RURAL OXIDANT AND OXIDANT TRANSPORT

R. M. Angus and E. L. Martinez, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina

Before 1970, surface measurements of oxidants in rural areas were made infrequently and did not indicate the presence of particularly high concentrations (1, 2). But in the course of a study conducted by the U.S. Environmental Protection Agency in 1970 (3), investigators found oxidant concentrations in a rural area of western Maryland and eastern West Virginia that frequently exceeded the present national ambient air quality standard (NAAQS) of 160 $\mu g/m^3$ (0.08 ppm) for a 1-hour average. Although the NAAQS is for photochemical oxidants, the measurement method prescribed is specific for ozone. Simultaneous oxidant and ozone specific measurements by Richter (4) during part of the 1970 study showed that virtually all of the oxidants measured were ozone. Follow-up studies of increasing magnitude were sponsored by EPA and were conducted in 1972, 1973, and 1974 (5, 6, 7). The extensive measurements carried out in the summer of 1974 were made at widely separated sites in the eastern Midwest.

The studies showed 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 1 (7) gives data on maximum ozone observed and frequency of ozone above the standard 160 $\mu g/m^3$ (0.08 ppm) for the monitoring locations shown in Figure 1. At DuBois, a small city in rural Pennsylvania, the oxidant standard was exceeded 341 hours during the period from June 14 to August 31, 1974. During the same period at Pittsburg, approximately 160 km (100 miles) southwest of DuBois, the standard was exceeded only 106 hours. The maximum hourly concentration measured at DuBois was 400 $\mu g/m^3$ (0.20 ppm); at Pittsburgh it was 280 $\mu g/m^3$ (0.14 ppm). Similar high values of ozone have also been measured in rural areas of New York (8, 9), New Jersey (10), Wisconsin, and Florida (12). Thus, in many areas of the eastern United States, high concentrations of oxidants are found in both rural and urban areas.

SOURCES OF RURAL OXIDANTS

Several possible sources of rural oxidants 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 that may move into rural areas while reacting to form oxidants and also the oxidants formed from man-made precursors that originate in the nonurban areas. The precursors are the nitrogen oxides and organic compounds that react to form oxidants 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, and industrial operations. 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. There are also 2 possible natural sources of surface level oxidants: (a) downward transport from the ozone-rich layers in the stratosphere into the lower troposphere near the surface and (b) photochemical generation

from hydrocarbons emitted by vegetation. The available evidence strongly indicates that frequent and persistent concentrations of ozone near the surface above 160 $\mu g/m^3$ (0.08 ppm) are not caused solely by natural sources and that the background that can be attributed to natural sources is usually 80 to 100 $\mu g/m^3$ (0.04 to 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 (13). These generally show ozone concentrations occurring at a maximum in the lower stratosphere, decreasing to low levels at or near the tropopause, and slightly decreasing toward the surface. Ozone levels near the surface that appear to be largely of stratospheric origin may at times range from 60 to 100 $\mu g/m^3$ (0.03 to 0.05 ppm) (15). 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 total ozone levels observed in rural areas (16).

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 40 to 100 $\mu g/m^3$ (0.02 to 0.05 ppm) (16). However, the atmospheric conditions that are conducive to higher ozone production by the photochemical process are not usually the same conditions associated with transport from the stratosphere. Therefore, the high values of nonurban 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 THAT AFFECT OXIDANT CONCENTRATION

Recent measurements downwind of urban centers [Houston (17), Phoenix (17), Ohio cities (7), and Philadelphia (10)] demonstrate that transport of oxidants from urban centers to locations as far as 50 to 80 km (30 to 50 miles) downwind takes place. In Los Angeles, where the magnitude of oxidant generation is greater, the distance can be extended to 120 km (75 miles) or more downwind (18). Beyond these distances, it is difficult to distinguish the individual urban contribution of ozone from general nonurban levels. Therefore, although transport of oxidants may partially explain the high oxidant levels at short range downwind of urban centers, it has not been definitely shown that transport is the principal cause of the high readings at more remote sites. [A recent study by Bell Laboratories presented convincing evidence, from a statistical and episodic analysis, that ozone resulting from emissions from the New York City metropolitan area is transported by prevailing winds on a 300-km (187-mile) northeast trajectory through Connecticut and as far as northeastern Massachusetts (11).]

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 160 $\mu g/m^3$ (0.08 ppm) have been found in which Freon 11 levels were not also above the background. Figure 2 shows ozone and Freon 11 measurements at Whiteface Mountain from July 24 to 27, 1974 (18). 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 ozone production was 100 $\mu g/m^3$ (0.05

Table 1. Ozone levels above NAAQS at rural and urban stations from June 14 to August 31, 1974.

