blocks of O₃ production, areas with large emissions of these primary pollutants would have the highest O3 concentrations. This is not the case. As it turns out, areas which are as far as 45 to 60 kilometers downwind of major sources of primary emissions, and which themselves have lesser emissions, can have the highest O_3 concentrations (3, 4). The reason for this is that the primary ingredients that lead to the eventual production of O_3 will, on contact with an O_3 molecule, destroy it. Thus no simple relationship exists between ozone concentrations and local emissions.

Much of the research on which air quality strategies have been based has been carried out with respect to the Los Angeles Basin. However, because primary emissions, background concentrations, and meteorology vary from one metropolitan region to another, it cannot be supposed that conclusions that are valid to Los Angeles can automatically be applied to another area. Rather, independent assessments need to be made. In this article we present such an assessment for a region in the Northeast with major air quality concerns: New Jersey, eastern New York, Connecticut, and Massachusetts.

As a result of research that has been carried out in recent years on the photochemical air pollution problem in the Northeast, three major conclusions relevant to air quality can now be stated:

1) Reductions of primary emissions of hydrocarbons and NO in the New York City metropolitan region (which includes parts of northern New Jersey and western Long Island) would reduce the concentrations of many trace contaminants but are not likely to have a major effect on concentrations of O_3 within the region itself, since the latter appear to be determined in large part by the O_3 already present in the air transported into the region.

2) Ozone maxima in Connecticut are increased by approximately 20 percent as a consequence of primary emissions in the New York City metropolitan region and meteorological transport. This results in Connecticut having the highest O_3 concentrations in the Northeast. Reductions of primary emissions in the New York City metropolitan region are likely to result in a decrease in O_3 concentrations in Connecticut.

3) Both within and downwind of the New York City metropolitan region, four of the five undesirable secondary products described earlier (sulfates, peroxyacetyl nitrate, nitric acid, and acro-

The authors are Members of Technical Staff at Bell Laboratories, Murray Hill, New Jersey 07974.



Fig. 1. Upper quartiles of daily maximum O_3 concentrations from June to August 1974 plotted against geographic locations; 1 unit = 16 ppb. Several sites discussed in the text are identified: A, Asbury Park, N.J.; BJ, Bayonne, N.J.; BY, Babylon, N.Y.; C, Chester, N.J.; G, Greenwich, Conn.; M, McGuire, N.J.; and S, Stamford, Conn.

lein) would decrease substantially if NO is reduced but would respond only slightly to hydrocarbon reductions. While concomitant reductions of both NO and hydrocarbons would reduce O₃ concentrations in areas downwind of the metropolitan region, there is not yet enough reliable information available to determine whether changing only NO or only hydrocarbon emissions would substantially reduce O₃. Nevertheless, in view of the much smaller computed response of most of the secondary products to hydrocarbon emission reductions, it appears that in the Northeast NO control is likely to be a more effective strategy for the overall reduction of photochemical air pollution.

In this article we will first present the evidence on which these conclusions rest and then discuss how the evidence leads to the conclusions.

Urban Photochemistry and Its

Investigation

A central set of reactions in O₃ production, involving NO, NO₂, and sunlight $(h\nu)$, is

$$NO_2 + h\nu \rightarrow NO + O$$
 (1)

$$O_2 + O \to O_3 \tag{2}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3}$$

The first equation demonstrates the role that solar radiation plays in O_3 formation. The third shows that O_3 destruction by NO is a direct process. Since NO is the principal oxide of nitrogen emitted by combustion sources, O_3 is removed near strong sources and formed by oxidized products when away from those sources (4). In addition to the effects of NO and NO₂, it has been argued (2) that hydrocarbon emissions affect O₃ concen-

trations, since peroxy radicals $(RO_2 \cdot)$, which result from hydrocarbons, provide a means for oxidizing NO to NO_2 without the O_3 loss involved in reaction 3 by the reaction

$$NO + RO_2 \rightarrow NO_2 + RO \rightarrow (4)$$

The chemistry involved is exceedingly complex and the importance of reaction 4 in the O_3 formation process is not yet fully delineated.

