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CONTROL OF PHOTOCHEMICAL OXIDANTS - TECHNICAL BASIS AND IMPLICATIONS OF RECENT FINDINGS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
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SUMMARY

As part of the Clean Air Act's mandate to protect public health and enhance the environment, the Environmental Protection Agency has developed a program to attain and maintain the National Ambient Air Quality Standard for Photochemical Oxidants. This program requires the reduction in emissions to the atmosphere of the precursor chemicals that are responsible for the formation of oxidants. Control measures have been instituted at both the Federal and State level and include the Federal Motor Vehicles Control Program, the Federal program for control of aircraft emissions, development of Federal New Source Performance Standards for stationary sources, and those measures taken by the States through State Implementation Plans to attain the oxidant standard. State measures include such programs as control of stationary sources and Transportation Control Plans to control in-use motor vehicles and reduce vehicular traffic in urban areas.

Oxidants are not emitted directly into the atmosphere but result primarily from a series of chemical reactions between oxidant precursor compounds in the presence of sunlight. The precursors are organic compounds and nitrogen oxides, primarily emitted from motor vehicles and stationary sources. Several fundamental facts concerning oxidant formation have been important in developing a strategy to reduce oxidant concentrations. These are: (1) organic compounds do not all react at the same rate in the chemical process and while some react within several minutes, others may take many hours; (2) in addition to the absolute concentrations of precursors, the ratio of organic compounds to nitrogen oxides is important in determining the concentration of oxidants formed; and (3) meteorological conditions, such as sunlight ultra-violet intensity, temperature, and atmospheric stability affect oxidant production.

These considerations and our knowledge of the nature and distribution of precursor emissions form the basis of EPA's program for reducing oxidant concentrations by reducing emissions of organic compounds from all significant sources through the various Federal and State programs. EPA also requires reductions in nitrogen oxide emissions to meet the National Ambient Air Quality Standard for nitrogen dioxide, but does not require their reduction in order to control oxidant concentrations.

To insure the technical accuracy of the oxidant control strategy and to refine that strategy where necessary, EPA has conducted a continuing program of research studies and data analysis. New findings based on laboratory and field studies accomplished over the last several years generally support the control measures currently being taken and further indicate that additional measures may be necessary in order to meet the oxidant standard nationwide. These recent studies have documented frequent violations of the oxidant standard in both urban and rural areas although, in some urban areas, both the maximum concentrations of oxidants and the frequency of violations have decreased over the past several years. At rural locations, the number of violations of the standard and the maximum concentrations are sometimes as high and even higher than in nearby urban areas. It is thus apparent that oxidants are a rural as well as an urban problem.

The recent studies show that: (1) man-made emissions are the predominant source of high levels of oxidants, even in remote rural areas; (2) the contribution of natural sources of oxidants is usually not more than 0.05 ppm, compared with the oxidant standard of 0.08 ppm; and (3) transport of oxidants and their precursor compounds has been demonstrated to about 50 miles downwind of urban areas and it is likely that transport over longer distances occurs. It also has been shown that the highest oxidant concentrations in the Midwest in both rural and urban areas occur during periods of stagnant conditions associated with high pressure weather systems.

In both urban areas and in many non-urban areas, there appear to be sufficient emissions of man-made precursors to account for the high oxidant levels observed. While transport of oxidants and their precursors may occur, most urban areas probably are responsible for their own oxidant problem. The high oxidant levels in non-urban areas appear to be the result of both locally produced precursors and precursors transported from urban and other non-urban sources. As a result, control strategies for non-urban areas will need to be directed at measures which reduce emissions from both non-urban sources as well as urban sources and which meet the specific needs of each of these areas.

The following implications from the new findings are suggested:

- Continued application of hydrocarbon control measures in the urban area. Because of the high precursor emission densities and the great numbers of people exposed to oxidants, continued emphasis on intensive

control measures within cities will be necessary to meet the oxidant standard in major urban areas.

- Increased control over wide geographic areas through Federal and State programs to meet standards in non-urban areas. In addition to the continued intensive control of hydrocarbon emissions in urban areas, it may be necessary to extend some measures under present State Implementation Plans to include non-urban areas as well as cities.

- Increased control of stationary sources. Although mobile source controls (including Transportation Control Plans) will continue to be a major part of the oxidant control program, there is a need for more stringent control of precursor emissions from stationary sources.

- Increased emphasis on controlling all reactive organics. Both under conditions of transport and under persistence of stagnant air masses there can be sufficient time for less reactive hydrocarbons to contribute to oxidant formation. This indicates the importance of controlling all organic compounds which can form oxidants.

- Control of nitrogen oxides as well as hydrocarbon emissions may become necessary to meet the oxidant standard nationwide. Nitrogen oxides emissions may be transported into rural areas and contribute to oxidant formation by reaction with locally emitted organic compounds. It may eventually become necessary to consider control of nitrogen oxides, coordinated with the control of hydrocarbons, as a part of the oxidant control strategy.

- Emissions from natural sources. Oxidant concentrations which can be attributed to natural sources are usually less than 0.05 parts per million compared with the oxidant standard of 0.08 parts per million. Because of emissions from natural sources, more stringent reductions of man-made emissions may be necessary in some areas.

Further refinement of the oxidant control strategy requires a more quantitative understanding of the chemical and the meteorological processes leading to high oxidant concentrations. EPA is engaged in an extensive program of laboratory and field studies to obtain the needed information. The program includes studies to quantify the relationship between emissions of precursors and concentrations of oxidants in the air at both urban and non-urban locations. More extensive data are being obtained on atmospheric levels of oxidants and precursors as well as

data on natural and man-made precursor emissions. It is expected that through this program the current strategy will evolve over the next several years to include the best measures needed to control oxidants in both urban and non-urban areas.

CONTROL OF PHOTOCHEMICAL OXIDANTS - TECHNICAL BASIS AND IMPLICATIONS OF RECENT FINDINGS

INTRODUCTION

The strategy used by the Environmental Protection Agency for reducing the concentrations of photochemical oxidants was largely formulated by 1972. Although the strategy has undergone some refinements, it still retains the main features developed at that time. Laboratory and field studies over the last several years have contributed much new information about oxidants. While the understanding of these new findings and of the overall oxidant problem is not yet complete, the new findings generally support the control measures that are being taken. Furthermore, the accumulating base of data indicates that additional measures may be needed in order to meet the oxidant standard nationwide.

This paper discusses the current strategy and its technical basis. It reviews the recent findings and discusses their implications for further increasing the effectiveness of the strategy. It identifies the topics which must be better understood before an optimum strategy can be developed and implemented, and it indicates the study programs underway or planned to provide the needed understanding.

EFFECTS OF OXIDANTS ON THE ENVIRONMENT AND THE OXIDANT STANDARD

Oxidants are strongly oxidizing compounds which are the primary constituents of photochemical smog. The oxidant found in largest amounts is ozone, a very reactive form of oxygen. Oxidants also include the group of compounds referred to collectively as PAN (peroxyacyl nitrates) and other compounds produced in much smaller quantities. The most accurate technique for determining oxidant concentrations is one that measures ozone rather than total oxidants. This measurement method (chemiluminescent) is the one recommended by EPA and was the method used to develop most of the data in this report. Consequently, although the term oxidant is used often in the text, the discussion of measurements refer to ozone values.

Adverse effects on human health resulting from exposures to very low concentrations of oxidants have been extensively documented for both man and experimental animals (Ref. 1, 2). Also low levels of oxidants have adverse effects on many forms of vegetation and microorganisms and on materials such as rubber, cotton, nylon, and polyesters. National Ambient Air Quality Standards have been established to protect human health (the primary standard) and to prevent adverse welfare effects (the secondary standard). For oxidants, both of these standards have been established at an ambient concentration of 0.08 parts per million (ppm) which is equivalent to 160 micrograms per cubic meter ($\mu g/m^3$) This is an hourly average not to be exceeded more than once a year.

FORMATION OF OXIDANTS IN THE ATMOSPHERE

This section presents the technical basis for the approach used by EPA to control oxidants. Oxidants are not emitted directly into the atmosphere but result primarily from a series of chemical reactions between oxidant precursors (nitrogen oxides and organic molecules) in the presence of sunlight. The principal sources of organic compounds are the hydrocarbon emissions from automobile and truck exhausts, gasoline vapors, paint solvent evaporation, open burning, dry cleaning fluids, and industrial operations. There are also natural sources such as seepage from the ground and emissions from vegetation. Nitrogen oxides are emitted primarily from combustion sources such as electric power generation units, gas and oil-fired space heaters, and automobile, diesel and jet engines. Nitric oxide (NO) is the major form of nitrogen oxide emitted in combustion processes. Nitrogen dioxide (NO_2) is formed from NO and is the compound which decomposes in sunlight to initiate the formation of ozone.

The factors which determine the concentrations of oxidants formed in the atmosphere include: (1) the amount and kinds of organic compounds initially present and the rate at which additional organics are emitted to the atmosphere; (2) the amount of nitrogen oxides initially present and their emission rates; and (3) sunlight ultra-violet intensity, temperature, and other meterological factors. The interaction of these factors and the chemical reactions involved are very complex and have been the subject of continuing scientific investigation during the last 20 years, including atmospheric studies, laboratory smog chamber studies, and computer simulation of the oxidant forming process.