Station	Maximum Hourly Average Concentration ($\mu g/m^3$)	Ninety-ninth Percentile ($\mu g/m^3$)	Days Exceeding Standard[a] (percent)	Hours Above Standard	
				Number	Percent
Rural					
Wilmington, Ohio	370	260	58	259	14.9
McConnelsville, Ohio	330	240	56	239	13.3
Wooster, Ohio	330	260	55	262	14.0
McHenry, Maryland	330	270	43	262	13.0
DuBois, Pennsylvania	400	310	54	341	20.5
Urban					
Canton, Ohio	280	230	44	148	8.0
Cincinnati, Ohio	360	220	20	54	3.5
Cleveland, Ohio	270	200	26	51	3.0
Columbus, Ohio	340	220	27	113	5.8
Dayton, Ohio	260	220	35	114	7.2
Pittsburgh, Pennsylvania	300	230	37	106	6.5

Note: 1 $\mu g/m^3$ = 0.0005 ppm.

[a]Based on data available from each station.

Figure 1. Location of ozone ground sampling stations in 1974 study.

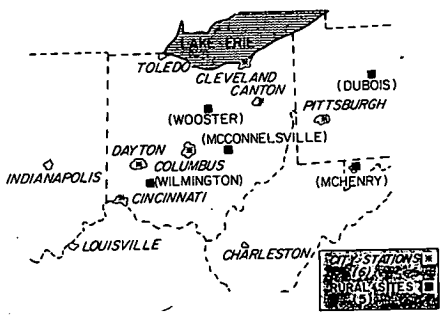
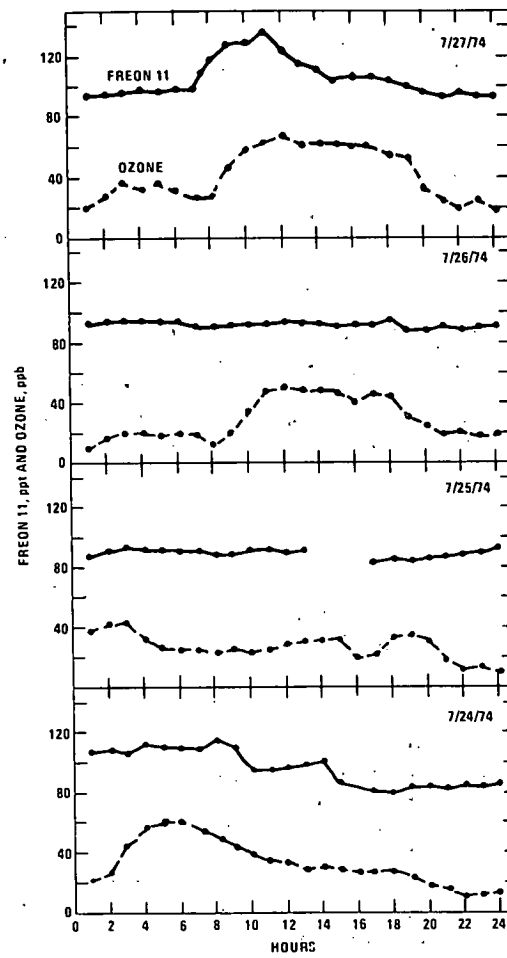


Figure 2. Hourly averages of Freon 11 and ozone at Whiteface, New York.



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. Similar studies were performed by investigators in England (20). They concluded that a significant portion of the ground-level ozone in southern England is caused by transport of precursors or ozone over distances of the order of 100 to 1000 km (160 to 1,600 miles).

Air parcel movement in the eastern United States was related to ozone concentration by Bach (21) using a trajectory computer program developed by the EPA Meteorology Laboratory. These trajectories computed air parcels arriving at the various nonurban ozone measuring sites in the summer of 1973. Sets of trajectories for 2 sites for the upper and lower decile of 12-hour average ozone concentrations are shown in Figures 3 and 4. The trajectories are for the 90-kPa (900-millibar) level [approximately 900 m (3,000 ft) above sea level], corresponding roughly to the mean afternoon mixing height.

Past positions at 12, 24, and 36 hours are plotted for 12-hour average ozone concentration periods falling in the upper and lower 10 deciles. The trajectories are inconclusive, showing no definitive pathway pattern differences between high and low ozone periods. It was significant, however, that for high ozone periods past positions are more closely spaced than for low ozone periods, indicating generally slower air movement. It is postulated that, for high rural ozone occurrence, light wind flow likely associated with longer reaction periods, slow-moving highs, and accumulation of ozone are of greater importance than the particular trajectories followed during long-range transport.