The oxidation of NO to NO_2 is only one of a large number of atmospheric reactions involving free radicals. In particular, the chains leading to the products discussed above are initiated by the hydroxyl radical

$$SO_2 \xrightarrow{HO} HSO_3 \xrightarrow{several} sulfates$$
 (5)

$$NO_2 \xrightarrow{HO} HNO_3$$
 (6)

Hydrocarbons $\xrightarrow{\text{HO}}$ RO₂ $\cdot \xrightarrow{\text{NO}_2}$ RO₂NO₂(7)

 $\stackrel{\text{NO}}{\longrightarrow}$ carbonyls (8)

(Peroxyacetyl nitrate is one of the group of products of reaction 7; the carbonyls produced in reaction 8 include acrolein, formaldehyde, and other aldehydes and ketones.)

A number of different, but related, scientific methodologies have been utilized to achieve the current understanding of the chemical and meteorological aspects of photochemical air pollution. One is smog chamber experimentation, in which primary emissions and sunlight are fed into a chamber and the concentrations of secondary products are measured. A second methodology is the development of chemical kinetic models in which differential equations, describing the rate of change of the various species, are solved to form theoretical time profiles of the concentrations. The inputs to

the models are a set of reactions, meteorological information, and emissions information. The virtue of both the smog chamber and modeling methodologies is that the effects of various emission reductions on photochemical air pollution can be studied by altering the inputs to the chamber or the model. The drawback is that results from the chamber or the model are only an approximation of the behavior in the real atmosphere. However, at least in the case of some chemical kinetic models, it has been demonstrated that they provide an approximation of the atmosphere which is sufficiently accurate to allow conclusions to be drawn.

A third methodology is the statistical analysis of atmospheric measurements of contaminants. The drawbacks here are that measurement technology is in some cases rather poor and that we cannot, as a practical matter, run experiments to check the effects of various control strategies. But the virtue, of course, is that it is the object of study which is being measured. In this article we focus on the results of this third methodology and of chemical kinetic modeling, since these two methodologies have been applied directly to investigate photochemical air pollution in the Northeast.

Emissions, Air Flow, and the Geographic Distribution of Ozone Concentrations

The New York City metropolitan region has very high levels of primary emissions. In fact, the region, which comprises 16 percent of the total area of the Northeast, accounts for 59 percent of the man-made emissions of hydrocarbons and 50 percent of the man-made emissions of NO (5). In addition, natural vegetative sources of hydrocarbons have been identified (6), although their magnitudes are not yet firmly established. During the months May to September (the time of year when levels of photochemical air pollution are high) the prevailing winds in the Northeast are from the southwest and west. The potential for transport of contaminants to the northeast and east from the New York City metropolitan region is therefore high. To aid in understanding the effect of the region on the photochemical air pollution problem in the Northeast, it is important to understand how the levels of O_3 vary from one geographic area to another.

The geographic distribution of O_3 concentrations is shown in Fig. 1, where the upper quartiles of daily maximum ozone concentrations from 1 June to 31

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August 1974 are plotted in coded form against geographic location. The highest O_3 concentrations are in the Greenwich-Stamford region of southwestern Connecticut; the next highest are in a belt that spreads out from there to the east and northeast.

Another important result is that O_3 concentrations at sites within the New York City metropolitan region are not higher than those upwind of the region. In fact, concentrations within and upwind of the region tend to be slightly lower at sites with high primary emissions than at sites with low emissions. For example, Fig. 2(7) shows the diurnal variation of O₃, NO, and NO₂ at three sites for workdays during the period 15 August to 30 September 1974. The values plotted for each hour are 10 percent trimmed means of the hourly averages. (The 10 percent trimmed mean is defined as the average of the observations between the highest and lowest deciles. This is an example of a robust statistical method-that is, one whose result is not distorted by a small fraction of the observations.)

For the NO and NO₂ curves the most noticeable feature is the greater magnitude of the concentrations at Bayonne than at the other two sites. Bayonne lies within the New York City metropolitan region, while the Chester and McGuire sites are located in relatively nonurban areas upwind. However, the total amount of O_3 is lowest at Bayonne. If the total areas under the curves in Fig. 2 are used as overall measures of the amounts of the pollutants at the sites, then for oxides of nitrogen (the area under the NO curve plus the area under the NO_2 curve) the order of the sites from the highest to lowest concentrations is Bayonne, McGuire, and Chester. For O₃ the order is reversed.