A large number of chemical reactions that may affect oxidant concentrations are now known (Ref. 3, 4, 5). A summary of the photochemical process for producing oxidants is shown in Figure 1 and a simplified summary of the reactions is presented in Table 1. In the oxidant forming process, organic compounds are oxidized to form peroxy radicals and aldehyde compounds. The peroxy radicals rapidly react with nitric oxide (NO) emissions to form nitrogen dioxide (NO_2). In the presence of ultra-violet light the NO_2 decomposes back to NO and

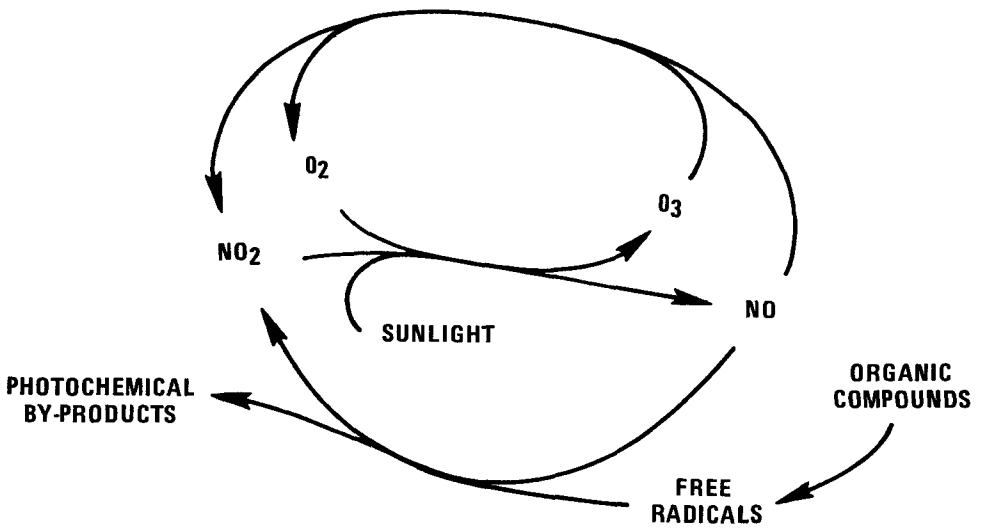


Figure 1. Photochemical production of oxidants.

TABLE 1. SIMPLIFIED SUMMARY OF CHEMICAL REACTIONS FOR PRODUCTION OF OXIDANTS

- OXIDATION OF ORGANIC COMPOUNDS TO FORM PEROXY RADICALS

  $CH_3CH = CH_2 + OH^{\cdot} \xrightarrow{O_2} CH_3CH_2\text{-}O\text{-}O^{\cdot} + H_2CO$

  PROPYLENE PEROXY RADICAL FORMALDEHYDE

- ALDEHYDES + O_2 + SUNLIGHT → ADDITIONAL PEROXY RADICALS

- PEROXY RADICALS CONVERT NO TO NO_2

  $CH_3CH_2\text{-}O\text{-}O^{\cdot} + NO \rightarrow NO_2 + CH_3\,CH_2\text{-}O^{\cdot}$

  $CH_3CH_2\text{-}O^{\cdot} + O_2 \rightarrow HO_2^{\cdot} + CH_3HCO$ ACETALDEHYDE

  $HO_2^{\cdot} + NO \rightarrow NO_2 + OH^{\cdot}$

  UP TO FOUR CONVERSIONS FOR EACH CARBON ATOM

- OZONE FORMING REACTION

  $NO_2 + O_2 \xrightarrow[\text{ULTRA-VIOLET}]{} NO + O_3$

- OZONE SCAVENGING REACTION

  $NO + O_3 \rightarrow NO_2 + O_2$

- PHOTOCHEMICAL BY-PRODUCTS FORMED

  ALDEHYDES, PAN, AEROSOLS, NITRIC ACID, H_2O_2, $OH^{\cdot}$, CO_2

simultaneously forms ozone (O_3). The NO_2 can also react with the peroxy radicals to form peroxyacyl nitrates (PAN). The importance of the organic compounds in the process is to convert the NO to NO_2. This reduces the concentration of the NO molecules which react to destroy ozone and also increases the concentration of the NO_2 needed to produce ozone. In the series of reactions that are possible, as many as four molecules of ozone can be generated for each carbon atom in the organic molecules.

Much of the information about the oxidant producing reactions has been obtained from smog chamber experiments. The results of a typical smog chamber experiment are presented in Figure 2 (Ref. 6). These results show a decrease in the reactive hydrocarbon, propylene, as the aldehyde compounds and the oxidants, ozone and PAN, are formed. The impact of the various reactions on the nitrogen oxides leads to low levels of NO and a maximum in the nitrogen dioxide concentration approximately one hour after the reactions start.

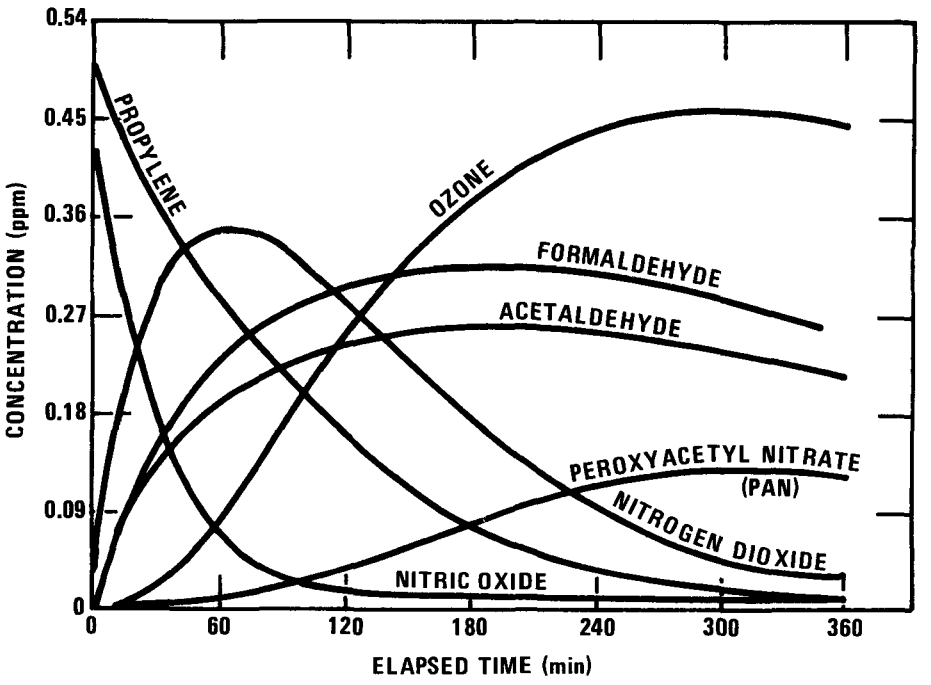


Figure 2. Results of a typical smog chamber experiment. Irradiation of a propylene-NO-NO_2 mixture in air. Initial experimental conditions - 0.5 ppm propylene, 0.45 ppm NO, and 0.05 ppm NO_2 in 760 torr of highly purified air.

Several observations are related to this oxidant forming process. They are:

1. It has been shown in smog chambers that organic compounds do not all react at the same rate in the photochemical process (Ref. 7). However,

given long irradiation times and sufficient amounts of nitrogen oxides, almost all organic compounds react to form oxidants. Very reactive compounds lead to high oxidant levels within a few hours of their emissions. Less reactive compounds form oxidants over longer times and may react as they move with an air mass and thus contribute to observed oxidant concentrations later in the day or far downwind of their source. There are thousands of organic compounds in typical use. Gasoline may contain more than two hundred compounds whose composition will vary by brand and by season of the year. Since the organics emitted to the air include many of these compounds, there is an extensive variety of reactions occurring in the atmosphere.

2. In the immediate vicinity of nitric oxide sources,such as near power plants and highways, relatively little ozone is found. Ozone reacts rapidly with nitric oxide and is destroyed, but NO_2 is formed. In the presence of sunlight, the NO_2 can later react to form ozone again. These interactions between ozone and the nitrogen oxides help explain several observations. Ozone concentrations are usually low at night in urban areas because the NO emissions act to destroy ozone and the absence of sunlight prevents additional ozone formation. City ozone concentrations are often lower than in adjacent suburban or rural areas because the NO emissions in the city are high and thus reduce the urban ozone concentrations.

3. In addition to the absolute concentration of precursors and the meteorological factors, such as sunlight and temperature, which directly affect the concentration of oxidants formed, the ratio of organic compounds to nitrogen oxides is important in determining the concentrations of oxidants formed. Smog chamber studies have shown that both very high and low ratios of organic compounds to nitrogen oxide suppress the amount of oxidants formed (Ref. 8). For intermediate ratios, the rate of formation and concentrations of oxidants formed depends on the type of organic compound and the ratio of organic to nitrogen oxide. For most urban areas, the ratio of organic compounds to nitrogen oxides in the atmosphere is such that reducing the ratio will help to reduce the oxidant concentration.

4. The highest concentrations of oxidants are most frequently observed in the afternoon hours. These highest levels of oxidants are formed by

reactions of the precursor organic compounds and nitrogen oxides that were emitted earlier in the day or had accumulated from previous days. Since both organics and nitrogen oxides are removed from the atmosphere during the photochemical reactions, the highest concentrations of these pollutants are thus usually observed during the early morning hours at the start of the photochemical process.

OXIDANT CONTROL STRATEGY

On the basis of the knowledge and understanding of oxidant formation presented above, EPA has approached the control of photochemical oxidants by requiring the reduction of atmospheric emissions of hydrocarbons and other organic compounds. Although a National Ambient Air Quality Standard has been established for hydrocarbons, this standard serves only as a guide for achieving the oxidant standard and is not based on health criteria. Since methane is the most naturally abundant and the most unreactive hydrocarbon species, only non-methane hydrocarbon compounds are specified in the air quality standard. This standard is 0.24 ppm (160 micrograms/cubic meter) for the 3-hour concentration measured from 6 to 9 a.m. A National Ambient Air Quality Standard also has been established for nitrogen dioxide (NO_2). This standard is based on the health effects of nitrogen dioxide. Reductions in nitrogen oxide emissions are required to meet this standard but are not required for the control of oxidant concentrations.

The reductions in emissions of hydrocarbons and other organic compounds are to be achieved through Federal and State programs which have been formalized in regulations (Ref. 9) promulgated under the Clean Air Act. The Federal programs provide for the reduction in emissions nationwide through the Federal Motor Vehicle Control Program, the Federal program for control of aircraft emissions, and the development of New Source Performance Stadards. The State programs provide for additional control measures through State Implementation Plans in those areas of the country where the Federal programs will not be sufficient to meet the air quality standard for oxidants. These programs are discussed in the following sections.