Temperature

It has generally been noted in the monitoring of ozone at various locations in this country that ozone concentrations above the NAAQS level occur during the warmer months of April through October. Seldom are such levels found to occur at other times of the year, except during warmer periods, mostly in the southern tier of states. Smog chamber experiments by Jeffries show that, at daily maximum temperatures below about 14.5 C (58 F), significant generation of ozone does not occur. For the 1973 field study data, Bach (21) correlated maximum hourly ozone concentrations for each day at each of the 4 sites with the maximum daily temperature at nearby surface stations of the National Weather Service. The paired stations were as follows:

Ozone Station	Temperature Station
McHenry, Maryland	Elkins, West Virginia
Kane, Pennsylvania	Youngstown, Ohio
Coshocton, Ohio	Columbus, Ohio
Lewisburg, West Virginia	Beckley, West Virginia

The results for 2 sites are shown in Figure 5. A consistent statistical relation was found with increase of maximum hourly ozone concentration related to increasing maximum temperature. The best correlation found was 0.71 for the McHenry-Elkins pair. In no case was an ozone concentration of greater than 160 $\mu g/m^3$ (0.08 ppm) found with temperatures less than 16.5 C (61.5 F).

The trend for higher ozone concentrations with greater maximum temperatures does not necessarily establish that a direct relation exists. Maximum temperature is also a function of other meteorological variables, including sky cover, synoptic weather features, wind speed, and past history of the air mass. However, direct or indirect,

Figure 3. Trajectories associated with high and low decile, 12-hour average ozone concentrations at McHenry, Maryland (squares and triangles indicate 12-hour past positions prior to arrival at indicated stations).

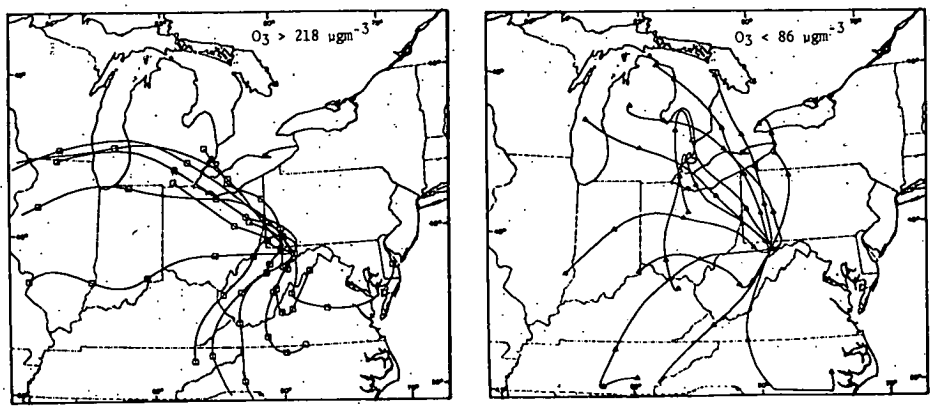


Figure 4. Trajectories associated with high and low decile, 12-hour average ozone concentrations at Coshocton, Ohio (squares and triangles indicate 12-hour past positions prior to arrival at indicated stations).

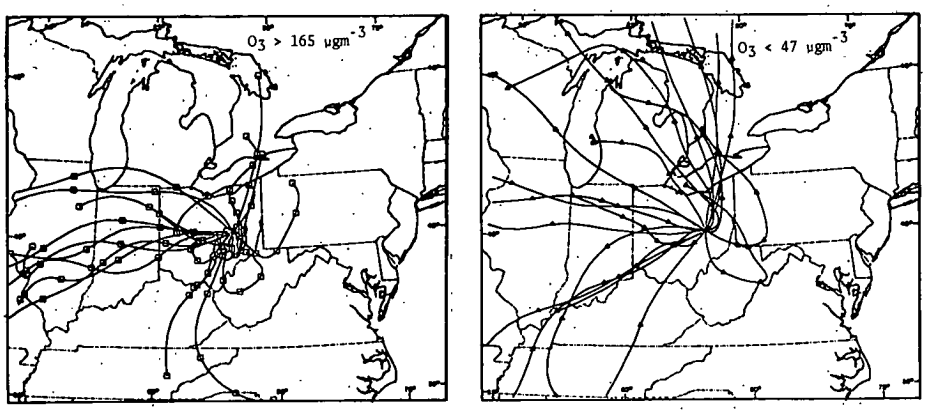


Figure 5. Scatter diagrams and least squares fit of daily maximum hourly ozone concentration and maximum daily temperature at indicated stations (A indicates 1 occurrence, and B indicates 2).