Meteorological Transport

Within the past few years it has generally become recognized that transport effects are important for air quality on a regional scale. The best demonstrations thus far concern $O_3(5, 8, 9)$ and airborne particulate matter (10). In the Northeast, transport is considered an important contributing factor in the high O₃ concentrations downwind of the New York City metropolitan region. The principal evidence is provided by a study (5) utilizing ground-level O3 measurements between 1 May and 30 September 1974 at 32 sites along a corridor from northern New Jersey to Boston, together with appropriate meteorological information.

The principal conclusion is that photochemical air pollution is transported from the New York City metropolitan area on a 300-kilometer northeast trajectory through Connecticut and as far as northeastern Massachusetts. This accounts for southwestern Connecticut having the highest O_3 concentrations in the Northeast and for a substantial increase in O_3 concentrations in Massachusetts.

We will describe, as an illustration, one of the analyses from (5) that led to the transport conclusion. At the 32 sites the dependence of O_3 on wind direction was investigated. Sites that lie in locations that are outside the New York City metropolitan region and that prevailing winds would reach after crossing the region show a clearly defined increase in O_3 concentrations when the air is flowing from the region to the sites. For example, with southwest winds a very substantial increase in O3 occurs in Connecticut and a moderate increase occurs in eastern and central Massachusetts. Asbury Park, New Jersey, which lies to the south and southeast of the New York City metropolitan region, and Babylon, New York, which lies to the east, are quite interesting, since these locations also are frequently downwind of the region but in different directions than the



Fig. 2. Concentrations of NO, NO_2 , and O_3 for three New Jersey sites plotted against time of day. For each hour of the day the values are 10 percent trimmed means of the hourly observations for workdays.

large number of sites to the northeast. Furthermore, these two sites, when downwind of the metropolitan region, are not downwind of the other urban areas along the eastern seaboard, such as Philadelphia and Baltimore. The analysis for Babylon and Asbury Park shows clearly defined peaks when the air is flowing from the metropolitan region to the sites.

It must be stressed, however, that O_3 concentrations of air entering the New York City metropolitan area are often already above the current federal standard of 120 parts per billion (ppb). For example, the Chester site referred to earlier lies in an area of New Jersey with low primary emissions which is infrequently downwind of the metropolitan region. On days with southwest winds the O₃ daily maxima at Chester are frequently above 120 ppb but are considerably lower than the daily maxima at Connecticut sites. Thus, on these days the O_3 content of the air entering the metropolitan region is frequently above the standard but is considerably less than the O_3 content of the air leaving the region and entering Connecticut.

Chemical Kinetic Modeling

Although a chemical simulation of an entire multistate region is currently intractable, chemical changes in air parcels upwind, within, and downwind of portions of the New York City metropolitan region on sunny summer workdays have been studied with the use of a chemical kinetic model. These calculational approaches were developed originally to simulate the air quality over the three northern New Jersey counties, Morris, Essex, and Hudson, and the computational results have been validated against air quality data (11). To extend this formulation to study downwind chemistry while avoiding the meteorologically complicating factors of the ocean-riverland system of New York City and Long Island, three fictitious counties were created; the resulting matrix is shown in Fig. 3. The emissions in Shopview County are set equal to those for Essex (less power plants). Those for Deerfield and Farmland counties are set equal to those for Morris County. Computations were performed (12) for each county on a sequential basis, following the typical westerly wind pattern. The resulting chemistry thus reflects both the local emissions of trace species and the advection from areas upwind.

The computed profile of O_3 maxima for the six-county calculation is shown in



Fig. 4, where the calculated concentrations resulting from primary emissions at current levels are indicated by circles. (The calculations depicted by the squares and triangles will be discussed later.) An O_3 decrease is seen as the urban area is approached from upwind, followed by an increase downwind to values above those of the background level. This, then, agrees with the pattern in the data.

The chemical explanation of the Fig. 4 results is straightforward. As one approaches the urban area, with its high density of combustion and motor vehicle sources of NO, the O_3 concentration decreases (Eq. 3). Downwind, the oxidation of NO by reactions such as 4 and

$$NO + HO_2 \rightarrow NO_2 + HO \rightarrow (9)$$

and the decrease in NO source density combine to increase the O_3 concentration.