FEDERAL PROGRAMS FOR OXIDANT CONTROL

Because roughly half of the hydrocarbons emitted to the ambient air in the United States are attributable to motor vehicles, a large portion of hydrocarbon reduction is to be achieved through the Federal Motor Vehicle Control Program. This program has required progressively stricter hydrocarbon controls on all light duty motor vehicles since the 1968 model year. In 1970, Section 202 of the Clean Air Act required that hydrocarbon emissions from light duty vehicles and

engines be reduced by at least 90% from emissions permissible in 1970 model year vehicles. This will eventually require emissions to be reduced to 0.41 grams per mile. Interim standards of 1.5 grams per mile (g/m) are now required on 1975 through 1977 model year vehicles. Regulations also exist to limit hydrocarbon emissions from other types of vehicles such as motorcycles, trucks, buses, and aircraft.

Section 111 of the Clean Air Act also authorizes EPA to promulgate "Standards of Performance for New Stationary Sources." These are standards for new sources which reflect the best demonstrated system of emission control, taking the cost of emission reduction into account. New sources are sources which are constructed or modified after the standard has been proposed. So far only one new source performance standard has been promulgated for hydrocarbon reductions. This is the standard for Storage Vessels for Petroleum Liquids (March 8, 1974, Federal Register). There are many other hydrocarbon emitting industrial operations where standards of performance may be appropriate. Some possible sources are industrial degreasing, fabric dry cleaning, service station gasoline transfers, automobile finishing and other industrial surface coating operations. EPA is currently studying each of these areas to gather background data. Standards of Performance for these sources are scheduled for promulgation between 1976 and 1978.

STATE PROGRAMS FOR OXIDANT CONTROL

Because the Federal programs will not be sufficient to meet the oxidant standard in all locations, each State has been required to develop plans for additional reduction in emissions of organic compounds in those areas which will not meet the oxidant standard.

To assist States in preparing Implementation Plans, EPA published guidelines in the August 14, 1971 Federal Register entitled, "Requirements for Preparation, Adoption and Submittal of Implementation Plans." Twenty-seven States have promulgated regulations to reduce hydrocarbon emissions in some portion of the State. In the other States, hydrocarbon regulations are left to local jurisdictions. The State Implementation Plans include regulations for existing stationary sources as well as the implementation, where necessary, of Transportation Control Plans.

For the development of Implementation Plans, it is necessary to determine how much the emissions of hydrocarbons and other organics must be reduced. It was realized that the relatively simple methods used for directly emitted pollutants

were not appropriate for the complex oxidant formation processes. Therefore, an attempt was made to quantify the amount of hydrocarbon reduction required to meet the oxidant standard. In 1970, the data to relate non-methane hydrocarbon to oxidant concentrations were available only from Denver, Los Angeles, Philadelphia, and Washington, D.C. The 6 to 9 a.m. average non-methane hydrocarbon concentrations were plotted against the peak hourly oxidant concentrations observed later in the day at the same measurement sites (Ref. 10). The points scattered because of the variations in the conditions which affect oxidant formation. A curved line was drawn to enclose these data points within an upper boundary. This upper limit curve depicted the highest oxidant levels observed for a given hydrocarbon concentration. From this curve the minimum hydrocarbon reductions required to meet the oxidant standard could be calculated. EPA published the result of this calculation as Appendix J in the August 14, 1971 Federal Register. Given a measured maximum oxidant level in an urban area, Appendix J is to be used to determine the amount of hydrocarbon control required in that area. In some cities the measured oxidant levels were above (greater than 0.28 ppm) the applicable range of Appendix J. These cities were permitted to reduce hydrocarbon emissions proportional to the amount that oxidant levels exceeded the standard.

Appendix B of the August 14, 1971 Federal Register also gives emission reductions which are attainable through the application of reasonably available emission control technology. These emission limitations emphasize reduction of total organic compound emissions, rather than substitution of less reactive organic compounds, because of the evidence that few organic compounds are photochemically unreactive. For organic solvent usage, however, such as in surface coatings and dry cleaning, the guidelines present a list of low reactivity compounds that may be considered for exemption for control. At present only fifteen States have rules controlling emissions from organic solvent usage. The rules differ in detail from State to State, but most of the States have adopted rules for organic solvents patterned after the Los Angeles Rule 66 (Ref. 11) rather than the Appendix B guidelines. This rule defines a group of photochemically highly reactive compounds and regulates the emissions of these defined compounds.

Transportation Control Plans (Ref. 12) provide for reductions in hydrocarbon emissions beyond the reductions achieved by the Federal Motor Vehicle Control Program and stationary source regulations set forth in approved State Implementation Plans. Pollutant reductions are to be achieved by such measures

as decreases in vehicle miles traveled, inspection and maintenance programs, retrofit emission controls for certain vehicles, gasoline supply limitation, and gasoline transfer vapor control. There are currently twenty-one Air Quality Control Regions which have transportation control plans for oxidant control. The compliance dates for six of these plans is May 31, 1975, while the other fifteen have attainment dates between 1975 and May 31, 1977.

RECENT FINDINGS

In addition to the control measures being taken under the regulations discussed above, EPA and others have been conducting field investigations and laboratory studies to better understand the oxidant problem. The recent studies have provided several new insights and strengthened the understanding of the oxidant formation process. Oxidant monitoring at various locations has provided data for determining concentration trends. Studies in the eastern United States have shown that the oxidant standard is often exceeded over large parts of that region and that oxidant concentrations in rural areas can be equal to or exceed those in urban areas. The studies have related the observed oxidant concentrations to atmospheric phenomena which affect oxidant formation and transport and to the man-made and natural sources of oxidants and their precursors. These studies and phenomena are summarized and discussed in the following sections.

RECENT TRENDS OF OXIDANT CONCENTRATIONS

Hydrocarbon emissions in the United States reached a maximum in 1968 and have decreased by about 7 percent between 1968 and 1972 as a result of emission control measures. At the same time nitrogen oxides emissions have increased by about 25 percent from 1968 to 1972 and had doubled from 1960 to 1970 (Ref. 13). Thus, in the typical urban environment, both the hydrocarbon emissions and the hydrocarbon to nitrogen oxide ratio has decreased. The result has been that in Los Angeles, in urban areas of New Jersey, and in other center cities, both oxidant levels and the number of violations of the oxidant standard has decreased (Ref. 14-16). For example, in Los Angeles and in the New Jersey areas, the number of days in which the oxidant standard has been exceeded decreased more than 50 percent between 1965 and 1972. In smaller urban areas of southern California, such as Riverside, Palm Springs, and Indio, maximum oxidant concentrations have also decreased from 1971 through 1974 although the number of violations has remained high (Ref. 17). These trends in maximum oxidant concentrations are presented in Figure 3. While these downward trends in oxidant levels are generally typical, there of course may be locations where levels have not been decreasing. The large increase in downtown Los Angeles for 1973 is because of unusual meterological conditions.

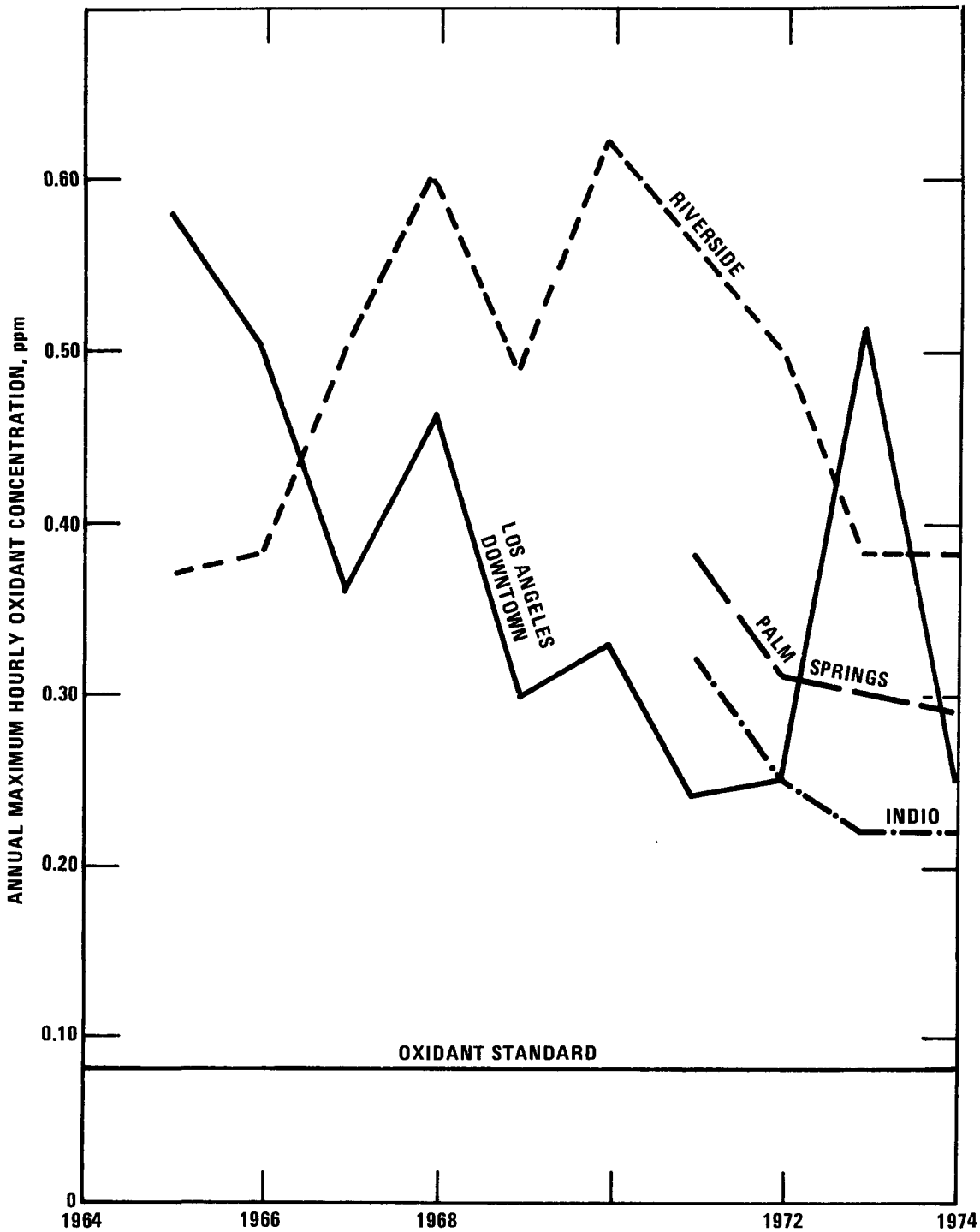


Figure 3. Southern California oxidant trends.