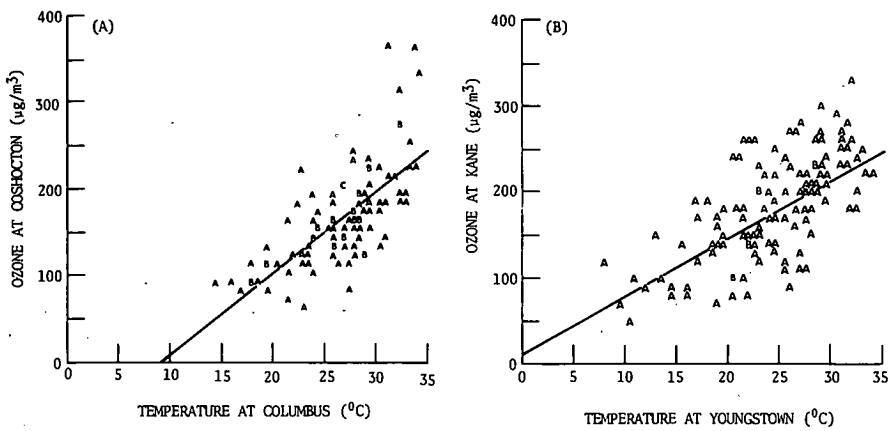


Figure 6. Time sequence of 12-hour average ozone concentrations at McHenry, Maryland, in 1972 (8 a.m. to 7 p.m. EDT is unshaded, 7 p.m. to 8 a.m. is shaded, and frontal passages are shown by double arrow).

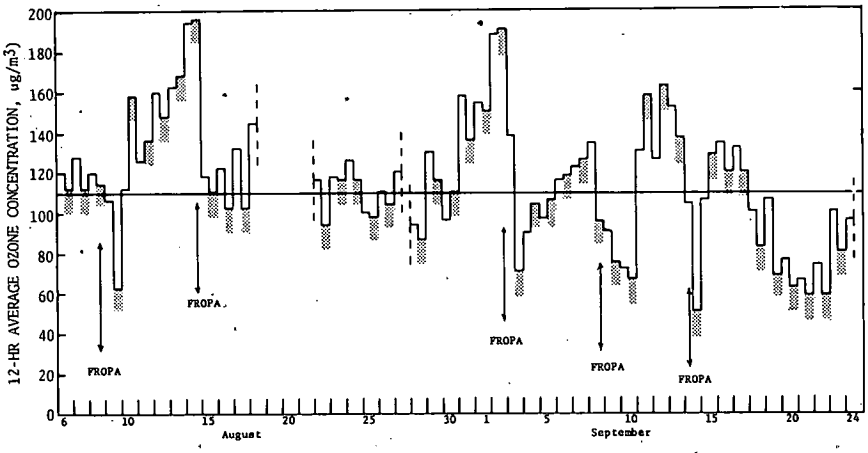
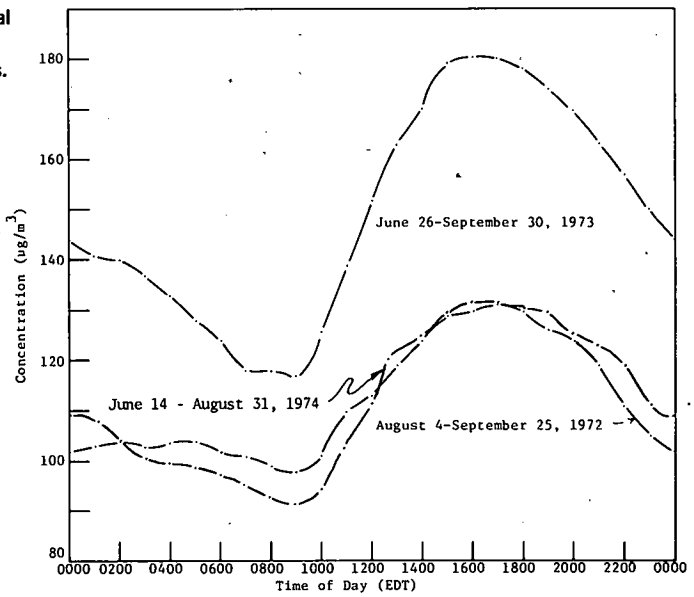


Figure 7. Comparison of mean diurnal ozone concentration at McHenry, Maryland, for indicated study periods.



maximum temperature appears to be a reliable indicator of the potential for high ozone concentrations to occur.