The influence of the urban "plume" on downwind air quality manifests itself in a variety of photochemical products in addition to these mentioned above. The geographical profiles of evening concentrations of the four photochemical products discussed earlier are shown for the six-county calculation in Fig. 5. In each case the product concentrations are higher downwind of the urban area than within the urban area itself. This prediction for gaseous chemical products has not yet been confirmed by field measurements.

Effects of Changes in Emission Patterns

Although the air quality consequences of changes in primary emissions are of substantial interest, extensive empirical data for such studies are unavailable. Some information, however, is provided by an analysis of the air quality resulting from the regular decrease in emissions on weekends (3). Sites that are downwind of the New York City metropolitan region with respect to prevailing winds (Massachusetts, Connecticut, and Long Island) generally show a reduction of the high level of daily maximum O₃ concentrations of approximately 10 to 25 percent on weekends. Sites within or upwind of the region show little change on weekends. In the downwind areas where a change occurs there is a reduction on weekends and on Monday, and then a gradual increase from Tuesday to Friday. Such a pattern mirrors the measured CO concentrations and traffic counts within the metropolitan region. Concentrations of O₃ in Connecticut are of particular importance since, as stated in an earlier section, they are the highest in the Northeast (13). It therefore seems important to have a clear and concise de-



Fig. 4. Computed diurnal maximum concentrations of NO, NO₂, and O₃ in the six counties. Symbols represent man-made emission rates equal to (Δ) 25 percent of current values for NO and hydrocarbons, (\bigcirc) current values for NO and hydrocarbons, and (\square) 150 percent of current values for NO and hydrocarbons.

scription of the weekend reduction in O_3 for the state as a whole. This was done by grouping together the data from all nine Connecticut sites. For concentrations above the current federal standard of 120 ppb, the weekend reduction is approximately 20 percent.

To illustrate the statistical methodology used to arrive at the weekend-weekday conclusion, we will describe one of the data analytic techniques, an empirical quantile-quantile (EQQ) plot (14), used in the analysis. The pth percentile (quantile) of a set of data is a value such that p percent of the data is less than or equal to the value. For instance, the median is the 50th percentile. On the EQQ plot, percentiles of one set of data (for example, weekends) are plotted against corresponding percentiles of the other set of data (for example, Tuesdays to Fridays). In the special case when both sets of data have the same number of observations this amounts to plotting the largest concentration from one data set against the largest from the other, the next largest against the next largest, and so on. If the distributions are nearly the same, then the points of the plot lie close to the line Y = X. The most important feature of the EQQ plot is that it allows comparison of values of the concentration distributions across the entire range of values from smallest to largest. EQQ plots were made comparing weekend and Tuesday-Friday daily maximum O₃ concentrations at all sites (3). One such plot is shown in Fig. 6. Most of the points of the plot lie below the line Y = X, which indicates higher concentrations on Tuesday to Friday than on the weekend.

As discussed earlier, one of the strengths of a chemical kinetic model is its potential for studying the effects of primary emission reductions by computationally varying the rate of emissions and analyzing the results. For this purpose, the upwind and downwind effects produced by changes in emissions have been studied (12) in two computations with the model described in the previous section. In the first of these, the primary man-made emissions were increased by 50 percent; in the second they were decreased by 75 percent. In both cases, natural emissions were held constant. Figure 4 shows the results of these two computations and the result of the computation with NO and hydrocarbons at current levels. In all counties NO and NO₂ decrease with decreasing emissions. However, the result for O_3 is mixed; in Essex and Hudson, which have high primary emissions, O₃ decreases with increasing emissions, while in the downwind county, Farmland, O₃ decreases with decreasing emissions. The result is quite consistent with the data analyses presented earlier.