Figure 4 shows how variable the year to year behavior of oxidant levels can be. This figure presents the average ozone readings by hour of the day for a rural site near McHenry, Maryland (Ref. 18). A possible reason for the variability was the fact that frontal movements recorded in 1973 were almost all classified as weak. Therefore, they may have lacked the vigorous vertical mixing and flushing action normally experienced during frontal passages. This may help to explain the generally higher ozone levels experienced in 1973 at McHenry relative to 1972 and 1974.

A related observation is that ambient levels of oxidant in urban areas are sometimes higher on the weekends than during weekdays, even though traffic and industrial emissions are presumably lower, particularly during the morning hours on Sunday. These results have been observed in a number of cities, including Los Angeles, Indianapolis, and Linden, New Jersey (Ref. 19).

The general observations are that daily average oxidant concentrations are higher on weekends and that, in some cities, levels above 0.08 ppm occur more frequently on weekend days than on weekdays. However, the highest oxidant concentrations do not appear to occur as frequently on weekends as on weekdays. The detailed investigation of temporal and spatial distribution of emissions, the meteorology, and chemical composition of the air in the cities has not yet been accomplished in sufficient detail to fully explain these observations. As explained below, many factors may be operating simultaneously to cause the higher weekend oxidant concentrations. Because these factors may be specific to weekend behavior, the observations of weekend oxidants should not be construed as a test of oxidant strategy measures. In urban areas where reductions in hydrocarbon emissions have been achieved, long-term reduction in oxidant concentration has occurred both during the week and on the weekends.

Several important observations can be made about the weekend oxidant concentrations. First, the air entering or remaining in the city on weekends may contain oxidants, precursors, and partially reacted intermediates which have persisted from earlier days. Secondly, detailed emission inventories are not available to completely specify the differences in emission patterns between weekdays and weekends. Saturday driving patterns are no doubt different from weekday patterns, but automobile emissions in the total metropolitan areas may not be significantly lower on Saturdays. In industrial areas on Saturday and Sunday, and in all urban areas on Sunday, it is likely that emissions of both hydrocarbons and nitric oxide (NO) are reduced considerably. Thirdly, there are data from Los

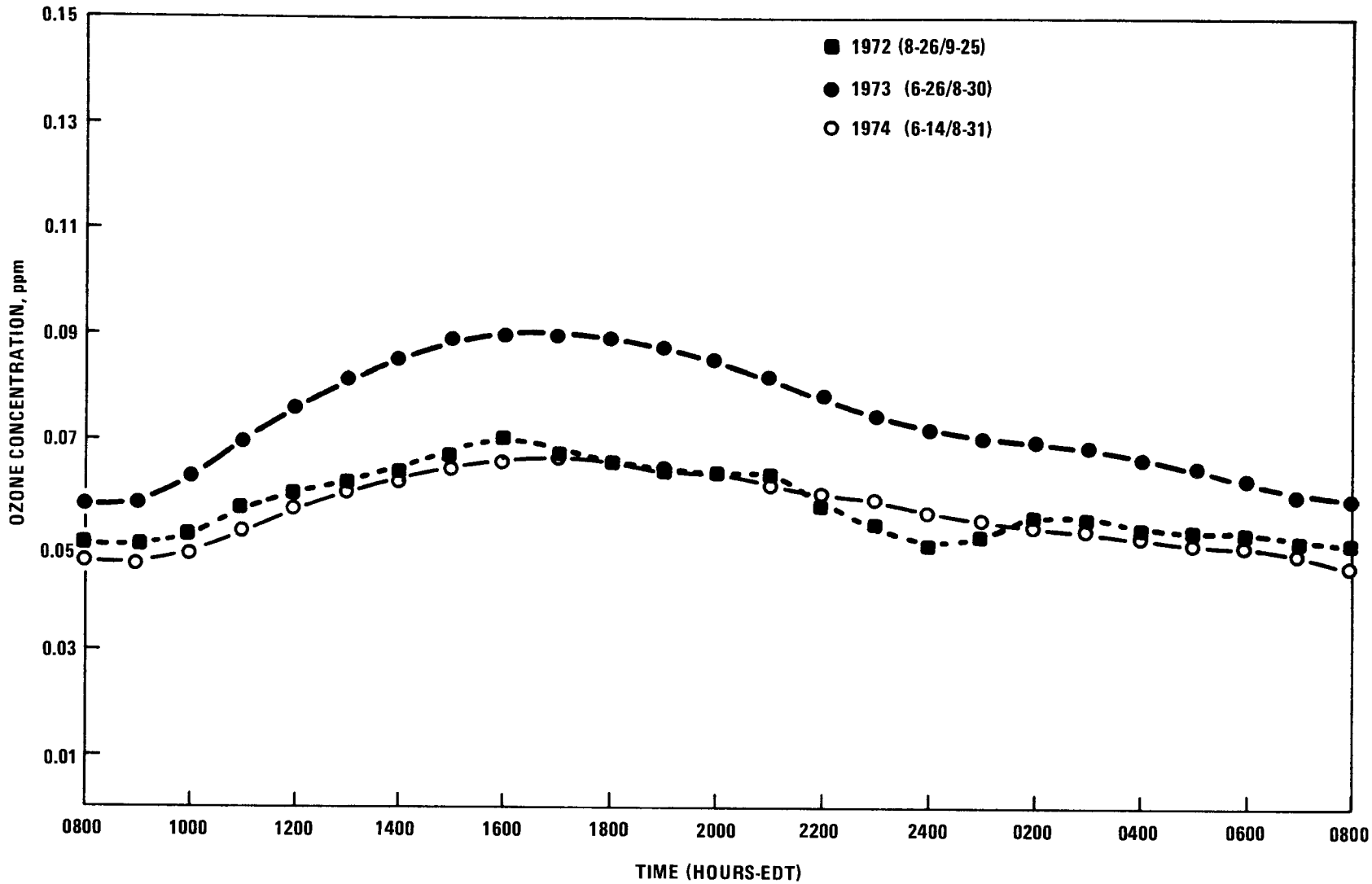


Figure 4. Mean diurnal ozone concentration at McHenry, Md. (Garrett County Airport) station for 1972, 1973, and 1974.

Angeles, urban New Jersey, and other cities to indicate that the ratio of NO to NO_2 is decreased on weekends. The hydrocarbon to nitrogen oxide ratio also increases on weekends. These last observations indicate that less NO may be available on weekends to scavenge ozone molecules, and that NO_2 concentrations, which can form oxidant, may have endured from prior days. Moreover, the weekend increase in the hydrocarbon to nitrogen oxide ratio cannot be explained by changes in traffic patterns alone. Finally, aerosols have been shown to be lower on weekends and solar radiation higher with the possible impact that scavenging reactions are reduced and photochemical reactions increased. The combination of these interacting factors results in the observations of higher average weekend oxidant concentrations.

RURAL OXIDANTS

Prior to 1970, measurements of oxidants in rural areas were made infrequently and did not indicate the presence of particularly high concentrations. But in the course of a study conducted by EPA in 1970, investigators found oxidant concentrations in a rural area of western Maryland and eastern West Virginia which frequently exceeded the national ambient air quality standard during the summer months. Follow-up studies of increasing magnitude were conducted in 1972, 1973, and 1974 (Ref. 18, 20, 21). The most extensive measurements were carried out in the summer of 1974 at widely separated sites in the eastern Midwest. It was found that the oxidant standard was exceeded on a significant number of days at both urban and rural sites. The rural sites exceeded the standard more often than urban sites and higher maximum concentrations were measured at the rural locations. Table 2 (Ref. 18) presents data on maximum ozone observed and frequency of ozone above the standard of 0.08 ppm (160 micrograms/cubic meter). Note that at DuBois, a small city in rural Pennsylvania, the oxidant standard was exceeded 341 hours during the period June 14 to August 31, 1974. During the same period at Pittsburgh, approximately 100 miles southwest of DuBois, the standard was exceeded only 106 hours. The maximum hourly concentration measured at DuBois was 0.20 ppm; at Pittsburgh it was 0.14 ppm. Similar high values of ozone have also been measured in rural areas of New York, New Jersey, Wisconsin, and Florida (Ref. 22). It thus appears that in many areas of the eastern United States high concentrations of oxidants are found in both rural and urban areas.

TABLE 2. OZONE DATA JUNE 14 - AUGUST 31, 1974

CITY	MAXIMUM CONCENTRATION (ppm)	DAYS EXCEEDING STANDARD (%)	NUMBER OF VIOLATIONS (TOTAL)
	RURAL		
WILMINGTON, OH.	0.18	58	259 HOURS
McCONNELSVILLE, OH.	0.16	56	239 HOURS
WOOSTER, OH.	0.17	55	262 HOURS
MCHENRY, MD.	0.17	43	262 HOURS
DUBOIS, PA.	0.20	54	341 HOURS
	URBAN		
CINCINNATI, OH.	0.18	44	54 HOURS
DAYTON, OH.	0.13	35	114 HOURS
COLUMBUS, OH.	0.15	27	113 HOURS
CANTON, OH.	0.14	44	148 HOURS
CLEVELAND, OH.	0.14	26	51 HOURS
PITTSBURGH, PA.	0.15	37	106 HOURS

SOURCES OF RURAL OXIDANTS

There are several possible sources of rural oxidants that must be considered in efforts to account for the observed concentrations. These sources include the large quantities of man-made precursors that are emitted in urban areas and which may move into rural areas while reacting to form oxidants, as well as oxidants formed from man-made precursors which originate in the non-urban areas. There are also two possible natural sources of rural oxidants. These are (1) downward transport from the ozone-rich layers in the stratosphere into the lower troposphere near the surface, and (2) photochemical generation from hydrocarbons emitted by vegetation. The available evidence strongly indicates that frequent and persistent concentrations of ozone near the surface above the oxidant air quality standard of 0.08 ppm are not caused solely by natural sources and that the background that can be attributed to natural sources is usually less than 0.05 ppm.