Fronts

In the analysis of the 1972 ozone measurements, a definite pattern seemed to be present of buildup of concentration levels followed by sharp decreases following frontal passages. This pattern is shown in Figure 6. This pattern is consistent with what is generally experienced with other pollutants, especially those in urban areas. A similar analysis was performed on the 1973 ozone data, but curiously the pattern exhibited the previous

year did not seem to repeat itself very often. A possible reason for the lack of repeatability 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 explain the data shown in Figure 7, in which generally higher ozone levels were experienced in 1973 relative to 1972 and 1974 at the rural site near McHenry, Maryland.

Vertical Distribution of Ozone

The data shown in Figure 7 indicate the diurnal variation in the average hourly concentrations. This pattern has been relatively consistent during the 1972 to 1974 studies. Generally, the highest ozone concentrations occur in the late afternoon and the lowest occur in the early morning. In general, there is no significant variation among monitoring locations, although the pattern is more pronounced at those rural locations that are subject to periodically strong inversion formation.

Figure 8 shows vertical ozone profiles that were taken 3 times during 1 day during the 1974 summer studies (7) and that illustrate the effect that low-level atmospheric stability has on ozone concentrations. These profiles are similar to other vertical measurements at Indianapolis and Canton, Ohio, and are consistent with ozone soundings of previous years. The concentrations of ozone decrease above the subsidence inversion near 2400 m (8,000 ft) as shown by the temperature profiles. The early morning profile indicates low ozone concentrations (40 $\mu g/m^3$ or 0.02 ppm) beneath a radiation inversion that occurred between the surface and 600 m (2,000 ft). Trapped between these 2 inversions is a layer of ozone above 180 $\mu g/m^3$ (0.09 ppm) that 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 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 concentrations that are low at night and that build up and become high 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. Also, during prolonged stagnation episodes, ozone concentrations build up without appreciable decrease in ozone levels at night. It is hypothesized that strong surface-based inversions fail to materialize at night during hazy or smoggy conditions so that vertical exchange within the lowest tropospheric layers may be sufficient to maintain high surface ozone concentrations.

Pressure Systems and Surface Winds

For some episodes of high ozone, studies have shown (8, 9) that similar ozone concentrations were measured at widely separated rural sites. During these episodes urban areas were also observed to experience high concentrations of ozone.

Analysis of data from the Research Triangle Institute summer studies indicates that ozone concentration variation is associated with large-scale weather features related to high-pressure weather systems (7). Figure 9 shows a smoothed graph of surface pressure and surface ozone concentrations for 1973 averaged over several eastern study sites. The highest oxidant readings occurred during periods of high pressure; however, as explained below, high pressure in itself does not lead to high ozone.

Figure 8. Ozone profile flight at Wilmington, Ohio, August 1, 1974.

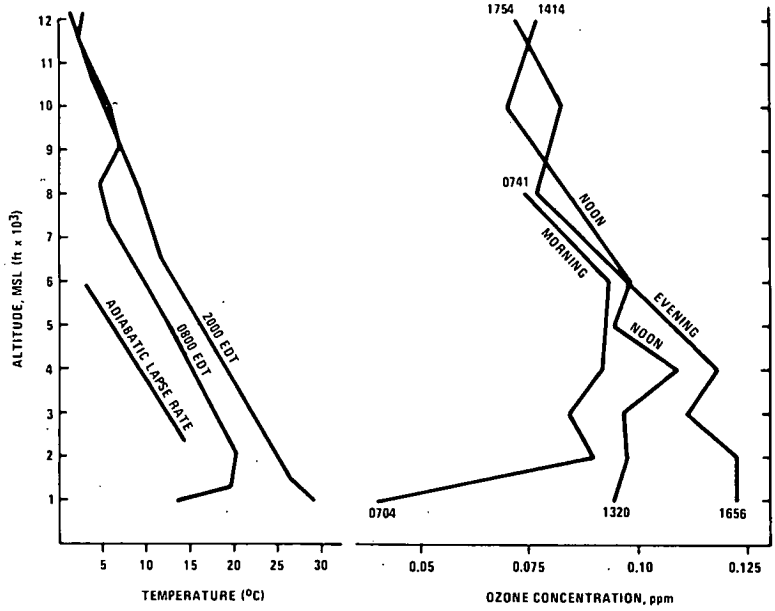


Figure 9. Smoothed variations for area average daily ozone and surface pressure (1973 time sequence).