Although no data exist on the effects of varying NO and hydrocarbons independently, the rather broad agreement of calculational results with data suggests that chemical kinetic model computations may provide some insight into these questions. Such computations have been performed with the model (12); representative results are given in Fig. 7. A very consistent pattern emerges for all of the secondary products shown, except for O₃. Major changes in hydrocarbon emissions have little effect on the generation rate of these products, while changes in the NO emissions produce major changes in the products, both within the urban area and downwind. This interesting circumstance results from the central position of the hydroxyl radical in urban photochemistry (for example, reactions 5 to 8). The concentration of the hydroxyl radical in northeast urban areas is controlled by the rate of the reaction

$$NO + HO_2 \rightarrow NO_2 + HO \rightarrow (10)$$

which is in turn controlled by the supply of NO available (12, 15). The supply of odd nitrogen compounds (NO, NO₂, HNO₃) thus appears to be very important in the production of many secondary contaminants (16).

In the case of O_3 , the response to changes in primary emissions cannot be expressed as simply. Increases or decreases in man-made hydrocarbon emissions are reflected (as a result of processes represented by reaction 4) in the calculated local and downwind O₃ concentrations, but the effects are small. For the specific conditions used in the calculation, man-made hydrocarbon emission changes of 50 percent resulted in less than 5 percent changes in O₃ concentrations. Within urban regions, increases in NO emissions result in decreased local O₃ levels, as a consequence of reaction 3. Downwind, the NO is increasingly oxidized to NO₂, the NO source density decreases, and the O₃ concentrations increase sharply. Our computations do not extend far enough downwind to show O₃ levels greater than those that occur under normal emission conditions. Such a result is suggested, however, by the dashed curve of Fig. 4 for concomitant increases in hydrocarbon and NO emissions and by the minimal response of O_3 to hydrocarbon emission changes.

Calculations performed with decreased levels of NO emissions show increases in O_3 in the densely populated 22 JUNE 1979



Fig. 5. Computed concentrations of the photochemical products acrolein, nitric acid, peroxyacetyl nitrate (PAN), and sulfate in the six counties at 7 p.m. for days with normal emissions, sun, and wind.

counties that are strong source regions. The O_3 increases downwind of the urban area are smaller than before, however. These responses indicate that the effects of changes in source configuration or strength can only be logically assessed on a regional basis.

It is tempting to try to generalize the above results on emissions reductions to other geographic areas, but compelling reasons exist for the restriction of their applicability. In particular, we note the large difference in the trace species content of the air supplies to the Northeast (17) and to the Los Angeles Basin (18). In both areas the concentrations of NO are sufficiently low that man-made emissions can readily perturb them. For nonmethane hydrocarbons, however, the clean oceanic air supply to the West Coast cities contrasts sharply with the continental air supply to the East Coast, the latter being preloaded with vegetative and man-made hydrocarbon emissions. The influence of local hydrocarbon emissions on total nonmethane hydrocarbon concentrations is therefore much greater on the West Coast than on the East.

Additional evidence for this may be provided by the observation of a correlation between winter rain and summer O_3 (19), the implication being that hydrocarbon emissions from vigorously growing vegetation are able to control atmospheric hydrocarbon chemistry. Finally, we note that in Houston a substantial reduction in man-made hydrocarbon emissions appears to have resulted in little change in O_3 (20). We thus conclude that the most important processes for air quality differ from region to region, and that remedial strategies must be developed individually for specific geographical areas.

Discussion

Three major conclusions regarding air quality in the Northeast United States were stated in the introduction. In the subsequent sections results from statistical analyses of contaminant and meteorological data and from chemical kinetic



Fig. 6 (left). Saturday-Sunday quantiles of O₃ daily maxima plotted against Tuesday-Friday quantiles of O₃ daily maxima for Danbury, Fig. 7 (right). Percent change in Conn. concentration of photochemical products at 7 p.m. in Hudson County, N.J., for different emission rates. The plots on the left show the results of varying hydrocarbon emissions with NO emissions held constant and equal to cur-



rent levels. Similarly, the plots on the right show the results of varying NO emissions with hydrocarbon emissions kept constant. In both cases the scale on the horizontal axis indicates the fraction by which current emissions are multiplied.

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modeling have been presented. In this section we discuss the derivation of the conclusions from the data analytic and modeling results.

Ozone concentrations in the New York City metropolitan region. The O₃ concentration of air as it enters the region differs little from the concentration within the region. In fact, at sites within the region that are near high NO emissions, the concentrations of O_3 are lower than at sites near low NO emissions. Thus, if all primary emissions in the region were eliminated, the O_3 content of the air within the region could be expected to be that of the air entering the region, which would be no less than it is now. Further verification of this conclusion is the fact that on weekends, when the primary emissions are reduced, the daily maximum O₃ concentration distribution within the region changes very little.