The amount of ozone transported from the stratosphere may be estimated from the numerous vertical ozone soundings of the atmosphere made in past years (Ref. 23). These generally show ozone concentrations at a maximum in the lower

stratosphere decreasing to very low levels at or near the tropopause and with a slight decrease downward toward the surface. Ozone levels near the surface that appear to be largely of stratospheric origin may at times range from 0.03 to 0.05 ppm. Temporary higher readings, however, are possible with unusually deep and vigorous vertical mixing induced by strong cold fronts, jet streams, thunderstorms, or some combination of these. These are sporadic, usually short-lived events lasting on the order of minutes or, less often, a few hours. Lightning from thunderstorms may also cause brief rises in ozone, but lightning by itself is considered an insignificant contributor to the ozone levels observed in rural areas (Ref. 24).

The natural organic compounds emitted by vegetation may react to form additional ozone or they may sometimes decrease it by scavenging reactions. The ozone added by reactions of natural hydrocarbons may increase the ambient ozone by 0.02 to 0.05 ppm (Ref. 25). However, the atmospheric conditions that are conducive to ozone production by the photochemical process are not usually the same conditions associated with transport from the stratosphere. Therefore, the high values of non-urban ozone that are frequently above the standard cannot be attributed only to natural sources, but rather, they appear to be primarily of man-made origin. The evidence for this conclusion is presented in the following section.

ATMOSPHERIC PHENOMENA WHICH AFFECT OXIDANT CONCENTRATION

Recent measurements downwind of urban centers (Houston, Phoenix, several Ohio cities, and Philadelphia) demonstrate that an identifiable urban plume of oxidants and oxidant precursors travels as far as 30-50 miles from the urban center (Ref. 18, 26, 27). In Los Angeles, where the magnitude of oxidant generation is greater, the distance can be extended to 75 miles or more downwind (Ref. 28). Beyond these distances, the individual urban contribution of pollutants becomes so mixed with other urban and non-urban contributions that the individual urban effect is difficult to distinguish. Therefore, while the transport of oxidants can partially explain the high oxidant levels at short ranges downwind of urban centers, it has been difficult to show definitely that transport is the principle cause of high readings at more remote sites. However, as described below, there is new evidence that oxidants and their precursors can be transported over longer distances.

To date, the most positive method for demonstrating that the high ozone concentrations observed at more remote locations are at least partially due to

emissions from man-made sources is by simultaneous measurements of ozone and compounds that are only emitted by human activity. Freon 11 is such a compound since it has no natural sources, is very stable in the lower atmosphere and has a measurable but slowly increasing global background concentration of approximately 90 parts per trillion. An increase above this background concentration is strong evidence for transport of air from areas of human activity. In studies during 1973 and 1974 at Whiteface Mountain, New York, at Elkton, Missouri, and in the Pacific Ocean between Seattle and San Diego, no levels of ozone above 0.08 ppm have been found in which Freon 11 levels were not also above the background. Figure 5 presents ozone and Freon 11 measurements at Whiteface Mountain from July 24-27, 1974 (Ref. 25). On July 24 ozone moved into the study area at 3 to 4 a.m. accompanied by an elevated Freon 11 level. July 25 was heavily overcast and there was little ozone formation. July 26 was sunny, Freon 11 was at normal background concentrations, and there was ozone production to 0.05 ppm during the day. On July 27 there were elevated Freon 11 concentrations, so that the ozone concentrations may have been due to local production and to ozone or precursors transported to the area. Thus, the higher levels of ozone measured on July 24 and July 27 are associated with high Freon 11 levels, which implies that these pockets of air had been transported from some area where man-made emission sources are present.

Certain meteorological phenomena may also help explain the high rural ozone concentrations. Figure 6 presents vertical ozone profiles taken at three times during one day during the 1974 summer studies (Ref. 18). These profiles are similar to other vertical measurements reported by other observers over Indianapolis and Canton, Ohio and are consistent with ozone soundings of previous years. The concentrations of ozone decrease above the subsidence inversion near 8000 feet as shown by the temperature profiles. The early morning profile indicates low ozone concentrations (0.02 ppm) beneath a radiation inversion that occurred between the surface and 2000 feet. Trapped between these two inversions is a layer of ozone above 0.09 ppm which had formed on previous days and had persisted through the night. In this layer, ozone has been separated from ground based scavenger pollutants and may persist for long periods of time and may be transported over long distances. At the surface below the radiation inversion, ground emissions of natural destructive agents and surface features provide a sink for the ozone. During the day, as the low level radiation inversion layer dissipates, the lower atmosphere becomes well mixed and oxidant, formed by

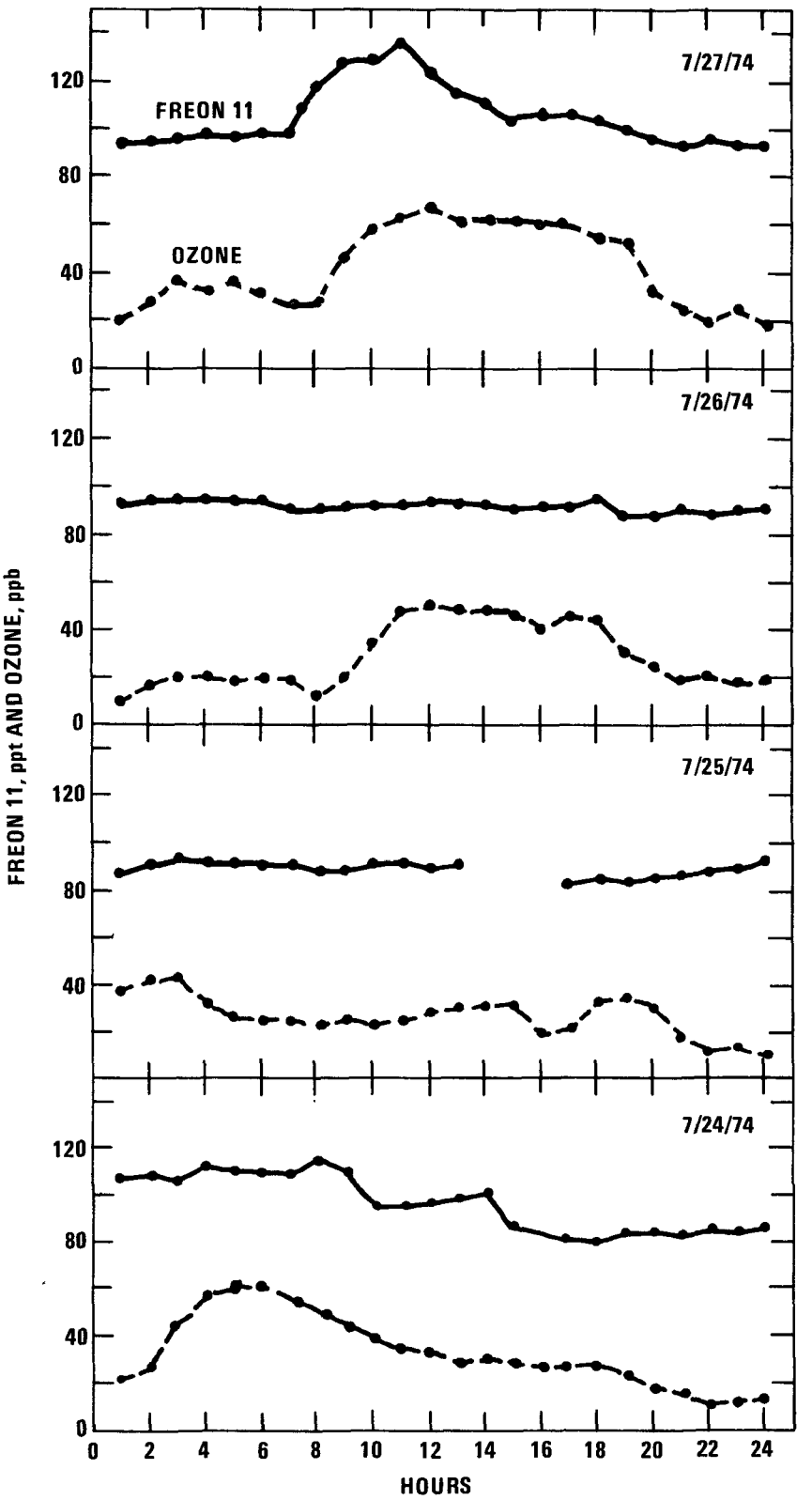


Figure 5. Hourly averages of Freon 11 and Ozone, Whiteface, New York.