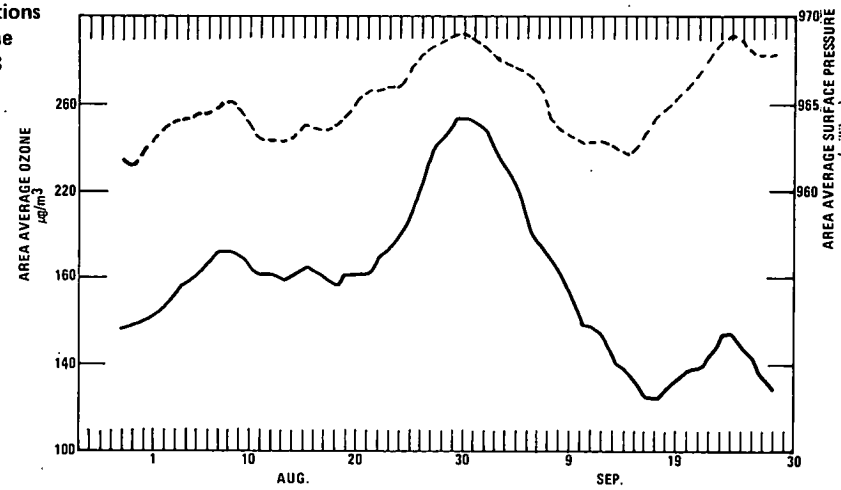
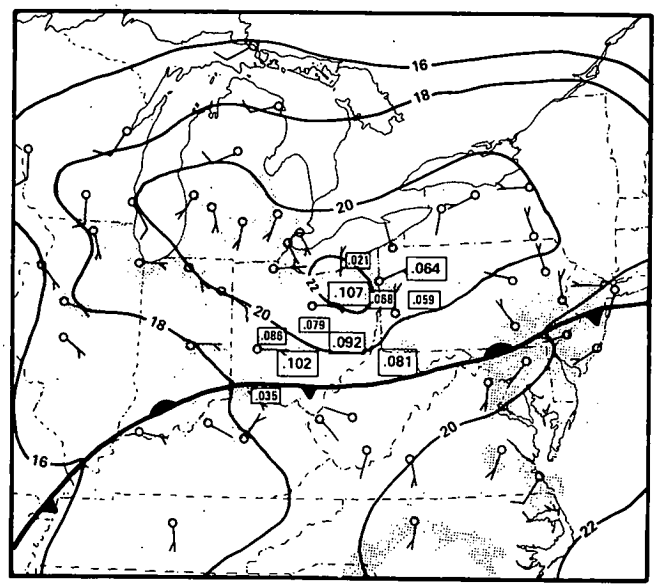


Figure 10. Average ozone concentration, July 6, 1974.



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 10 and Figure 11 (7). These are 2 of several cases studied. The 5 numbers in large boxes are the 8-hour afternoon averages of ozone concentrations in parts per million observed at the rural monitoring sites. The 6 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 10) and is indicated by the line numbered 22 (102.2 kPa or 1,022 millibars). On July 8 (Figure 11) 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 3500 kg/km^2/year (10 tons/mile^2/year). In the urban areas emission densities are between 35 000 and 350 000 kg/km^2/year (100 and 1,000 tons/mile^2/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 160 to 320 km (100 to 200 miles) in diameter, environmental conditions are most conducive to high oxidant buildup. Apparently, near the center of the high-pressure area, there are light disorganized winds, sufficient ultraviolet radiation, and high temperatures; and if sufficiently large emissions of precursor compounds are present, oxidants will be formed. Thus, in a slow-moving high, a virtual outdoor smog chamber develops in which locally generated oxidants are added to oxidants and precursors that may have been transported into the area as the high-pressure cell was developing.

The summer studies by Rasmussen (17) in the Canton, Ohio, area also related high concentrations of ozone to slowly moving high-pressure systems. He found that Canton frequently experienced advection of oxidant from contamination sources that became a part of the anticyclonic (high-pressure) air mass. The model developed by Rasmussen (17) is shown in Figure 12. Behind the central portion of the high-pressure system, the high concentrations appeared late in the day or early in the morning, when photochemical reactions from local pollutants would not be occurring.

Whether the highest concentrations of ozone occur in the center or on the trailing edge of the high-pressure system will depend on the source of emissions and the specific movement of the system. The conclusion of the above studies is that migratory anticyclones achieve a widespread level of ozone in the air mass and that the urban areas with high precursor emissions are the predominant sources of the high rural ozone concentrations.