Chemical kinetic computer modeling has reproduced these results and has provided an explanation of the phenomenon in terms of the reaction of NO with O_3 . Furthermore, the model has shown that O_3 concentrations within the region do not decrease when primary emissions in the model are reduced. In fact, when NO is increased, O_3 decreases near strong NO sources, just as is shown by measurements.

Ozone concentrations in Connecticut. The northern New Jersey-New York City metropolitan region accounts for roughly 50 percent of the total emissions of NO and hydrocarbons in the northeast United States but only 16 percent of the total area. The air mass over the metropolitan region with these high concentrations of primary emissions frequently moves into Connecticut, since the prevailing winds during the summer months are from the southwest and the west. The O₃ concentrations at the Connecticut sites (and one site on Long Island) are approximately 20 percent higher than those at sites within or upwind of the New York City metropolitan region. Thus the presence of the region would appear to be the cause of the increase at the Connecticut sites, which have the highest O₃ concentrations in the Northeast. Increases in O3 concentrations at similar distances from major metropolitan areas have recently been reported for the Los Angeles (21) and St. Louis (22) regions as well.

Further verification that the metropolitan region is the cause of the 20 percent increase is the fact that sites which are frequently downwind of the region have the highest O₃ concentrations when the wind is blowing from the direction of the metropolitan region. In addition, the chemical kinetic model shows an increase in O₃ concentrations in areas that are downwind of the metropolitan region and provides a chemical explanation of the phenomenon.

Since the metropolitan region appears to be a direct source of the 20 percent O_3 increase in Connecticut, it seems likely that primary emission reductions within the region would decrease the O₃ concentrations in Connecticut. This is verified both from the data and from the kinetic model. On weekends, when primary emissions are reduced during the morning and afternoon because of decreased motor vehicle and industrial activity, O_3 concentrations are reduced by approximately 20 percent in Connecticut to levels that are similar to those upwind of the metropolitan region. Reductions of primary emissions in the chemical kinetic model also lead to reductions in O_3 concentrations in the areas that are downwind of the metropolitan region.

It is not precisely clear why the weekend reduction in primary emissions throughout the Northeast does not result in a decrease in O₃ concentrations at sites within and upwind of the New York City metropolitan region. A tentative explanation is that since the O_3 entering the region is the result of emissions occurring over a very large portion of the country, including the Midwest and the metropolitan regions to the southwest, the movement and diffusion of air masses would tend to smear out the effects of weekend reductions over all days of the week. However, since the Connecticut increase is due to a relatively close emission source, from which the movement into Connecticut can take just a few hours, the effect of the weekend reduction can be seen.

Effects of changes in nitric oxide and hydrocarbon emissions. Simultaneous reductions in both NO and hydrocarbon emissions result in O₃ increases within the New York City metropolitan region but lead to decreases downwind. The chemical kinetic calculations have shown that reductions solely in hydrocarbon emissions result in a slight local O₃ decrease while reductions solely in NO emissions lead to an increase in O_3 . But the increase diminishes in successive downwind "counties," with the implication that even farther downwind the trend would be reversed. In any case, further calculations, particularly those in which extreme meteorological inversion conditions are used, are needed before firm conclusions about the effects on O₃ of individual reductions of NO and hydrocarbons can be drawn.

It should be remembered that O₃ is only one of many constituents of photochemical air pollution. Among the other undesirable secondary products are sulfates, nitric acid, peroxyacetyl nitrate, and acrolein. Although these are not all of the undesirable products, they are, together with O₃, a representative cross section whose concentrations serve as a good characterization of the overall level of photochemical air pollution. The results of the chemical kinetic calculations indicate that reductions solely in NO emissions reduce the concentrations of these four products, both within and downwind of the New York City metropolitan region. But the calculations also show that major variations solely in hydrocarbon emissions cause little local or downwind change in these four products. Thus the evidence at this time suggests that in the Northeast NO control is the more effective strategy for an overall reduction of photochemical air pollution.

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