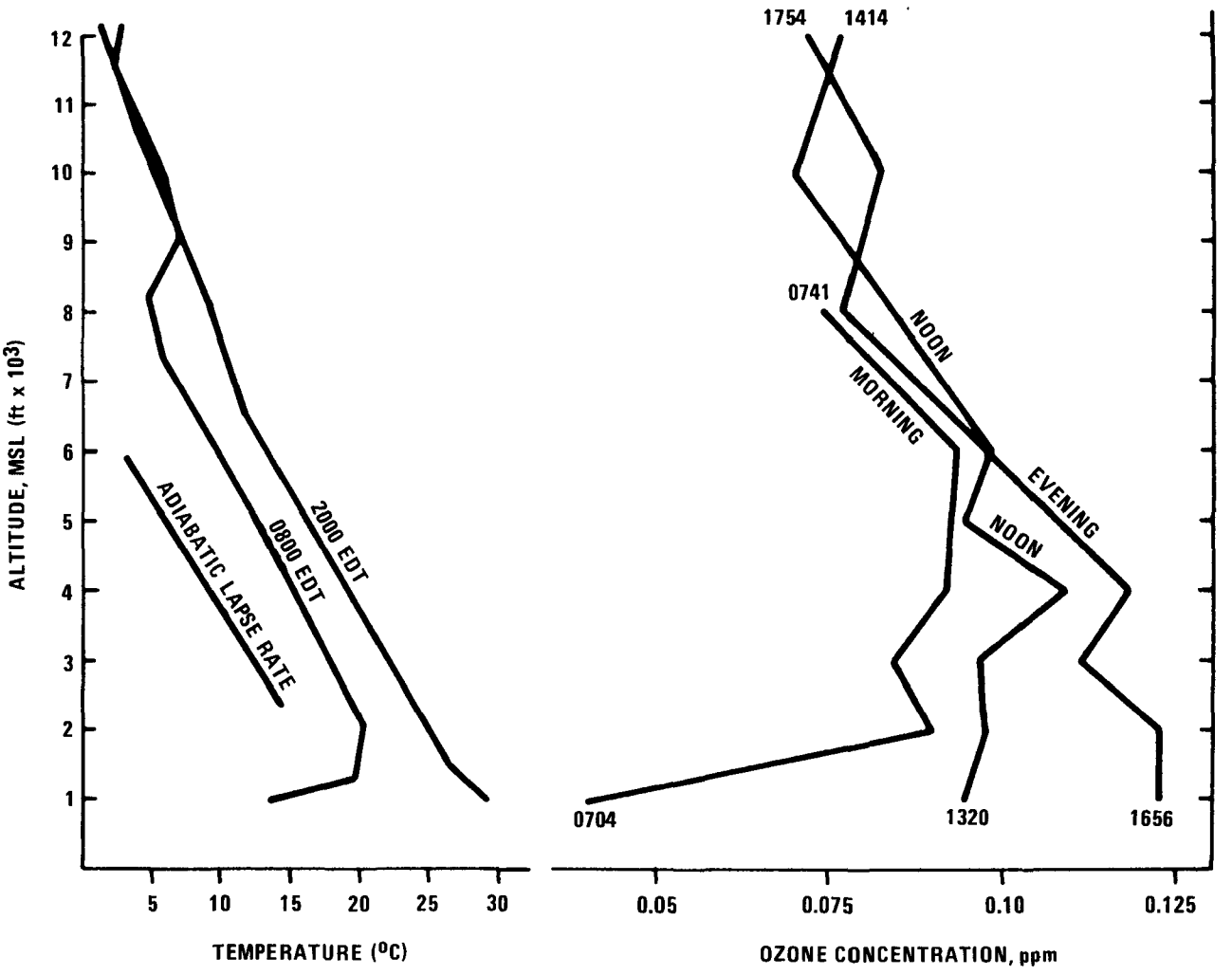


Figure 6. Ozone profile flight, Wilmington, Ohio, August 1, 1974.

photochemistry from precursors emitted at the surface or from hydrocarbons left over from the previous day, mixes with the layer of ozone that had persisted through the night. As the day progresses, more oxidant is formed as shown by the high oxidant concentrations measured in the afternoon. This typical pattern explains the usual diurnal oxidant concentrations measured at ground based rural monitors. This pattern usually shows low concentrations at night with build-up to high concentrations in the afternoon. Exceptions occur when high oxidant concentrations have been measured at night under atmospheric conditions that dissipate or prevent formation of the surface-based inversion.

Preliminary analysis of data from the 1974 summer studies indicates that ozone concentration variation also is associated with large scale weather features related to high pressure weather systems (Ref. 18). Figure 7 presents a smoothed graph

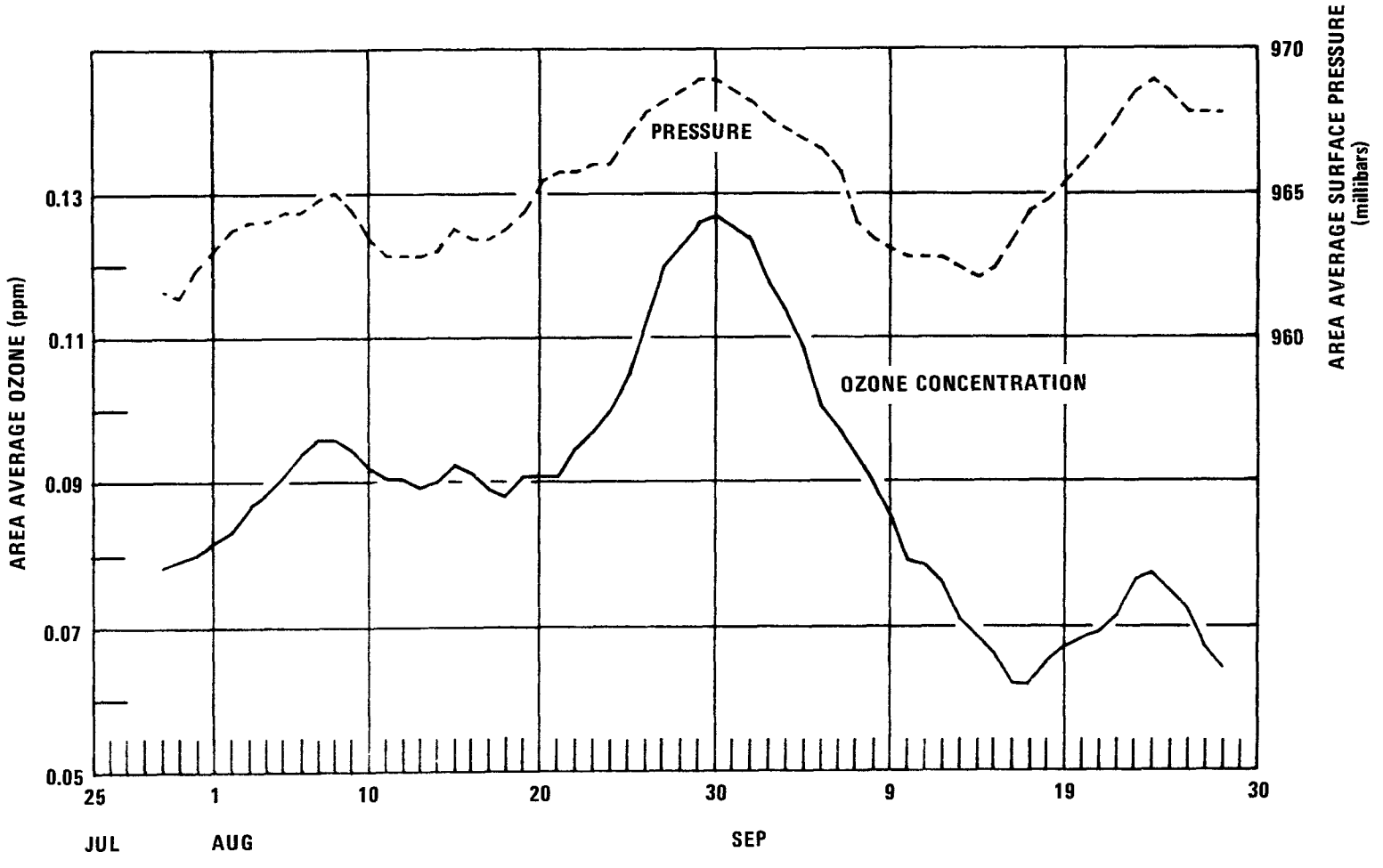


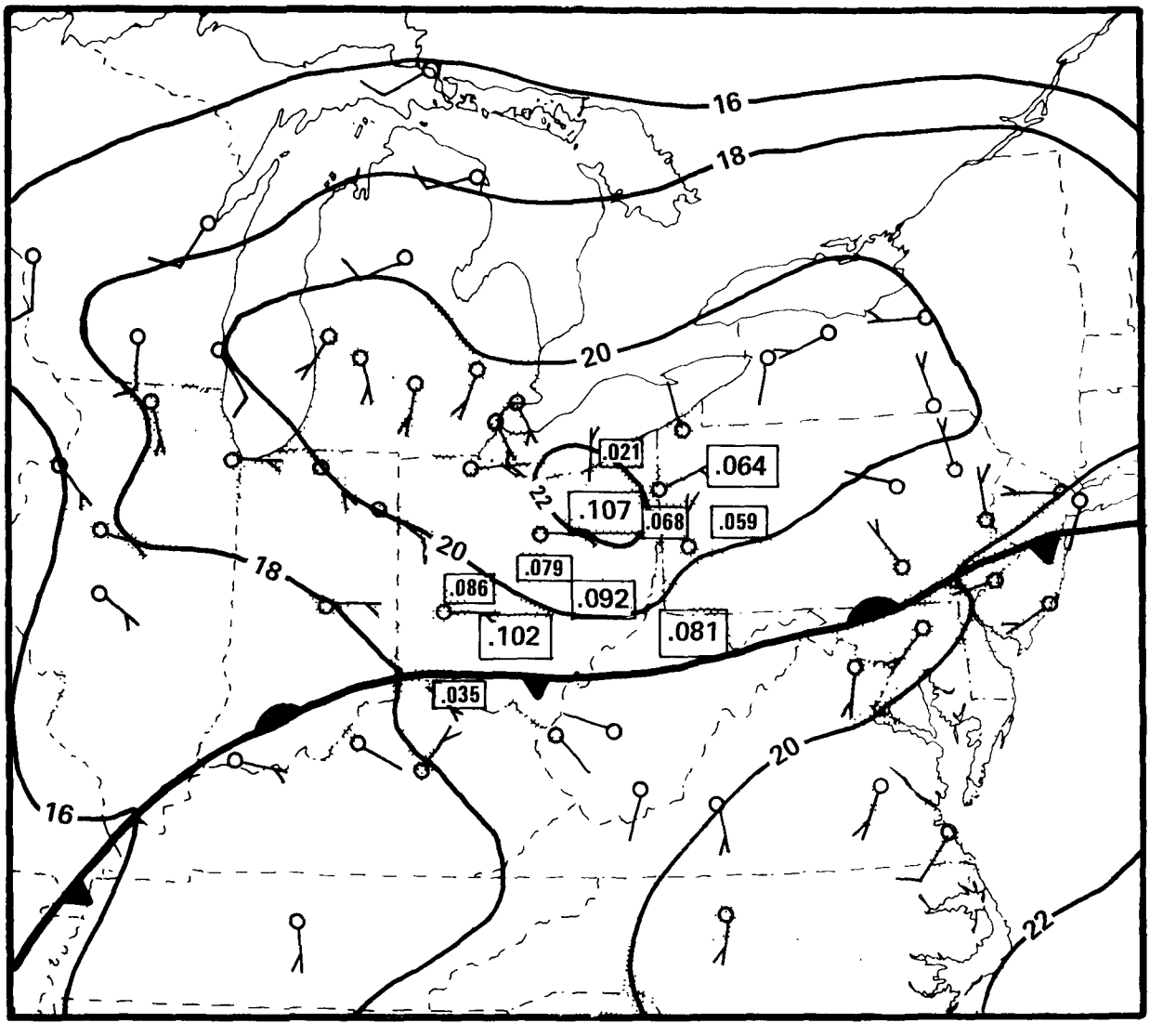
Figure 7. Smoothed variations of area average daily ozone - surface pressure - 1973 time sequence.