ASSESSMENT OF RURAL OZONE STUDIES

The recent laboratory and field investigations of oxidant formation have provided several new insights or strengthened past understanding. It is now apparent that oxidants are a rural as well as an urban problem. Oxidants can be formed during long time periods of 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. Figure 13 shows a qualitative model of the components of the origins of ozone measured in the rural to urban to rural movement of ozone (15). This model indicates the man-made, stratospheric, and natural hydrocarbon sources of ozone upwind of a city. It indicates the scavenging effect of the emissions in the urban area and the buildup of an ozone plume downwind of the urban center. It is the conclusion of the recent studies that, although natural sources of oxidants may at times contribute to ozone concentrations reaching levels near the oxidant standard, man-made emissions are the predominant source of the highest levels of ozone. The occurrence of high levels of ozone in rural areas also indicates that additional control measures may be required in order to achieve the oxidant standard nationwide (22).

Figure 11. Average ozone concentration, July 8, 1974.

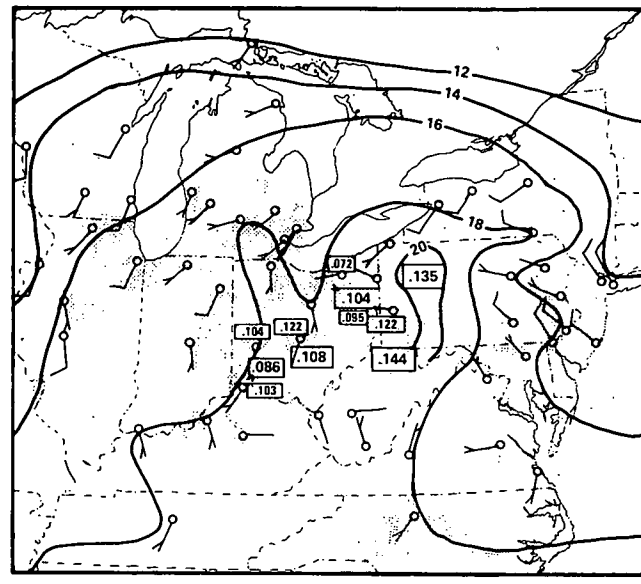


Figure 12. Ozone behavior within a high-pressure air mass.

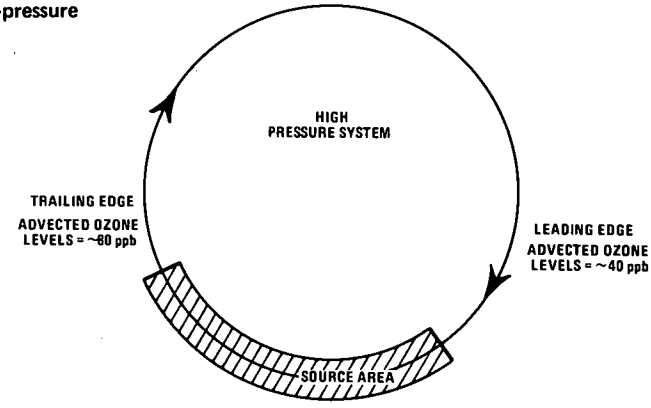
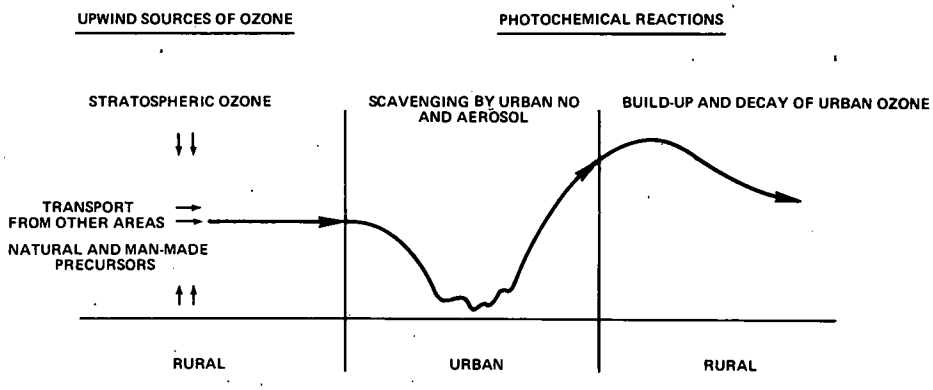


Figure 13. Surface ozone formation and transport.



SUMMARY

The information presented in this paper is based on recent field-monitoring programs for ozone in nonurban areas. The paper presents a discussion of the factors that may lead to and affect the observed ozone concentrations. Several meteorological parameters including transport of ozone and its precursor compounds are examined as factors affecting rural ozone levels that exceed the national ambient air quality standard. The conclusion is that man-made sources of precursor compounds are primarily responsible for the violations of the air quality standards. Transport of ozone or ozone precursors from cities into nonurban areas and the importance of synoptic-scale pressure systems are discussed.