of surface pressure and surface ozone concentrations for 1973 averaged over several eastern study sites. This shows that the highest oxidant readings occurred during periods of high pressure; however as explained below, high pressure in itself does not lead to high ozone.

On a spatial basis, the higher ozone concentrations generally seem to occur near the central portion of high pressure cells and decrease outward. The spatial distribution of ozone in a high pressure system is shown on weather maps for July 6 and July 8, 1974 in Figure 8 and Figure 9 (Ref. 18). These are two of several cases studied. The five numbers in large boxes are the 8-hour afternoon averages of ozone concentrations in parts per million observed at the rural monitoring sites. The six numbers in smaller boxes are the ozone concentrations at urban locations. The contour lines are lines of constant pressure. The center of the high pressure system is over Cleveland on July 6 (Figure 8) and is indicated by the line numbered 22 (1022 millibars). On July 8 (Figure 9) the high pressure cell is centered over western Pennsylvania. The wind direction and velocity is shown by the arrows. The shading indicates areas of high man-made hydrocarbon emissions where emission densities are greater than 10 tons per square mile per year. In the urban areas emission densities are between 100 and 1000 tons per square mile per year. Emission densities are high in most of this region and are sufficient to account for the measured ozone concentrations. The evidence suggests that near the center of a high pressure area, perhaps 100-200 miles in diameter, environmental conditions are most conducive to high oxidant build-up. Apparently, near the center of the high pressure area, there are light disorganized winds, sufficient ultra-violet radiation and high temperatures as well as sufficiently high emissions of precursor compounds. Thus, in a slow moving high, a virtual outdoor smog chamber develops in which locally generated oxidants are added to oxidants and precursors which may have been transported into the area as the high pressure cell was developing.

ASSESSMENT OF RECENT TECHNICAL FINDINGS

The recent field investigations and laboratory studies of oxidant formation and control have provided several new insights. It is now apparent that oxidants are a rural as well as an urban problem. Oxidants can be formed over long time periods during stagnant conditions in high pressure systems or during transport of oxidants and precursors. This implies that the long-term behavior of oxidants and precursors is an important contributor to oxidant concentrations. It also implies



1. AVERAGE DAYLIGHT OZONE CONCENTRATION (1200 TO 2000 EDT) IN PPM

   A. SMALL BOX - URBAN
   B. LARGE BOX - RURAL

2. SURFACE PRESSURE (1700 EDT) IN MILLIBARS

3. 24-HOUR RESULTANT SURFACE WINDS

4. HYDROCARBON EMISSION DENSITY (> 10 tons/year-sq. mile) (SCREENED AREA)

Figure 8. Average ozone concentration 06 July 1974.

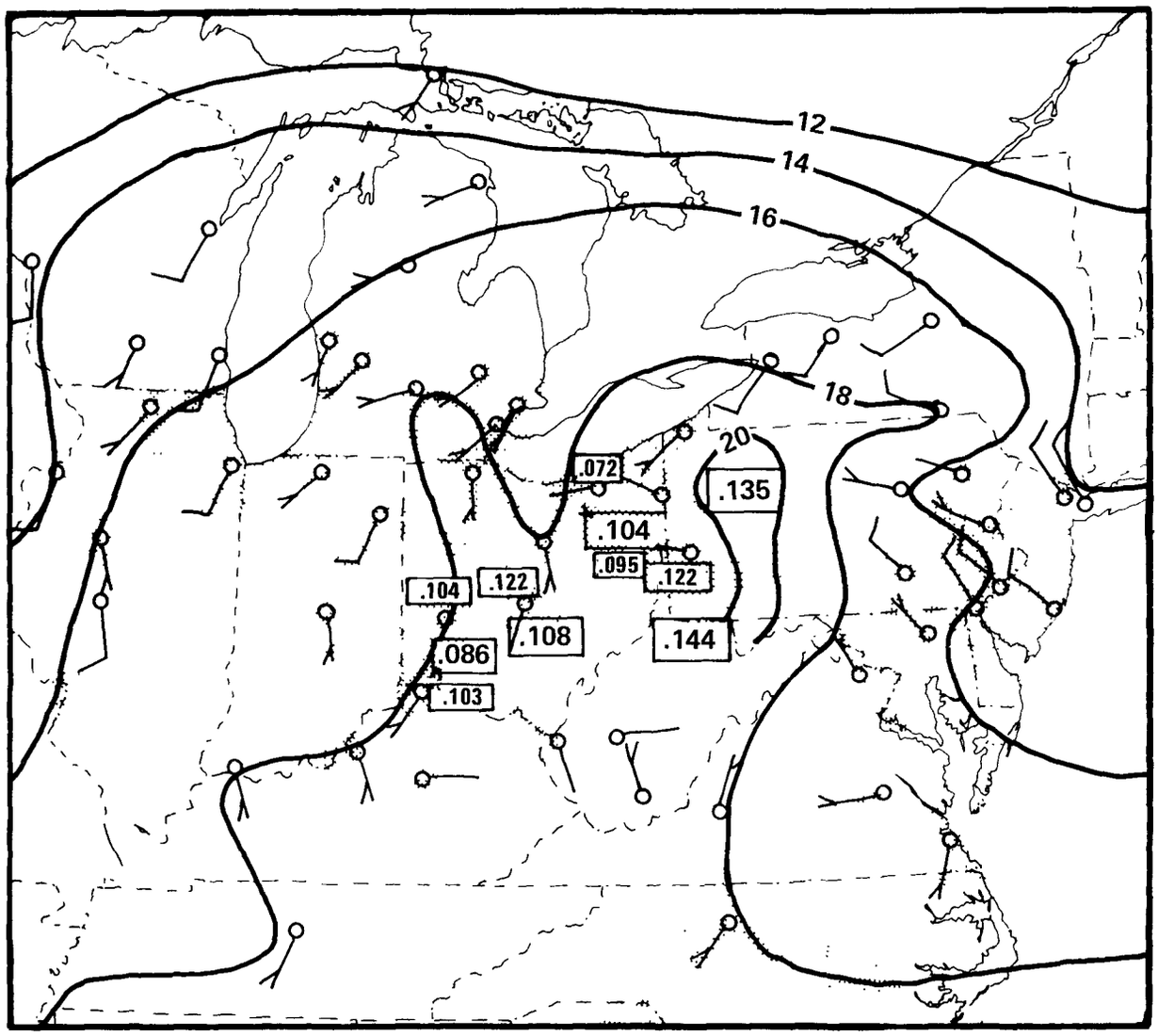


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Figure 9. Average ozone concentration 08 July 1974.

that less reactive organic compounds as well as the more reactive compounds can contribute to observed oxidant levels. There are also natural sources of oxidants which at times may contribute to oxidant concentrations reaching levels near the oxidant standard. The studies indicate that man-made emissions of hydrocarbons are, however, the predominant source of the highest levels of oxidant.

IMPLICATIONS OF RECENT FINDINGS FOR OXIDANT CONTROL STRATEGIES

Recent trends indicate that the current strategy is leading to reduction in oxidant levels in urban areas. However, it appears that measures in addition to those planned under the current strategy will need to be developed in order to achieve the oxidant standard nationwide. The implications suggested are discussed in detail in the following sections.

GENERAL IMPLICATIONS

It is clear that high oxidant levels are a problem in many non-urban as well as urban areas. The large cities and major urban areas are, of course, concentrated major sources of organic compounds and nitrogen oxides. However, non-urban areas also generate substantial man-made precursor emissions. These areas are not necessarily rural, but may include many medium and smaller sized cities that may account for significant fractions of population. In the state of Ohio, where the rural oxidant studies discussed in the preceding section were largely conducted, the ten largest cities (population greater than 100,000) account for approximately 60 percent of the total man-generated hydrocarbon emissions. This leaves 40 percent of these emissions coming from the non-metropolitan areas of the state. It would follow then that the major steps needed to control oxidants in both urban and non-urban areas are those measures that effectively reduce the emissions in each of these areas and which take into account the individual characteristics of each area. These findings in no way indicate that there should be less control of the urban fraction of hydrocarbons.

It will, of course, be necessary to consider the interaction of urban and non-urban areas since transport of oxidants and their precursors occurs. As discussed in the previous section, there is evidence that transport can take place. The highest oxidant levels in both urban and non-urban locations of the eastern U.S., however, appear to occur within areas of a high pressure system. Since winds are usually light within these systems, transport beyond about fifty miles may not be important under these conditions. This would support a view that within high pressure systems the urban centers and the non-metropolitan areas are both principal contributors to their own oxidant problems.

Because controlling urban and non-metropolitan oxidants may present different problems they are discussed under separate headings in the following sections.

IMPLICATIONS FOR CONTROL OF URBAN OXIDANTS

Most urban areas are characterized by a large population at risk and high precursor emission densities. The oxidant problem in these metropolitan areas can be largely attributed to those mobile and stationary source emissions generated within the community itself. Based on recent studies in the Midwest, this is particularly true during meteorological conditions characterized by stagnant high pressure systems, the same conditions during which the highest oxidant levels have been observed. For these reasons, the continued application of intensive control measures in our urban areas is essential if we are to attain the oxidant standard and prevent adverse effects to human health.

Of particular importance in achieving this objective are those measures designed to reduce mobile source emissions. Estimates for several major metropolitan areas show that as much as 70 percent of total urban hydrocarbon emissions are attributable to light and heavy duty vehicles. To effectively handle this problem, continued emphasis will be required on Transportation Control Plans to augment the Federal Motor Vehicle Emission Control program. These plans are a key element in achieving the oxidant standard in urban areas and offer the only viable approach to achieving mobile source emissions reductions beyond those resulting from the Federal Motor Vehicle Emission programs.

Although the present strategy recommends controlling all reactive hydrocarbons or organic compounds, it does provide for substitution of less reactive for moderate and highly reactive materials where reduction of all organics is not feasible or economic. Within large cities this approach can contribute to reduced oxidant levels, and it may be necessary to continue to permit these substitutions where measures for total hydrocarbon reduction are not practical. However, recent findings suggest that the less reactive hydrocarbons within an urban area can persist from one day to the next under stagnant conditions and thus have time to react and contribute to oxidant levels. Also, under conditions when transport of oxidants and precursors occurs, there can be sufficient time for the less reactive organics to contribute to oxidant levels in neighboring areas. Therefore, while continued use of reactivity oriented measures can be of value to a city, the recent findings place increased emphasis on the need to control all organic compounds that can participate in oxidant formation.

Another implication concerns the ultimate need to control nitrogen oxides emissions as part of the strategy for achieving the oxidant standard. The oxidant strategy relies on reduction of hydrocarbon emissions to meet this objective. Our understanding of the underlying chemistry continues to indicate that emphasizing hydrocarbon control is the most effective way to reduce the high levels of oxidants seen in major urban areas. However, this strategy can leave unreacted nitrogen oxides in the atmosphere which may be transported into suburban and rural areas to interact with further infusions of organic material and give oxidant concentrations which exceed the standard in these areas. The observation of elevated weekend oxidant levels in some cities may also be related to varying relative rates of organic and nitrogen oxides emissions.

The strategy leading to control of oxidants in urban, suburban, and rural areas will continue to be based on the reduction of organic compounds. Eventually, however, as oxidant levels are reduced toward the standard, it is likely that coordinated reductions of both organics and nitrogen oxides will be required. In a coordinated approach, cities could take advantage of the beneficial effect of a low organic to nitrogen oxides ratio while sufficient control of nitrogen oxides would be necessary to control oxidant formation downwind or during extended stagnation conditions.

IMPLICATIONS FOR CONTROL OF NON-METROPOLITAN OXIDANTS

Non-metropolitan areas, in contrast to the major urban centers, have their emission sources spread over wide geographic areas. Control measures that need to be taken must be effective over these broad areas. The Federal control programs for mobile and stationary sources apply nationwide and therefore have this character. The States can also extend their hydrocarbon control regulations statewide. These regulations now tend to be confined to major urban areas within the States. Through the State Implementation Plans, further reductions in emissions can be achieved from both stationary and mobile sources in non-metropolitan areas that have an oxidant problem. Thus, in the future, it may be determined that certain States need to adopt statewide stationary source controls and possibly certain transportation measures such as vehicle inspection/-maintenance. This latter measure employed throughout a State would help assure maximum effectiveness of the Federal Motor Vehicle Control Program.

To characterize the need for stationary source control, a preliminary estimate can be made of the effectiveness of Federal programs in reducing oxidants in the

non-urban areas throughout the U. S. under present nationwide control timetables. Table 3 shows estimates of national emissions of hydrocarbons from various mobile sources and from stationary sources projected through 1985. These estimates include factors for expected growth in each category and reductions based on Federal programs now being implemented or required in the near future. In the case of light duty vehicles the estimates are based on EPA's recent recommendations on extension of interim and statutory standards. For the mobile sources, the retirement of older vehicles and the projected deterioration of control devices is also included.

TABLE 3. NATIONWIDE HYDROCARBON EMISSIONS (MILLIONS OF TONS PER YEAR)

YEAR	LIGHT-DUTY VEHICLES	LIGHT-DUTY TRUCKS	HEAVY-DUTY VEHICLES	OTHER MOBILE SOURCES*	TOTAL MOBILE SOURCES	STATIONARY SOURCES	TOTAL HC EMISSIONS
1972	10.3	2.0	2.4	1.9	16.6	12.5	29.1
1975	9.1	1.7	2.2	2.2	15.2	13.7	28.9
1985	3.6	1.3	2.1	3.4	10.4	14.7	25.1

*AIRCRAFT, VESSELS, OFF-HIGHWAY, RAIL

Since rural oxidant levels in excess of 0.16 ppm have been measured as was reported in Table 2 and natural background concentrations of 0.04 ppm and possibly higher may occur, it is possible that at least a two-thirds reduction in man-made oxidants will be needed to meet the oxidants standard in some non-urban regions. Assuming that the relative reductions in nationwide emissions shown in Table 3 approximate the effect of the Federal programs over broad geographic areas, it is not likely that they will be sufficient to achieve the needed oxidant reductions. It appears from the above estimates that more needs to be done than is currently planned to solve the non-urban problem. Although it may be possible to improve the controls for heavy duty vehicle emissions and other mobile sources, the most promising area for achieving the broad area control needed for non-urban areas would appear to be stationary sources. In 1972 these sources accounted for less than half of the total emissions nationwide whereas by 1985 they will account for almost two-thirds of the nationwide hydrocarbon emissions. This distribution may not be true in some rural areas where motor vehicles could remain the dominant source of emissions.

The recent findings have additional implications for control of the non-urban oxidants problem. Both the more reactive and the less reactive organics, under the conditions of light winds associated with persistent high pressure systems,

may have sufficient time to generate oxidants. Thus, reduction of total emissions and not just reduction of the more reactive compounds would need to be emphasized in non-urban areas. Control of organic rather than nitrogen oxides emissions appears to be the most effective route to reduce oxidant levels in rural areas. However, to attain the standard, coordination of both organic and nitrogen oxides emissions control may be necessary.

Finally, consideration of natural contributions of oxidants and precursors is likely to be an important consideration in non-urban areas. While recent findings suggest that natural sources do not in themselves lead to oxidant levels above the standard, they may in combination with man-made emissions lead to levels in excess of the standard. Therefore, stricter controls on the man-made emissions may be needed to compensate for the contributions from natural sources. It may also be found that the natural source contribution is sufficiently high in some areas that small additions of man-made emissions may cause the standards to be exceeded. In these cases it will still be possible to significantly reduce oxidants but it may not be possible to attain the standards at all times and places.

The implications of the recent findings for the control of oxidants in both urban and non-urban areas may be summarized as: most organic compounds need to be controlled; eventually the coordinated control of both organics and nitrogen oxides may be necessary; present regulations need to be expanded into non-metropolitan areas; continued emphasis on mobile sources must be supplemented by reductions in stationary sources; and natural sources should be considered in determining required emissions reduction measures.

EPA PROGRAMS
LEADING TO MORE EFFECTIVE CONTROL STRATEGIES

Substantial progress has been made in the last several years in understanding the occurrence and formation of photochemical oxidants in the atmosphere. It is apparent from all the available information that the reduction in emissions of organic compounds will lead to reduction of oxidant concentrations. The recent studies indicate that additional measures will be needed in order to meet the standard everywhere. There is still not sufficient information, however, to define exactly what control measures will be needed to meet the oxidant standard everywhere. EPA is sponsoring an extensive program of laboratory and field studies, including development of improved mathematical modeling techniques, to obtain the needed information. The studies will:

- Determine and quantify the effect of intermediate and long-range transport on oxidant levels in both urban and rural areas.
- Quantify the role of local emissions of hydrocarbons and nitrogen oxides on the generation of rural and urban oxidants.
- Determine the long-term behavior of oxidant levels in air masses in which oxidant precursors are being intermittently or continually injected.
- Quantify the relative roles of hydrocarbons and nitrogen oxides in oxidant formation particularly at oxidant levels near the standard.
- Determine the contribution of natural sources and sinks of hydrocarbons, nitrogen oxides and oxidants on oxidant levels in the lower atmosphere in both rural and urban areas.
- Develop more reliable methods for relating emissions of precursors and the concentrations of oxidants observed in the atmosphere.
- Expand the aerometric data base for oxidants and precursors throughout the United States.
- Develop detailed emission inventory data by place, time of day, and year for both anthropogenic and natural sources of oxidant precursors.

- Develop control technology for stationary sources at reasonable cost.

Much of the needed information from these studies will become available over the next few years. In some other areas several more years of effort may be required. However, as soon as the information in any area is sufficient to support an addition or change in strategy, the improvement can be made. Thus, it is expected by this process that the current strategy will evolve into an optimum strategy over the next several years.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The report assesses laboratory and field studies conducted over the past several years and discusses how the findings affect current and projected programs to control oxidants. Both maximum concentrations and the frequency of violations of the air quality standards for oxidants have decreased in some urban areas as a result of recently initiated controls. However, long thought to be primarily an urban problem, oxidant levels well in excess of the standard have been observed in broad areas in the eastern third of the U.S. Although naturally occuring sources such as vegetation and the stratosphere do contribute to these high levels, man's activity is their predominant cause. Instances are noted in which oxidants and their precursor compounds have been carried up to 50 miles, and probably farther. More extensive control of oxidant-producing compounds will be required in rural areas while emphasis continues to be placed on control in the cities.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
photochemical oxidants		

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