REFERENCES

1. W. S. Hering and T. R. Borden. Ozone Observations Over North America. U.S. Air Force Cambridge Research Laboratories, Bedford, Mass., Vol. 1, 1964, Vol. 2, 1965, and Vol. 3, 1967.
2. V. H. Regener. Vertical Flux of Atmospheric Ozone. Journal of Geophysical Research, Vol. 62, 1957, pp. 221-228.
3. Mount Storm, West Virginia—Gorman, Maryland—Keyser, West Virginia Air Pollution Abatement Activity. U.S. Environmental Protection Agency, Research Triangle Park, N.C., Publ. APTD-0656, April 1971.
4. H. G. Richter. Special Ozone and Oxidant Measurements in Vicinity of Mount Storm, West Virginia. Research Triangle Institute, Research Triangle Park, N.C., Oct. 1970.
5. D. R. Johnston et al. Investigation of High Ozone Concentrations in the Vicinity of Garret County, Maryland, and Preston County, West Virginia. U.S. Environmental Protection Agency, Research Triangle Park, N.C., Rept. R4-73-019, Jan. 1973.
6. D. R. Johnston et al. Investigation of Ozone and Ozone Precursor Concentrations at Nonurban Locations in the Eastern United States: Phase I. U.S. Environmental Protection Agency, Research Triangle Park, N.C., Rept. 450/3-74-034, May 1974.
7. C. D. Decker et al. Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies. U.S. Environmental Protection Agency, Research Triangle Park, N.C., Rept. 450/3-75-036.
8. W. N. Stasiuk and P. Coffey. Rural and Urban Ozone Relationships in New York State. Journal of Air Pollution Control Association, Vol. 24, 1974, p. 564.
9. P. Coffey and W. N. Stasiuk. Evidence of Atmospheric Transport of Ozone into Urban Areas. Environmental Science and Technology, Vol. 9, 1975, pp. 59-62.
10. W. S. Cleveland and B. Kleiner. The Transport of Photochemical Air Pollution From the Camden-Philadelphia Urban Complex. Environmental Science and Technology, Vol. 9, 1975, pp. 869-871.
11. W. S. Cleveland and B. Kleiner. The Analysis of Ground-Level Ozone Data From New Jersey, New York, Connecticut, and Massachusetts: Transport From the New York City Metropolitan Area. Bell Laboratories, Oct. 1975.
12. 1973 South Florida Ozone Study: Ambient Air Quality Monitoring. Region 4, U.S. Environmental Protection Agency, Nov. 21, 1974.
13. H. U. Dutsch. Photochemistry of Atmospheric Ozone. In Advances in Geophysics, Academic Press, Vol. 15, 1971, pp. 219-322.
14. P. R. Sticksel. The Stratosphere as a Source of Surface Ozone. Presented at 68th Annual Meeting of Air Pollution Control Association, June 1975.
15. R. A. Rasmussen and E. Robinson. Journal of Air Pollution Control Association, Vol. 25, 1975, p. 17.
16. A. Shlanta and C. D. Moore. Ozone and Point Discharge Measurements Under Thunderclouds. Journal of Geological Research, Vol. 77, Aug. 20, 1972, pp. 4500-4510.
17. R. A. Rasmussen et al. Measurement of Light Hydrocarbons in the Field and

Studies of Transport Beyond an Urban Area. Washington State Univ., final rept. of contract 68-02-1232, 1976.
18. D. L. Blumenthal and W. H. White. The Stability and Long Range Transport of Ozone or Ozone Precursors. Presented at 68th Annual Meeting of Air Pollution Control Association, June 1975.
19. R. A. Rasmussen and E. Robinson. The Role of Trace Atmospheric Constituents in the Surface Ozone Model. Washington State Univ., Pullman, 1975.
20. R. A. Cox et al. Long Range Transport of Photochemical Ozone in Northwestern Europe. Nature, Vol. 255, May 8, 1975.
21. W. D. Bach. Investigation of Ozone and Ozone Precursor Concentrations at Non-urban Locations in the Eastern United States. U.S. Environmental Protection Agency, Research Triangle Park, N.C., Rept. 450/3-74-034-a, Feb. 1975.
22. E. L. Martinez. Temporal-Spatial Variations of Non-Urban Ozone Concentrations and Related Meteorological Factors. Presented at Conference on Air Quality Measurements, Austin, Texas, March 1975.
23. Control of Photochemical Oxidants: Technical Basis and Implications of Recent Findings. U.S. Environmental Protection Agency, Rept. 450/2-75-005.